Chemical Engineering Thermodynamics II

(CHE 303 Course Notes)

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Chapter 1

Introduction

1.1 Basic Definitions

Thermodynamics is the science that seeks to predict the amount of energy needed to bring about a change of state of a system from one equilibrium state to another. While thermodynamics tells us nothing about the mechanisms of energy transfer, rates of change, and time associated with a system changing from one equilibrium state to another, it is still the lynch-pin that allow us to answer these questions.

- Definition of 'heat': Heat is energy in transit solely as a result of a temperature difference.

- Definition of 'work': Work is energy exchange between system and surroundings due to any phenomenon except a temperature difference.

- Definition of 'temperature': Temperature is a measure of the mean kinetic energy of molecules. Absolute zero (0^oK) is a state of complete motionless of molecules.

- 'Rate': 'Rate' implies an element of speed, how fast an event happens, and time.

- 'System': In thermodynamics, the universe can be divided into two parts. One part is the system, the other part is the rest of the universe called the surroundings. System can be classified as (1) *isolated system* where no mass or energy is transferred across the system boundaries, (2) *closed system* (*system*) where only energy is transferred across the system boundaries, or (3) *open system* (*control volume*) where mass and energy can be transferred across the system boundaries. A system is any designated region of a continuum of fixed mass. The boundaries of a system may be deformable but they always enclose the same mass.
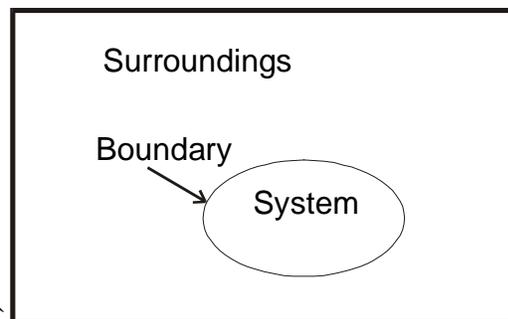
Figure 1.1 Schematic diagram of the "universe", showing a system and the surroundings.

- 'Control volume': A 'control volume' is also any designated region of a continuum except that it may permit matter to cross its boundaries. If the boundaries of a control volume are such that matter may not enter or leave the control volume, the control volume is identical to a system. In these respects, a 'system' is a subset of a 'control volume'.

- 'Equilibrium': 'Equilibrium' means that there are no spatial differences in the variables that describe the condition of the system, also called the 'state' of a system, such as its pressure, temperature, volume, and mass (P, T, V, m), and that any changes which occur do so infinitesimally slowly.

The laws of thermodynamics are applicable only to equilibrium states which means that the state does not really change significantly with time, differences in variables between the state of a system and its surroundings are of infinitesimal magnitude and that within the system itself there are no spatial variations of the variables that determine its state. Using thermodynamics, we can predict the amount of energy needed to change a system from an equilibrium state to another. For example it will take about 75 kJ to change 1 kg of air at 25°C and 1 atm to 100°C and 1 atm. It will take much more energy, about 2257 kJ, to change 1 kg of water at 100°C and 1 atm to water vapor (steam) at the same temperature and pressure.
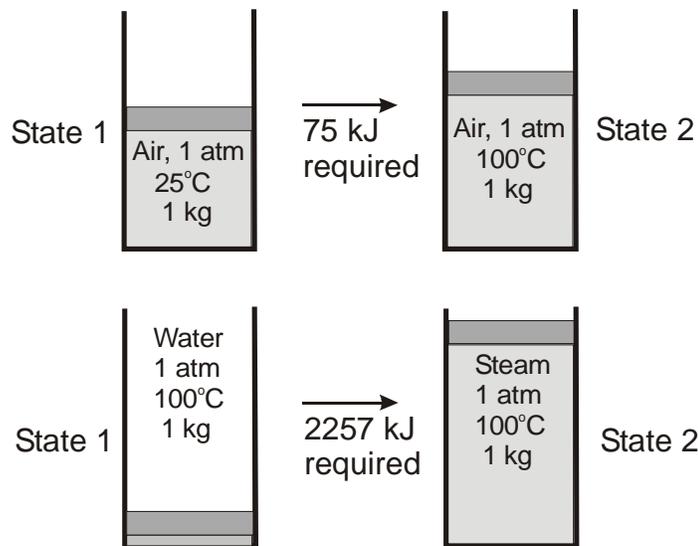
Figure 1.1 Energy required changing air or water from state 1 to state 2.

1.2 Property

A property is a macroscopic characteristic of a system such as pressure, temperature, volume, and mass. At a given state each property has a definite value independent of how the system arrived at that state. The properties of air in state 1 shown in Figure 1.1 are: pressure at 1 atm, temperature at 25°C, and mass of 1 kg.

A property can be classified as extensive or intensive. An extensive property depends on the size of the system while an intensive property is independent on the size of the system. Consider systems (1) and (2) shown in Figure 1.2 both at 100°C and 1 atm containing 2 and 5 kg of steam, respectively.
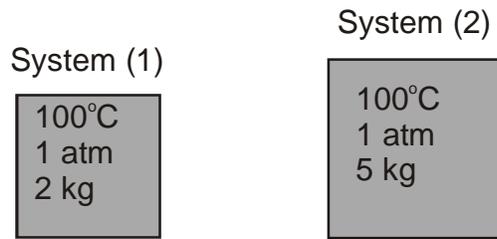
Figure 1.2 Example of intensive and extensive properties.

Temperature, pressure, and specific volume of both systems are intensive properties. Total mass and total volume of each system are extensive property. At 100°C and 1 atm, the specific volume v of each system is 1.674 m³/kg. The mass of system (1) is $m_1 = 2$ kg and that of system (2) is $m_2 = 5$ kg. The total volume of system (1) is $V_1 = m_1v = $ (2 kg)(1.674 m³/kg) = 3.348 m³. The total volume of system (2) is $V_2 = m_2v = $ (5 kg)(1.674 m³/kg) = 8.37 m³. An intensive property might be obtained from an extensive propery by dividing the extensive property by the mass of the system.

1.3 Units

The SI units (Système International d'Unitès, translated Internal System of Units) are used in this text. It happens that seven primary quantities are needed to completely describe all natural phenomena[1]. The decision as to which quantities are primary is arbitrary. The units of the primary quantities and their symbols are listed in Table 1.3-1 and are defined arbitrarily as follows:

Meter: the length of the trajectory traveled by light in a vacuum per 1/299,792,458 s,

Kilogram: the mass of the platinum cylinder deposited at the International Office for Weights and Measures, Sèvres, France,

Second: 9,192,631,770 times the period of radiation in energy level transitions in the fine spectral structure of ^{133}Cs,

Kelvin: 1/273.16 of the triple point temperature of water with naturally occurring amounts of H and O isotopes,

Amperes: the current which, on passing through two parallel infinite conducting wires of negligible cross section, separated by 1 m and in vacuum, induces a force (per unit length) of 2×10^{-7} N/m,

Mole: the amount of a matter containing the number of particles equal to the number of atoms in 0.012 kg of the pure isotope ^{12}C,

Candela: the amount of perpendicular light (luminosity) of $1/60\times10^{-6}$ m² of the surface of an absolute black body at the melting temperature of platinum and a pressure of 101,325 Pa.

Table 1.3-1 The seven primary quantities and their units in SI

Primary quantity	Unit
Length	Meter (m)
Mass	Kilogram (kg)
Time	Second (s)
Temperature	Kelvin (K)
Electric current	Ampere (A)
Amount of matter	Mole (mol)
Amount of light	Candela (cd)

Several of the derived quantities with units are listed in Table 1.3-2. A derived unit is a quantity expressed in terms of a product and/or quotient of two or more primary units.

Table 1.3-2 The derived quantities and their units in SI

Derived quantity	Unit
C_p, specific heat capacity	J/kg·K
E, energy	J = N·m, joule
F, force	N = kg·m/s^2, newton
k, thermal conductivity	W/m·K
p, pressure	Pa = N/m^2, pascal
q, heat transfer rate	W = J/s = kg·m^2/s^3, watt
q'', heat flux	W/m^2 = J/s·m^2
q''', heat generation rate per unit volume	W/m^3
μ, viscosity	N/m^2=kg/s·m
ρ, density	kg/m^3

1.4 Pressure

Any force acting on a surface consists of a component perpendicular to the surface and a component parallel to the surface. These two components are called normal force and shear force as shown in Figure 1.4-1. *Pressure* is defined as a normal force per unit area on which the force acts. The SI pressure unit, N/m^2, is called a *pascal* (Pa). Pressure at any point is a fluid is the same in any direction.

Normal stress = Normal force/A
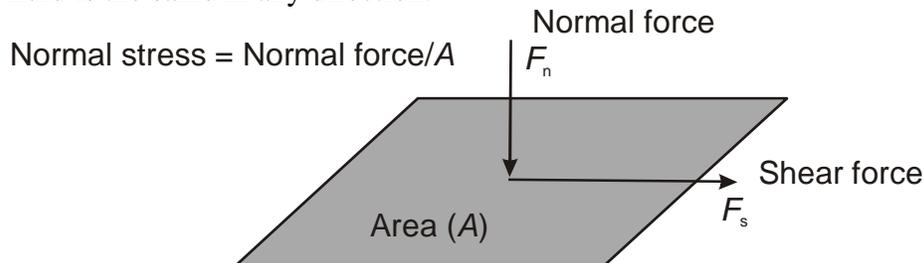
Figure 1.4-1 Normal and parallel components of a force on a surface.

Consider a hole in the wall of a tank or a pipe as shown in Figure 1.4-2. The fluid pressure p may be defined as the ratio F/A, where F is the minimum force that would have to exerted on a frictionless plug in the hole to keep the fluid from emerging[1]
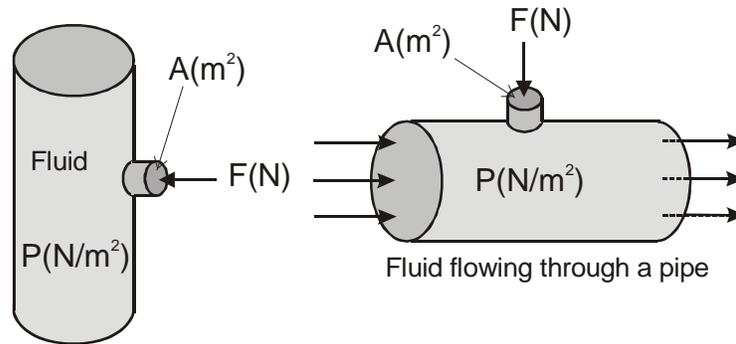
Figure 1.4-2 Fluid pressure in a tank and a pipe.

The pressure at a given position measured relative to absolute zero pressure or absolute vacuum is called the *absolute pressure*. Most pressure-measuring devices are calibrated to read zero in the atmosphere as shown in Figure 1.4-3. These pressure gages indicate the difference between the absolute pressure and the local atmospheric pressure. Pressures below atmospheric pressure are called *vacuum pressures* and are measured by vacuum gages that indicate the difference between the atmospheric pressure and the absolute pressure. Absolute, gage, and vacuum pressures are all positive quantities and are related to each other by

$$P_{gage} = P_{abs} - P_{atm}$$

$$P_{vac} = P_{atm} - P_{abs}$$
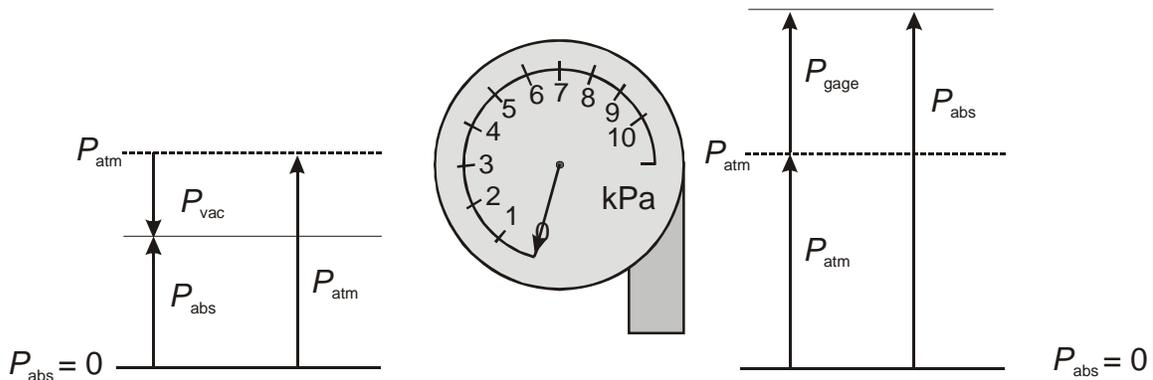
Figure 1.4-3 Absolute, gage, and vacuum pressures.

Two common pressure units are the *bar* and *standard atmosphere*:

1 bar $= 10^5$ Pa $= 0.1$ Mpa $= 100$ kPa

1 atm $= 101,325$ Pa $= 101.325$ kPa $= 1.01325$ bar $= 14.696$ psi

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[1] R. M. Felder and R. W. Rousseau, <u>Elementary Principles of Chemical Processes</u>, Wiley, 2000, p.54.

1.5 Temperature

When two objects are brought into contact and isolated from the surrounding, energy tends to move spontaneously from one to the other. The object that gives up energy is at a *higher* temperature, and the object that receives energy is at a *lower* temperature. We would be able to observe that the electrical resistance of the warmer object decreases with time, and that of the colder block increases with time; eventually there would be no change in the electrical resistances of these objects. The two objects are then in *thermal equilibiurm*. They are at the same *Temperature*. We could then define temperature as a measure of the tendency of an object to spontaneously give up energy to its surroundings.

Any object with at least one measurable property that changes as its temperature changes can be used as a thermometer. Most thermometers operate on the principle of thermal expansion: Materials tend to occupy more volume at a given pressure when they are at a higher temperature. A mercury thermometer is just a convenient device for measuring the volume of a fixed amount of mercury. To define actual units for temperature we arbitrary assign 0 to the freezing point and 100 to the boiling or steam point of water. We then mark these two points on our mercury thermometer, measure off a hundred equally spaced intervals in between, and declare that this thermometer now measures temperature on the Celsius (or centigrade) scale, by definition.

The *Kelvin scale* is an absolute temperature scale that measures temperature from absolute zero instead of from the freezing point of water. The relationship between these two temperature scales is given by

$$T(^{o}C) = T(K) - 273.15 \qquad (1.6\text{-}1)$$

By definition, the *Rankin scale*, is related to the *Kelvin scale* by a factor of 1.8:

$$T(^{o}R) = 1.8T(K) \qquad (1.6\text{-}2)$$

A degree of the same size as that on the Rankine scale is used in the *Fahrenheit scale* but the zero point is shifted according to the relation

$$T(^{o}F) = T(^{o}R) - 459.67 \qquad (1.6\text{-}3)$$

From equations (1.6-1), (1.6-2), and (1.6-3) the Fahrenheit scale can be related to the Celsius scale by

$$T(^{o}F) = 1.8T(^{o}C) + 32$$

Many of the equations of thermodynamics are correct only when you measure temperature on the absolute scale, Kelvin or Rankine. There will be no problem in using the Celcius and Fahrenheit scales when the *difference* between two temperatures is needed.

1.6 Energy Balance

Energy balance is the cornerstone of heat transfer analysis. The first law of thermodynamics is the conservation of energy, which states that energy is neither created nor destroyed. The first law can be written for a system as

$$\delta Q \ = \ \delta W + dE$$

where

$\delta Q =$ heat transfer between the system and the surroundings
$\delta W =$ work exchanged between the system and the surroundings
$dE =$ accumulated energy of the system

The first law postulates the existence of a "*function of state*" called the accumulated energy such that for an adiabatic system ($\delta Q = 0$) the work output is balanced by a reduction in the accumulated energy:

$$dE \ = \ - \delta W$$

While δQ and δW are not themselves a "*function of state*", the difference $\delta Q \ - \ \delta W$ is a *function of state*.
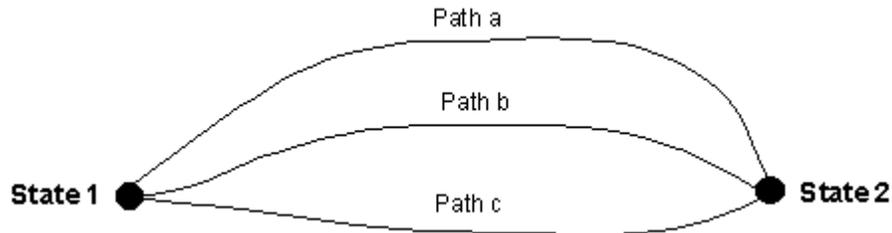
A quantity is a *function of state* when the difference in its values between two states only depends on the initial and final states and not on the paths connecting these two states. The accumulated energy E is a state function so that,

$$\left[E(T_2,P_2,...) - E(T_1,P_1,...)\right]_a \ = \ \left[E(T_2,P_2,...) - E(T_1,P_1,...)\right]_b$$

The differential of E is an exact differential for which the integral from state 1 to state 2 is simply the difference $E(T_2,P_2,...) - E(T_1,P_1,...)$.

$$\int_1^2 dE \ = \ E\big|_1^2 \ = \ E(T_2,P_2,...) - E(T_1,P_1,...)$$

Heat and work are path functions and the differentials of heat and work, δQ and δW, respectively, are nonexact differentials so that $\int_1^2 \delta Q \neq Q_2 - Q_1$ and $\int_1^2 \delta W \neq W_2 - W_1$. The following example will show that work is path dependent.

Example 1.6-1

A gas is contained within a cylinder and piston system shown. Assuming a 'simple' system (expansion and compression work only), calculate the work done by the system in transforming from state P_1, V_1 to state P_2, V_2.
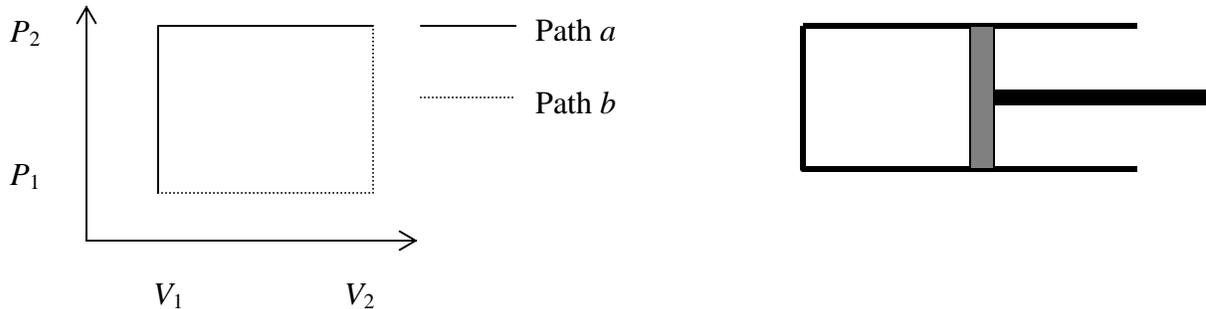
Solution

1. Compute the work using path a with constant volume followed by constant pressure

$$\int_1^2 \delta W = \int_{P_1,V_1}^{P_2,V_2} PdV = \int_{P_1,V_1}^{P_2,V_1} PdV + \int_{P_2,V_1}^{P_2,V_2} PdV = 0 + P_2(V_2 - V_1) = W_a$$

2. Compute the work using path b with constant pressure followed by constant volume

$$\int_1^2 \delta W = \int_{P_1,V_1}^{P_2,V_2} PdV = \int_{P_1,V_1}^{P_1,V_2} PdV + \int_{P_1,V_2}^{P_2,V_2} PdV = P_1(V_2 - V_1) + 0 = W_b$$

Clearly $W_a \neq W_b$

It should be noted that a constant pressure process makes δW a function of state.

$$PdV = d(PV) - VdP$$

$$\int_1^2 \delta W = \int_1^2 d(PV) - \int_1^2 VdP$$

$\int_1^2 d(PV)$ is a function of state while $\int_1^2 VdP$ is not a function of state. For constant P

$$\int_1^2 \delta W = \int_1^2 d(PV) = PV\big|_1^2 = P_2V_2 - P_1V_1 = P_{1 \text{ or } 2}(V_2 - V_1)$$

A function of state is one whose integral of a differential of itself recovers the original function, for example

$$\int dU = U \;;\; \int dP = P \;;\; \int d(PV) = PV$$

First law as a rate equation
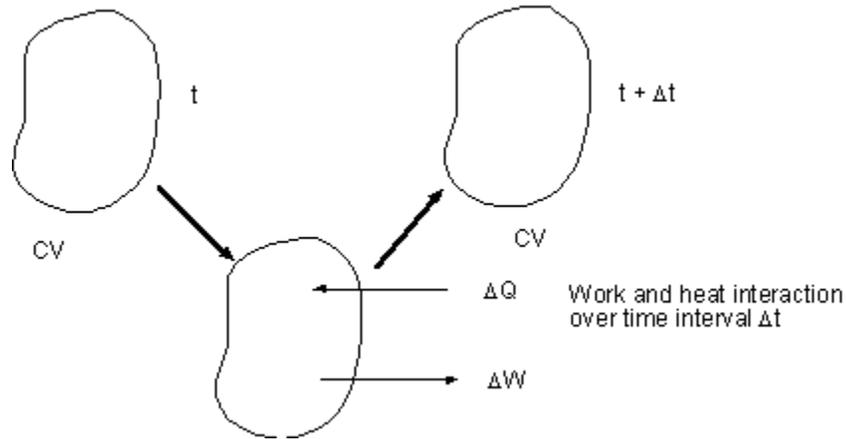
Apply the first law to the system shown over time interval Δt

$$\Delta Q = \Delta W + \Delta E \tag{1.6-1}$$

Divide the above equation by Δt

$$\frac{\Delta Q}{\Delta t} = \frac{\Delta W}{\Delta t} + \frac{\Delta E}{\Delta t} \tag{1.6-2}$$

We are departing from the classical thermodynamic view that deals with equilibrium because time is not a relevant parameter for equilibrium systems. Take the limit of Eq. (1.6-2) as $\Delta t \to 0$

$$\lim_{\Delta t \to 0} \frac{\Delta Q}{\Delta t} = \lim_{\Delta t \to 0} \frac{\Delta W}{\Delta t} + \lim_{\Delta t \to 0} \frac{\Delta E}{\Delta t}$$

$$\frac{\delta Q}{\delta t} = \frac{\delta W}{\delta t} + \frac{dE}{dt} \tag{1.6-3}$$

$$q = \dot{W} + \frac{dE}{dt} \tag{1.6-4}$$

where q = net heat input plus heat generated (W)

$$q = q_{in} - q_{out} + q_{gen} \tag{1.6-5}$$

$\dot{W}$ = net work output (W)

$\dfrac{dE}{dt}$ = accumulated energy change (W)

A control volume must be defined to apply Eqs. (1.6-4) and (1.6-5).

Example 1.6-2. --
Saturated steam at 99.63°C condenses on the outside of a 5-m long, 4-cm-diameter thin horizontal copper tube by cooling liquid water that enters the tube at 25°C at an average velocity of 3 m/s and leaves at 45°C. Liquid water density is 997 kg/m³, c_p of liquid water is 4.18 kJ/kg°C. **(a)** Determine the rate of heat transfer to water. **(b)** If the rate of heat transfer to water is 200 kW, determine the rate of condensation of steam

Solution --

Condensing steam Q

T_i T_e
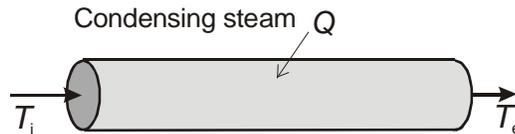
(a) The rate of heat transfer to water is given by

$$\dot{Q} = \dot{m}\, c_p (T_e - T_i)$$

In this equation, the mass flow rate of water is given by

$$\dot{m} = \rho V_{vel} A_{tube}$$

$$\dot{m} = (997 \text{ kg/m}^3)(3 \text{ m/s})(\pi \times 0.02^2 \text{ m}^2) = 3.7586 \text{ kg/s}$$

The heat transfer rate is then

$$\dot{Q} = (3.7586 \text{ kg/s})(4.18 \text{ kJ/kg°C})(45 - 25)°C = \textbf{314.2 kW}$$

(b) If the rate of heat transfer to water is 200 kW, determine the rate of condensation of steam.

We need the enthalpy for saturated liquid and saturated vapor

Temp C	Pressure MPa	Specific Enthalpy kJ/kg	Quality	Phase
99.63	0.1	2675	1	Saturated Vapor
99.63	0.1	417.5	0	Saturated Liquid

The rate of heat transfer to water can also be determined from

$$\dot{Q} = \dot{m}_{steam} (h_g - h_f) \Rightarrow \dot{m}_{steam} = \frac{\dot{Q}}{h_g - h_f}$$

$$\dot{m}_{steam} = \frac{200 \text{ kJ/s}}{(2675 - 417.5) \text{ kJ/kg}} = \textbf{0.0886 kg/s}$$

1-10

Chapter 2

Thermodynamic Relations

2.1 Types of Thermodynamic Properties

The thermodynamic state of a system can be characterized by its properties that can be classified as measured, fundamental, or derived properties. We want to develop relationships to relate the changes in the fundamental and derived properties in terms of the measured properties that are directly accessible from laboratory measurements. Some of the measured properties are P, v, T, composition, c_p, and c_v. The small letters are used to denote specific quantities for example v is specific volume.

The fundamental properties are internal energy u and entropy s. These properties arrive from the first and second law of thermodynamics. The first law states that energy is conserved, and the second law states that entropy of the universe always increases.

The derived properties are defined to facilitate the energy balance of systems in which the combination of internal energy and other properties often occurs. In open systems, the mass that crosses the boundary between the surroundings and the system always contributes to two terms in the energy balance: internal energy and flow work (Pv). For convenient we can define an enthalpy (h) as

$$h = u + Pv \qquad\qquad (2.1\text{-}1a)$$

In terms of the total enthalpy H, we have

$$H = U + PV \qquad\qquad (2.1\text{-}1b)$$

We can then make an enthalpy balance for an open system in which the flow work is included in the enthalpy term. Figure 2.1-1 shows a raindrop created from the surrounding super saturated vapor in the atmosphere. Not only the energy U of the raindrop is needed but also some additional energy, equal to PV, is required to push the atmosphere out of the way to make room for the drop.

A raindrop with volume
V and internal energy U
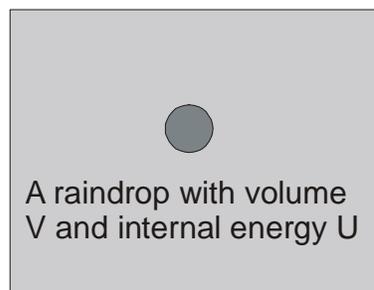
Figure 2.1-1 An energy of $U + PV$ is required to create a raindrop.

Enthalpy is the total energy we would need, to create a system out of nothing and put it in an environment with constant pressure P. Or, if we could completely annihilate a system, H is

the energy we could recover: the system's energy plus the work done by the collapsing atmosphere.

However, we usually are not interested in the total energy needed or the total energy that can be recovered from a system. We will be more interested in the work involved in a system. For isothermal surroundings, the system can extract heat from the surroundings for free, so the work required to create the system from nothing is equal to the internal energy minus the heat received. And if we annihilate the system, we generally cannot recover all its energy as work since we have to dispose of its entropy by dumping some heat into the surroundings. Therefore it is more convenient to define the *Helmholtz free energy*, A, for an environment at constant temperature T

$$A = U - TS \tag{2.1-2}$$

A is the energy that must be provided as work if we create the system out of nothing. The heat extracted from the surroundings is $T\Delta S = T(S_f - S_i) = TS_f$ where S_f is the system final entropy and S_i the system zero initial entropy. If we annihilate a system with initial entropy S_i, A is the amount of recovered work, since we have to dump some heat, equal to TS_i, into the environment to get rid of the system's entropy.

Equation (2.1-2) includes all work, even the work done by the system's surroundings. If the system is in an isothermal and isobaric environment, it is more convenient to use the *Gibbs free energy*

$$G = U - TS + PV \tag{2.1-3}$$

Gibbs free energy is the work required to create a system from nothing in an environment with constant P and constant temperature T.

We usually are more interested in the change in states of a system rather than its creation or annihilation. We then want to look at the changes in A and G. The change in A at constant temperature is given by

$$\Delta A = \Delta U - T\Delta S = Q + W - T\Delta S \tag{2.1-4}$$

In this expression Q is the heat added and W is the work done on the system. If the process is reversible then $Q = T\Delta S$ and the change in A is precisely equal to the work done on the system. If the process is irreversible then $Q < T\Delta S$ and $\Delta A < W$, the change in A is less than the work done on the system.

For an environment with constant P and constant temperature T, the change in G is given by

$$\Delta G = \Delta U - T\Delta S + P\Delta V = Q + W - T\Delta S + P\Delta V \tag{2.1-5}$$

For any process we have

$$Q - T\Delta S \leq 0 \text{ (equal sign for reversible processes)} \tag{2.1-6}$$

The work term W consists of the work done by the environment, $-P\Delta V$, and any "other" work done on the system.

$$W = -P\Delta V + W_{other} \qquad (2.1\text{-}7)$$

Substituting equations (2.1-6) and (2.1-7) into equation (2.1-5) we obtain

$$\Delta G \leq W_{other} \text{ at constant } T, P \qquad (2.1\text{-}8)$$

Example 2.1-1. --
Determine the electrical work required to produce one mole of hydrogen in the electrolysis of liquid water at 298°K and 1 atm. The chemical reaction is

$$H_2O(l) \rightarrow H_2(g) + 0.5O_2(g)$$
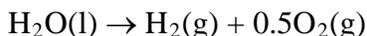
Data (at 298°K and 1 atm): $\Delta H = 286$ kJ for this reaction, $S_{H2O} = 70$ J/°K, $S_{H2} = 131$ J/°K, and $S_{O2} = 205$ J/°K.

Solution --

$$G = H - TS$$

At constant T we have

$$\Delta G = \Delta H - T\Delta S$$

The change in system entropy is given by

$$\Delta S = S_{H2} + 0.5S_{O2} - S_{H2O} = 131 + 0.5(205) - 70 = 163.5 \text{ J/°K}$$

The change in G is then

$$\Delta G = 286 \text{ kJ} - (298°K)(163.5 \text{ J/°K}) = \textbf{237 kJ}$$

This is the amount of energy in terms of electrical work required to produce one mole of hydrogen by electrolysis.

If we burn one mole of hydrogen, the amount of heat we would get is 286 kJ. If we can combine one mole of hydrogen and half a mole of oxygen in a fuel cell to produce water we can extract 237 kJ of electrical work. The difference $\Delta H - \Delta G = T\Delta S = 49$ kJ is the waste heat that must be expel by the fuel cell to get rid of the excess entropy that was in the gases. Therefore the maximum efficiency, $\varepsilon_{fuel\ cell}$, of the fuel cell is

$$\varepsilon_{fuel\ cell} = 237/286 = 0.829$$

This efficiency is higher than the 40% efficiency of electrical power plants.

Example 2.1-2. ---
In a hydrogen fuel cell shown in Figure 2.1-2, hydrogen and oxygen gas pass through porous electrodes and react to form water. Electrons are released at the anode (negative electrode) and deposited at the cathode (positive electrode). The overall reaction is

$$H_2(g) + 0.5O_2(g) \rightarrow H_2O(l)$$
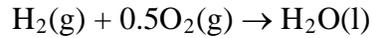
Calculate the voltage of the cell.

Data (at 298°K and 1 atm): $\Delta G = -237$ kJ for this reaction.
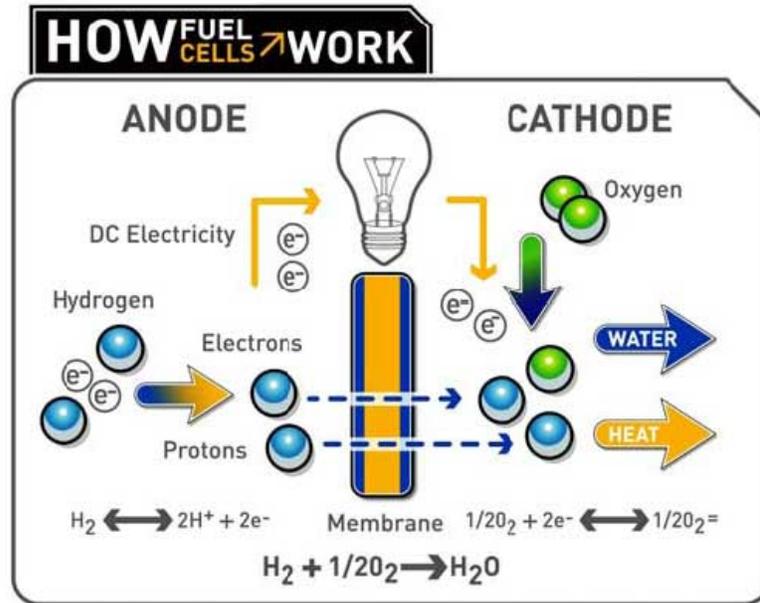
Figure 2.1-2 A hydrogen fuel cell

Solution --

In a hydrogen fuel cell[1], the steps of the chemical reaction are

Anode Reaction: $H_2 \Rightarrow 2H^+ + 4e^-$

Cathode Reaction: $0.5O_2 + 2H^+ + 2e^- \Rightarrow H_2O$

Two electrons are pushed through the circuit each time the full reaction occurs. The electrical work produced per electron is

237 kJ/$(2 \times 6.02 \times 10^{23}) = 1.97 \times 10^{-19}$ J $= 1.23$ eV

(Note: 1 eV $= 1.602 \times 10^{-19}$ J)

Since 1 volt is the voltage needed to give each electron 1 eV of energy, so the fuel cell has a voltage of 1.23 V.

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[1] Schroeder, D. V., <u>An Introduction to Thermal Physics</u>, Addision Wesley Longman, 2000

2.2 Fundamental Property Relations

The first law for a closed system undergoing reversible process with only PV work is given by

$$dU = \delta Q_{rev} + \delta W_{rev}$$

From the second law, $\delta Q_{rev} = TdS$, the first law can be written as

$$dU = TdS - pdV \tag{2.2-1}$$

We can write the change in internal energy in terms of two independent variables S and V, that is, $U = U(S, V)$:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{2.2-2}$$

Comparing equations (2.2-1) and (2.2-2) we have

$$T = \left(\frac{\partial U}{\partial S}\right)_V \text{ and } p = -\left(\frac{\partial U}{\partial V}\right)_S \tag{2.2-3}$$

The four functions U, H, A, and G are collectively called *thermodynamic potentials*. The expression represented by $U = U(S, V)$ results in the partial derivatives of the thermodynamic potentials corresponding to thermodynamic properties T and p as defined in Eq. (2.2-3). While U can be a function of any two properties, no other grouping of independent properties x and y, $U = U(x, y)$, allows us to write partial derivatives in terms of thermodynamic properties as given by Eq. (2.2-3). The three properties $\{U, S, V\}$ form a **fundamental grouping**.

Similarly, the change in enthalpy ($H = U + pV$) is given by

$$dH = dU + d(pV) = TdS - pdV + pdV + Vdp$$

$$dH = TdS + Vdp \tag{2.2-4}$$

The change in enthalpy in terms of two independent variables S and p is

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial p}\right)_S dp \tag{2.2-5}$$

Comparing equations (2.2-4) and (2.2-5) we have

$$T = \left(\frac{\partial H}{\partial S}\right)_P \text{ and } V = \left(\frac{\partial H}{\partial p}\right)_S \tag{2.2-6}$$

We have two more relations for the change in *Helmholtz free energy*, dA, and the change in *Gibbs free energy*, dG,

$$dA = -SdT - pdV \qquad (2.2\text{-}7)$$

$$dG = -SdT + VdpP \qquad (2.2\text{-}8)$$

The fundamental groupings $\{A, T, V\}$ and $\{G, T, p\}$ result in

$$S = -\left(\frac{\partial A}{\partial T}\right)_V \text{ and } p = -\left(\frac{\partial A}{\partial V}\right)_T \qquad (2.2\text{-}9)$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \text{ and } V = \left(\frac{\partial G}{\partial p}\right)_T \qquad (2.2\text{-}10)$$

The grouping can be obtained from the following diagram where there properties at a corner form a fundamental grouping, for example $\{A, T, V\}$ and $\{G, T, p\}$.

Great **p**hysicists **H**ave **S**tudy
Under **V**ery **A**ble **T**eachers

Thermodynamic properties can then be obtained from the partial derivative of the thermodynamics potentials. Temperature can be obtained from the derivative of H or U. In both cases, the variable opposite T in the diagram will be in the denominator of the derivative and the remaining variable belong to the grouping will be the variable keeping constant.

Using this rule, we have

$$T = \left(\frac{\partial U}{\partial S}\right)_V \text{ and } T = \left(\frac{\partial H}{\partial S}\right)_P$$

Similarly, p can be expressed in terms of the partial derivative of thermodynamic potentials using the following diagram. Note the minus sign since V is in the negative direction of P.

2-6

$$p = -\left(\frac{\partial U}{\partial V}\right)_S \text{ and } p = -\left(\frac{\partial A}{\partial V}\right)_T$$

Similarly, we have
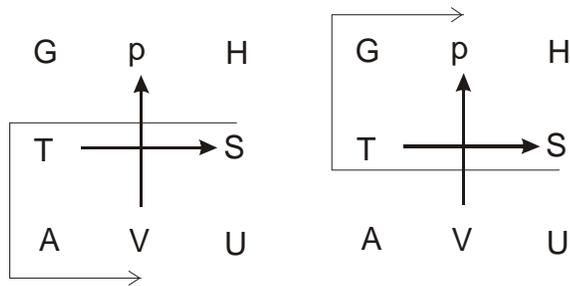
$$S = -\left(\frac{\partial A}{\partial T}\right)_V \text{ and } S = -\left(\frac{\partial G}{\partial T}\right)_P$$

and
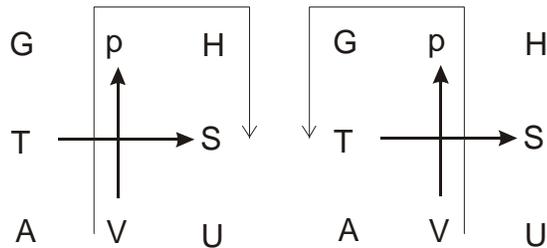
$$V = \left(\frac{\partial H}{\partial p}\right)_S \text{ and } V = \left(\frac{\partial G}{\partial p}\right)_T$$

When we study phase equilibrium, the Gibbs free energy will be use frequently to obtain the relations between the measured properties.

Example 2.2-1.[2] --

For the Van Der Waals isotherm shown in the following figure, show that the saturation pressure can be determined by locating the horizontal, two-phase segment of the isotherm so that two equal areas are enclosed between it and the Van de Waals curve.
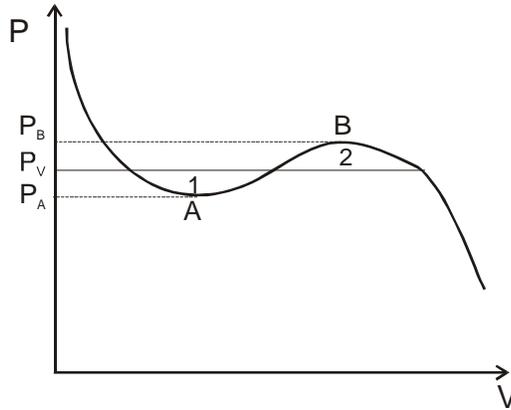
Solution --
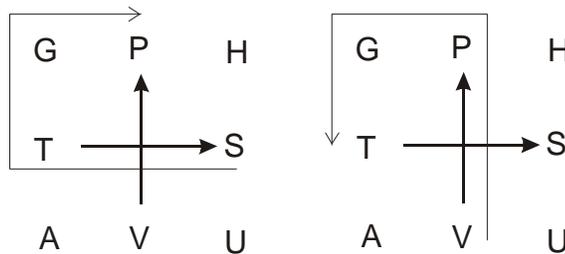
From the grouping $\{G, T, P\}$, we have $G = G(T, P)$, therefore

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP = -SdT + VdP$$

Along an isotherm of the equation of state, $dT = 0$, therefore $\Delta G = \int_{P_1}^{P_2} VdP$

At the saturation pressure $\Delta G = G^V - G^L = 0$, we have

$$\Delta G = G^V - G^L = \int_{P_V}^{P_A} VdP + \int_{P_A}^{P_V} VdP + \int_{P_V}^{P_B} VdP + \int_{P_B}^{P_V} VdP = 0$$

Since **area (1)** $= -\int_{P_V}^{P_A} VdP - \int_{P_A}^{P_V} VdP$, and **area (2)** $= \int_{P_V}^{P_B} VdP + \int_{P_B}^{P_V} VdP$, the saturation pressure can be determined by locating the horizontal, two-phase segment of the isotherm so that two equal areas are enclosed between it and the Van Der Waals curve.

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[2] Kyle, B.G., Chemical and Process Thermodynamics, Prentice Hall, 1999

Maxwell Relations

The fundamental property relations are written so that the left-hand side is the differential of a state function as follow

$$dU = TdS - PdV \tag{8.3-1a}$$

$$dH = TdS + VdP \tag{8.3-1b}$$

$$dA = -SdT - PdV \tag{8.3-1c}$$

$$dG = -SdT + VdP \tag{8.3-1d}$$

The exact differential of a function $z = z(x, y)$ is written as

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = Mdx + Ndy \tag{8.3-2}$$

In this expression, we have

$$M = \left(\frac{\partial z}{\partial x}\right)_y \text{ and } N = \left(\frac{\partial z}{\partial y}\right)_x$$

A useful property of exact differential is that the order of partial differentiation does not matter. That is

$$\left(\frac{\partial}{\partial y}\left[\frac{\partial z}{\partial x}\right]_y\right)_x = \left(\frac{\partial}{\partial x}\left[\frac{\partial z}{\partial y}\right]_x\right)_y \tag{8.3-2}$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{8.3-3}$$

Applying equation (8.3-3) to equation (8.3-1a) we get

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{8.3-4a}$$

This relation is called the Maxell relation. Similarly, from the other three fundamental property relationships we have

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P, \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \text{ and } -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \tag{8.3-4b,c,d}$$

The Maxwell relations can be used to calculate entropy from *PVT* data. The derivative relations of equations (8.3-1a)–(8.3-1d) then enable us to calculate *U*, *H*, *A*, and *G*. The Maxwell relations can also be obtained from the diagram
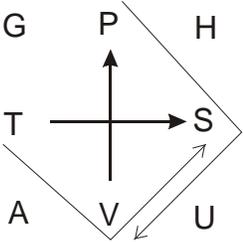
$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

The sign of the derivative is obtained from multiplication of the individual sign of each variable in a group. For *TVS* the sign is $(-)(-)(+) = +$, for *PSV* the sign is $(+)(+)(-) = -$. Similarly, for the other three Maxwell relations we have

$$\Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\Rightarrow -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

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Chapter 2

2.3 Equations of State

In the calculations of energy, enthalpy, and entropy of a substance we need an accurate representation of the relationship among pressure, volume, and temperature. Besides the tabular and graphical presentations of the *p-v-T* relationship, analytical formulations, called *equation of state*, constitute another way of expressing the *p-v-T* relationship. The equations of state are convenient for performing the mathematical operations required to calculate *u*, *h*, *s*, and other thermodynamic properties. We will discuss the virial, Van de Walls, and Soave-Redlick-Kwong (SRK) equation of states.

2.3-1 The Virial Equation of State

The virial equation of state can be derived from the principle of statical mechanics to relate the *p-v-T* behavior of a gas to the forces between molecules. A virial equation of state expresses the quantity $\dfrac{p\bar{v}}{RT}$ as a power series in the inverse of molar volume $\bar{v}$.

$$Z = \frac{p\bar{v}}{\bar{R}T} = 1 + \frac{B(T)}{\bar{v}} + \frac{C(T)}{\bar{v}^2} + \frac{D(T)}{\bar{v}^3} + \ldots \tag{2.3-1}$$

In this equation, *B*, *C*, and *D* are called *virial coefficient* and are functions of temperature. For a truncated virial equation with two terms we have

$$\frac{p\bar{v}}{\bar{R}T} = 1 + \frac{B(T)}{\bar{v}} \tag{2.3-2}$$

In this equation, $B(T)$ can be estimated from the following equations:

$$B(T) = \frac{\bar{R}T_c}{p_c}(B_0 + \omega B_1) \tag{2.3-3}$$

$$B_0 = 0.083 - \frac{0.422}{T_R^{1.6}}, \qquad B_1 = 0.139 - \frac{0.172}{T_R^{4.2}}$$

In equation (2.3-3), ω is the Pitzer acentric factor, which is a parameter reflecting the geometry and polarity of a molecule. In the limiting case where there are no interactions between the molecules, all the virial coefficients are equal to zero. Eq. (2.3-1) becomes

$$Z = \frac{p\bar{v}}{\bar{R}T} = 1 \tag{2.3-4}$$

Eq. (2.3-4) is the ideal gas equation of state. Example 2.3-1 will illustrate the use of the virial equation of state with one virial coefficient.

Example 2.3-1 --
A three-liter tank contains two gram-moles of nitrogen at $-150.8^{\circ}C$. Estimate the tank pressure using the ideal gas equation of state and then using the virial equation of state truncated after the second term. Taking the second estimate to be correct, calculate the percentage error that results from the use of the ideal gas equation at the system conditions. Data for nitrogen: $T_c = 126.2$ K, $p_c = 33.5$ atm, and $\omega = 0.040$[12].

Solution ---

$$\bar{v} = 3.0 \text{ L}/2 \text{ mol} = 1.5 \text{ L/mol}, \ T = -150.8 + 273.2 = 122.4 \text{ K}$$

From the ideal gas law,

$$p_{\text{ideal}} = \frac{\bar{R}T}{\bar{v}} = \frac{(0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(122.4 \text{ K})}{1.50 \text{ L/mol}} = \textbf{6.696 atm}$$

From the truncated virial equation,

$$\frac{p\bar{v}}{\bar{R}T} = 1 + \frac{B(T)}{\bar{v}}$$

$$T_R = 122.4/126.2 = 0.970$$

$$B_0 = 0.083 - \frac{0.422}{T_R^{1.6}} = 0.083 - \frac{0.422}{0.97^{1.6}} = -0.360$$

$$B_1 = 0.139 - \frac{0.172}{T_R^{4.2}} = B_1 = 0.139 - \frac{0.172}{0.97^{4.2}} = -0.0566$$

$$B(T) = \frac{\bar{R}T_c}{p_c}(B_0 + \omega B_1)$$

$$B(T) = \frac{(0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(126.2 \text{ K})}{33.5 \text{ atm}}[-0.36 + (0.04)(-0.0566)] = -0.112 \text{ L/mol}$$

$$p = \frac{\bar{R}T}{\bar{v}}\left(1 - \frac{0.112}{1.5}\right) = \frac{(0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(122.4 \text{ K})}{1.50 \text{ L/mol}}(0.9253)$$

$$\textbf{\textit{p} = 6.196 atm}$$

Error in using ideal gas law

$$\varepsilon = \frac{p_{ideal} - p}{p} \times 100 = 8.07 \text{ \%}$$

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[12] Felder R. M., Rousseau R. W., <u>Elementary Principles of Chemical Processes</u>, Wiley, 2005, pg. 202

2.3-2 The Van de Walls Equation of State

We will use the Van de Walls equation of state to illustrate the evaluation of thermodynamic properties. Both the Van de Walls and the SRK equations of state have two adjustable constants but the Van de Walls equation is simpler. The Van de Walls equation of state is

$$P = \frac{\overline{R}T}{\overline{v} - b} - \frac{a}{\overline{v}^2} \tag{2.3-5}$$

In this equation, the constant b accounts for the finite volume occupied by the molecules and the term $\dfrac{a}{\overline{v}^2}$ accounts for the attractive forces between molecules.
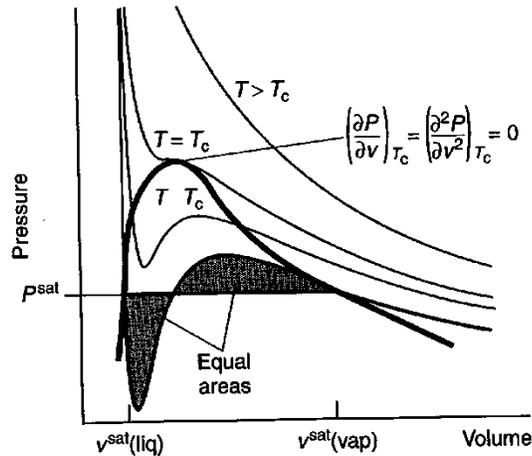
Figure 2.3-1 Isotherms from the Van der Waals equation.

The Van der Waals parameters a and b can be determined from the critical properties since there is an inflection point at the critical isotherm as shown in Figure 2.3-1. At the critical point we have

$$\left(\frac{\partial P}{\partial \overline{v}} \right)_{T_c} = \left(\frac{\partial^2 P}{\partial \overline{v}^2} \right)_{T_c} = 0 \tag{2.3-6}$$

The isotherm passing through the critical point is given by

$$P = \frac{\overline{R}T_c}{\overline{v} - b} - \frac{a}{\overline{v}^2}$$

The first and second derivatives of P with respect to v are given by

$$\left(\frac{\partial P}{\partial \overline{v}} \right)_{T_c} = - \frac{\overline{R}T_c}{\left(\overline{v}_c - b \right)^2} + \frac{2a}{\overline{v}_c^3} = 0 \tag{2.3-6a}$$

$$\left(\frac{\partial^2 P}{\partial \bar{v}^2}\right)_{T_c} = \frac{2\bar{R}T_c}{\left(\bar{v}_c - b\right)^3} - \frac{6a}{\bar{v}_c^4} = 0 \tag{2.3-6b}$$

We can solve the two equations (2.3-6a) and (2.3-6b) for the two unknowns a and b. Multiplying equation (2.3-6a) by 2 and equation (2.3-6b) by $(\bar{v}_c - b)$ and add them together we get

$$\frac{4a}{\bar{v}_c^3} - \frac{6a}{\bar{v}_c^4}(\bar{v}_c - b) = 0 \tag{2.3-7}$$

$$4a\bar{v}_c - 6a\bar{v}_c + 6ab = 0 \Rightarrow \bar{v}_c = 3b \tag{2.3-8}$$

Substituting $b = \bar{v}_c/3$ into equation (2.3-6a) and solving for a gives

$$a = \frac{9}{8}\bar{v}_c \bar{R} T_c$$

At the critical point we have

$$P_c = \frac{\bar{R}T_c}{\bar{v}_c - b} - \frac{a}{\bar{v}_c^2} \tag{2.3-9}$$

We can use equation (2.3-9) to solve for $\bar{v}_c$ in terms of critical temperature and critical pressure. Substituting $a = \dfrac{9}{8}\bar{v}_c \bar{R}T_c$ and $b = \bar{v}_c/3$ into equation (2.3-9) we obtain

$$P_c = \frac{3\bar{R}T_c}{2\bar{v}_c} - \frac{9\bar{v}_c \bar{R}T_c}{8\bar{v}_c^2} = \frac{3\bar{R}T_c}{2\bar{v}_c}\left(\frac{3}{2} - \frac{9}{8}\right) = \frac{3\bar{R}T_c}{8\bar{v}_c}$$

Solving for $\bar{v}_c$ in terms of P_c and T_c we have

$$\bar{v}_c = \frac{3\bar{R}T_c}{8P_c}$$

Hence

$$a = \frac{9}{8}\bar{v}_c \bar{R} T_c = \frac{27}{64}\frac{(\bar{R}T_c)^2}{P_c}$$

Using $\bar{R} = 8.314$ J/(mol·°K) $= 8.314\times10^{-5}$ m³·bar/(mol·°K) and for propane, $T_c = 369.9$°K, $P_c = 42.46$ bar, we have

$$a = \frac{27}{64}\frac{(\bar{R}T_c)^2}{P_c} = \frac{27}{64}\frac{(8.314\times10^{-5}\times369.9)^2}{42.46} = 9.36\times10^{-6} \text{ m}^6\text{·bar/mol}$$

Example 2.3-2.[3] --
One mole of propane gas is to be expanded from 0.001 m³ to 0.040 m³ while in contact with a heating bath at 100°C. The expansion is not reversible. The heat extract from the bath is 600 J. Determine the work for the expansion using the Van der Waals equation of state.

$$P = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}^2}$$

Solution --

From the first law we have $\Delta u = q + w$. Since the amount of heat transfer q is given (600 J/mol), we only need to evaluate Δu to find w.

We write u as a function of the independent variables T and v since the values of these two variables are given in the problem

$$u = u(T, v) \Rightarrow du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

Since the process occurs at constant T, $dT = 0$, we have

$$du = \left(\frac{\partial u}{\partial v}\right)_T dv$$

We need to express $\left(\frac{\partial u}{\partial v}\right)_T$ in terms of measurable properties by using the diagram
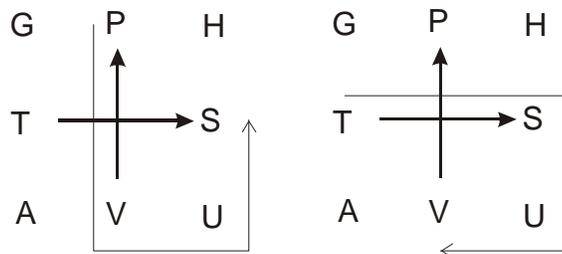
$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv = Tds - Pdv$$

Therefore

$$du = \left(\frac{T\partial s - P\partial v}{\partial v}\right)_T dv = \left[T\left(\frac{\partial s}{\partial v}\right)_T - P\right]dv$$

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[3] Koresky M.D., Engineering and Chemical Thermodynamics, Wiley, 2004, pg. 222
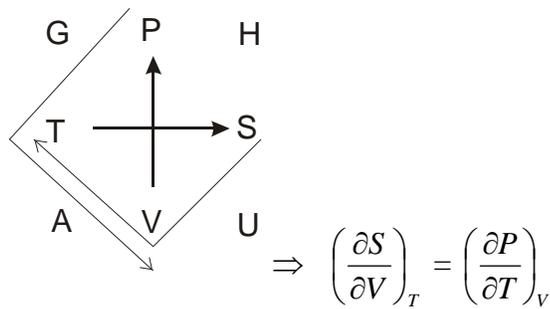
$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Using the Maxwell relation we have $\left(\dfrac{\partial s}{\partial v}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_v$, the change in internal energy can now be expressed solely in terms of measurable properties:

$$\mathrm{d}u = \left[T\left(\frac{\partial P}{\partial T}\right)_v - P \right]\mathrm{d}v$$

In terms of molar quantities

$$\mathrm{d}\bar{u} = \left[T\left(\frac{\partial P}{\partial T}\right)_v - P \right]\mathrm{d}\bar{v}$$

From the Van der Waals equation: $\qquad P = \dfrac{\bar{R}T}{\bar{v}-b} - \dfrac{a}{\bar{v}^2}$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{\bar{v}-b} \Rightarrow \left[T\left(\frac{\partial P}{\partial T}\right)_v - P \right] = \frac{a}{\bar{v}^2}$$

Hence

$$\Delta\bar{u} = \int_{0.001m^3}^{0.04m^3} \left[T\left(\frac{\partial s}{\partial \bar{v}}\right)_T - P \right]\mathrm{d}\bar{v} = \int_{0.001m^3}^{0.04m^3} \frac{a}{\bar{v}^2}\,\mathrm{d}\bar{v} = -\frac{a}{\bar{v}}\bigg|_{0.001m^3}^{0.04m^3}$$

Using $\bar{R} = 8.314$ J/(mol·°K) $= 8.314\times10^{-5}$ m³·bar/(mol·°K) and for propane, $T_c = 369.9$°K, $P_c = 42.46$ bar, we have

$$a = \frac{27}{64}\frac{(\bar{R}T_c)^2}{P_c} = \frac{27}{64}\frac{(8.314\times10^{-5}\times369.9)^2}{42.46} = 9.36\times10^{-6}\ \text{m}^6\text{·bar/mol}$$

Therefore

$$\Delta\bar{u} = -9.36\times10^{-6}\left(\frac{1}{0.04} - \frac{1}{0.001}\right) = 913\times10^{-5}\ \text{m}^3\text{·bar/mol}$$

$$\Delta \bar{u} = 913 \text{ J/mol}$$

The required work for the expansion is

$$w = \Delta \bar{u} - q = 913 - 600 = \textbf{313 J/mol}$$

2.3-3 Soave-Redlick-Kwong (SRK) Equation

The Soave-Redlick-Kwong (SRK) equation belongs to a class of cubic equations of state because, when expanded, they yield third-degree equations for the specific volume. The SRK equation of state is

$$p = \frac{\bar{R}T}{\bar{v} - b} - \frac{\alpha a}{\bar{v}(\bar{v} + b)} \tag{2.3-10}$$

In this equation, the parameter a, b, and α are empirical functions of the critical temperature and pressure, the Pitzer acentric factor, and the system temperature. The following correlations can be used to estimate these parameters:

$$a = 0.42747 \frac{\left(\bar{R}T_c\right)^2}{p_c}$$

$$b = 0.08664 \frac{\bar{R}T_c}{p_c}$$

$$m = 0.48508 + 1.55171\omega - 0.1561\omega^2$$

$$\alpha = \left[1 + m\left(1 - \sqrt{T_R}\right)\right]^2$$

Example 2.3-3 --
A gas cylinder with a volume of 2.50 m^3 contains 1.00 kmol of carbon dioxide at $T = 300$ K. Use the SRK equation of state to estimate the gas pressure in atm. Data for carbon dioxide: $T_c = 304.2$ K, $p_c = 72.9$ atm, and $\omega = 0.225$[4].

Solution --

$$T_R = 300/304.2 = 0.9862$$

$$\bar{R}T_c = (0.08206 \text{ L·atm/mol·K})(304.2 \text{ K}) = 24.96 \text{ L·atm/mol}$$

$$a = 0.42747 \frac{\left(\bar{R}T_c\right)^2}{p_c} = 0.42747 \frac{\left(24.96 \text{ L·atm/mol}\right)^2}{72.9 \text{ atm}} = 3.6539 \text{ L}^2\text{·atm/mol}^2$$

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[4] Felder R. M., Rousseau R. W., Elementary Principles of Chemical Processes, Wiley, 2005, pg. 203

$$b = 0.08664 \frac{\bar{R}T_c}{p_c} = 0.08664 \frac{24.96 \text{ L·atm/mol}}{72.9 \text{ atm}} = 0.0297 \text{ L/mol}$$

$$m = 0.48508 + 1.55171\omega - 0.1561\omega^2 = 0.8263$$

$$\alpha = \left[1 + m\left(1 - \sqrt{T_R}\right)\right]^2 = \left[1 + 0.8263\left(1 - \sqrt{0.9862}\right)\right]^2 = 1.0115$$

$$p = \frac{\bar{R}T}{\bar{v} - b} - \frac{\alpha a}{\bar{v}\left(\bar{v} + b\right)}$$

$$p = \frac{(0.08206 \text{ L·atm/mol·K})(300 \text{ K})}{(2.50 - 0.0297) \text{ L/mol}} - \frac{(1.0115)(3.654 \text{ L}^2 \cdot \text{atm/mol}^2)}{(2.50 \text{ L/mol})(2.50 + 0.0297) \text{ L/mol}}$$

p = 9.38 atm

Example 2.3-4 --
A stream of propane at temperature $T = 423$ K and pressure p(atm) flows at a rate of 100.0 kmol/hr. Use the SRK equation of state to estimate the volumetric flow rate $\dot{V}_{flow}$ of the stream for $p = 0.7$ atm, 7 atm, and 70 atm. In each case, calculate the percentage differences between the predictions of the SRK equation and the ideal gas equation of state. Data for propane: $T_c = 369.9$ K, $p_c = 42.0$ atm, and $\omega = 0.152$[5].

Solution --

We first calculate a, b, and α from the following expressions:

$$a = 0.42747 \frac{\left(\bar{R}T_c\right)^2}{p_c}, \qquad\qquad b = 0.08664 \frac{\bar{R}T_c}{p_c}$$

$$m = 0.48508 + 1.55171\omega - 0.1561\omega^2, \qquad \alpha = \left[1 + m\left(1 - \sqrt{T_R}\right)\right]^2$$

The SRK equation is written in the form

$$f(\bar{v}) = p - \frac{\bar{R}T}{\bar{v} - b} + \frac{\alpha a}{\bar{v}\left(\bar{v} + b\right)} = 0$$

$\bar{v}$ is then calculated using Newton's method: $\bar{v} = \bar{v} - \dfrac{f(\bar{v})}{f'(\bar{v})} = \bar{v} - d\bar{v}$, where

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[5] Felder R. M., Rousseau R. W., <u>Elementary Principles of Chemical Processes</u>, Wiley, 2005, pg. 204

$$f'(\bar{v}) = \frac{\bar{R}T}{(\bar{v}-b)^2} - \frac{\alpha a(2\bar{v}+b)}{\left[\bar{v}(\bar{v}+b)\right]^2}$$

The initial value for $\bar{v}$ is obtained from ideal gas law: $\bar{v}_{ideal} = \dfrac{\bar{R}T}{p}$. The iteration process stops when $\bar{v}/d\bar{v}$ is less than 0.0001. The percentage difference between $\bar{v}_{SRK}$ and $\bar{v}_{ideal}$ is

$$\frac{\bar{v}_{ideal} - \bar{v}}{\bar{v}} \times 100\%$$

Once $\bar{v}$ is known for a given p, the volumetric flow rate corresponding to a molar flow rate of 100.0 kmol/hr is obtained as

$$\dot{V}_{flow} \text{ (m}^3\text{/hr)} = \bar{v} \text{ (L/mol)} \frac{10^3 \text{ mol}}{\text{kmol}} \frac{1 \text{ m}^3}{10^3 \text{ L}} (100 \text{ kmol/hr}) = 100 \bar{v} \text{ (L/mol)}$$

The calculations are performed using the following Matlab program:

```
% Example 2.4-3
Tc=369.9; % K
pc=42.0; % atm
w=0.152; % acentric factor
Rg=0.08206; % L*atm/(mol*K)
T=423; % K
p=input('p(atm) = ');
Tr=T/Tc;
a=0.42747*(Rg*Tc)^2/pc;
b=0.08664*(Rg*Tc)/pc;
m = 0.48508 + 1.55171*w - 0.1561*w^2;
alfa=(1+m*(1-Tr^0.5))^2;
videal=Rg*T/p;v=videal;
for i=1:20;
   f=p-Rg*T/(v-b)+alfa*a/(v*(v+b));
   df=Rg*T/(v-b)^2-alfa*a*(2*v+b)/(v*(v+b))^2;
   dv=f/df;
   v=v-dv;
   if abs(dv/v)<1e-4, break, end
end
Di=(videal-v)/v*100;
Flowrate=100*v;
fprintf('videal   =   %6.2f,   v(L/mol)   =   %6.2f,   Percentage   Difference   =
%6.3f\n',videal,v,Di)
fprintf('Flow rate (m3/hr) = %6.1f\n', Flowrate)
```

```
>> ex3d4d5
p(atm) = .7
videal = 49.588, v(L/mol) = 49.406, Percentage Difference =   0.37
Flow rate (m3/hr) = 4940.6

>> ex3d4d5
p(atm) = 7
videal =  4.959, v(L/mol) =  4.775, Percentage Difference =   3.86
Flow rate (m3/hr) =  477.5

>> ex3d4d5
p(atm) = 70
videal =  0.496, v(L/mol) =  0.289, Percentage Difference =  71.57
Flow rate (m3/hr) =   28.9
```

The SRK equation of state (and every other equation of state) is itself an approximation. At 423 K and 70 atm, the actual value for $\bar{v}$ is 0.2579 L/mol. The percentage error in the SRK estimate ($\bar{v}$ = 0.289 L/mol) is 12%, and that in the ideal gas estimate ($\bar{v}$ = 0.50 L/mol) is 92%.

Chapter 2

2.4 Properties Evaluations

This section will show the use of equation of state and property relations to evaluate thermodynamic properties in several examples.

Example 2.4-1. [6] --
Propane at 350°C and 600 cm³/mol is expanded in an isentropic turbine. The exhaust pressure is atmospheric. What is the exhaust temperature? *PvT* behavior has been fit to the Van der Waals equation with $a = 92{\times}10^5$ [(atm·cm⁶)/mol²] and $b = 91$ [cm³/mol]. Solve this using *T* as *v* as the independent variables, that is $s = s(T, v)$. The Van der Waals equation is given as

$$P = \frac{\bar{R}T}{v - b} - \frac{a}{v^2}$$

The ideal gas heat capacity for propane is $\dfrac{c_p}{R} = 1.213 + 28.785{\times}10^{-3}T - 8.824{\times}10^{-6}T^2$

Solution --

Since propane is expanded in an isentropic turbine, we can construct a path such that the sum of Δs is zero.
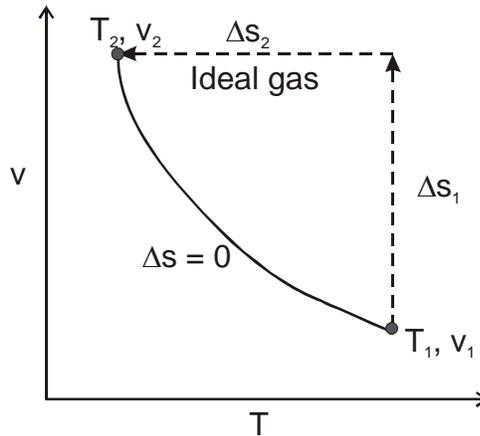
Choosing *T* and *v* as the independent variables the change in entropy is given by

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

Since $\partial s = \dfrac{\partial Q}{T} \Rightarrow \left(\dfrac{\partial s}{\partial T}\right)_v = \dfrac{1}{T}\left(\dfrac{\partial Q}{\partial T}\right)_v = \dfrac{c_v}{T}$

---

[6] Koresky M.D., <u>Engineering and Chemical Thermodynamics</u>, Wiley, 2004, pg. 245

Using Maxwell relation as shown on the following diagram, we have

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$\Rightarrow \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$
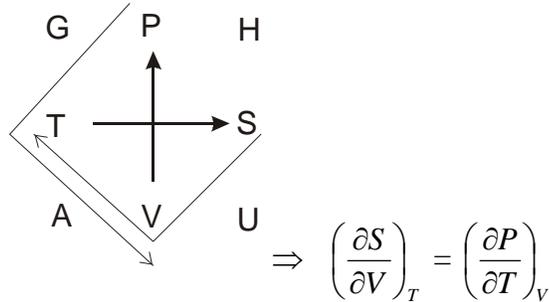
Therefore $\quad ds = \dfrac{c_v}{T}\,dT + \left(\dfrac{\partial P}{\partial T}\right)_v dv$

From the Van der Waals equation: $\quad P = \dfrac{RT}{v-b} - \dfrac{a}{v^2} \Rightarrow \left(\dfrac{\partial P}{\partial T}\right)_v = \dfrac{R}{v-b}$

For an isentropic process, we have

$$\Delta s = \int_{T_1}^{T_2} \frac{c_v}{T}\,dT + \int_{v_1}^{v_2} \frac{R}{v-b}\,dv = 0$$

$$\frac{c_v}{R} = \frac{c_p}{R} - 1 = 0.213 + 28.785\times10^{-3}T - 8.824\times10^{-6}T^2$$

$$0.213\ln(T_2/T_1) + 28.785\times10^{-3}(T_2 - T_1) - 4.412\times10^{-6}(T_2^2 - T_1^2) + \ln\left(\frac{v_2 - b}{v_1 - b}\right) = 0 \quad \text{(E-1)}$$

In terms of molar quantities

$$0.213\ln(T_2/T_1) + 28.785\times10^{-3}(T_2 - T_1) - 4.412\times10^{-6}(T_2^2 - T_1^2) + \ln\left(\frac{\bar{v}_2 - b}{\bar{v}_1 - b}\right) = 0 \quad \text{(E-1)}$$

Since $\bar{R} = 82.06$ cm^3·atm/mol·K, $\bar{v}_2 = \dfrac{\bar{R}T_2}{P_2} = \dfrac{82.06T_2}{1} = 82.06T_2$

Substituting the following numerical values: $T_1 = 350^oC = 623.15^oK$, $\bar{v}_1 = 600$ cm^3/mol, $P_2 = 1$ atm, and $b = 91$ [cm^3/mol] into equation (E-1), we have

$$0.213\ln(T_2/623.15) + 28.785\times10^{-3}(T_2 - 623.15) - 4.412\times10^{-6}(T_2^2 - 623.15^2)$$

$$+ \ln\left(\frac{82.06T_2 - 91}{509}\right) = 0 \tag{E-2}$$

We can use the following Matlab statements to solve the nonlinear equation

```
>> fun=inline('0.213*log(x/623.15) + 28.785e-3*(x -623.15) - 4.412e-6*(x^2 -
623.15^2)+log((82.06*x-91)/509)');
>> T2=fsolve(fun,500,optimset('Display','off'))
T2 =
  448.2512
>>
```

The temperature of the exhaust from the turbine is **448.3^{o}K.**

Example 2.4-2.[7] --
Develop a general relationship for the change in temperature with respect to pressure at constant entropy

$$\left(\frac{\partial T}{\partial P}\right)_s$$

(a) Evaluate the expression for an ideal gas.

(b) From the result in part (a), show that for an ideal gas with constant c_P, an isentropic expansion from state 1 and state 2 yields equation $Pv^k = const$.

(c) Evaluate the expression for a gas that obeys the Van der Walls equation of state.

Solution ---
(a) Evaluate the expression for an ideal gas

The cyclic rule can be employed to give

$$\left(\frac{\partial T}{\partial P}\right)_s = -\left(\frac{\partial T}{\partial s}\right)_P\left(\frac{\partial s}{\partial P}\right)_T$$

Substituting the relation $\left(\frac{\partial s}{\partial T}\right)_P = \frac{c_P}{T}$ and $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$ yields

$$\left(\frac{\partial T}{\partial P}\right)_s = \frac{T}{c_P}\left(\frac{\partial v}{\partial T}\right)_P$$

For an ideal gas: $Pv = RT \Rightarrow \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$

Therefore,

$$\left(\frac{\partial T}{\partial P}\right)_s = \frac{RT}{P}\frac{1}{c_P} = \frac{v}{c_P}$$

(b) Show that for an ideal gas with constant c_P, an isentropic expansion from state 1 and state 2 yields equation $Pv^k = const$.

Separation of variables provides

$$\frac{\partial T}{T} = \frac{R}{c_P}\frac{\partial P}{P}$$

[7] Koresky M.D., <u>Engineering and Chemical Thermodynamics</u>, Wiley, 2004, pg. 245

Integration provides

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{P_2}{P_1}\right)^{\frac{R}{c_P}}$$

This expression can be rewritten as $\dfrac{T_2}{T_1} = \left(\dfrac{P_2}{P_1}\right)^{\frac{R}{c_P}}$

The ideal gas law is now employed

$$\frac{P_2 v_2}{P_1 v_1} = \left(\frac{P_2}{P_1}\right)^{\frac{R}{c_P}} \Rightarrow P_2^{\left(1-\frac{R}{c_P}\right)} v_2 = P_1^{\left(1-\frac{R}{c_P}\right)} v_1$$

where

$$1 - \frac{R}{c_P} = \frac{c_P - R}{c_P} = \frac{c_v}{c_P} = \frac{1}{k}$$

If we raise both sides of the equation by a power of k, we find

$$P_2 v_2^k = P_1 v_1^k \Rightarrow P v^k = const.$$

(c) Evaluate the expression for a gas that obeys the Van der Walls equation of state.

In Part (a), we found $\left(\dfrac{\partial T}{\partial P}\right)_s = \dfrac{T}{c_P}\left(\dfrac{\partial v}{\partial T}\right)_P$

Using the derivative inversion rule, we find for the van der Waals equation

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{Rv^3(v-b)}{RTv^3 - 2a(v-b)^2}$$

Therefore, $\left(\dfrac{\partial T}{\partial P}\right)_s = \dfrac{1}{c_P}\dfrac{RTv^3(v-b)}{RTv^3 - 2a(v-b)^2}$

Example 2.4-3.[8] --
Your company has just developed a new refrigeration process. This process uses a secret gas
called Gas A. You are told that you need to come up with thermodynamic property data for
this gas. The following data have already been obtained for the superheated vapor:

	$P = 10$ bar		$P = 12$ bar	
T [°C]	v [m³/kg]	s [kJ/kg·°K]	v [m³/kg]	s [kJ/kg·°K]
80	0.16270	5.4960	0.13387	?
100	0.17389		0.14347	

As accurately as you can, come up with a value for s in the table above. Clearly indicate your
approach and state any assumptions that you make. Do not assume ideal gas behavior.

Solution --

In order to solve this problem we need to relate the change in entropy from 10 to 12 bar to
the change in molar volume (for which we have complete data). First, we can rewrite the
change in entropy as

$$\Delta s = s_2 - s_1 = \int_{10\,\text{bar}}^{12\,\text{bar}} \left(\frac{\partial s}{\partial P} \right)_T dP$$

Applying a Maxwell relation, we can relate the above equation to the change in molar
volume:

$$s_2 = s_1 + \int_{10\,\text{bar}}^{12\,\text{bar}} \left(\frac{\partial s}{\partial P} \right)_T dP = s_1 + \int_{10\,\text{bar}}^{12\,\text{bar}} -\left(\frac{\partial v}{\partial T} \right)_P dP$$

As 10 bar:

$$\left(\frac{\partial v}{\partial T} \right)_P \cong \left(\frac{\Delta v}{\Delta T} \right)_P = 5.60 \times 10^{-4} \left[\frac{m^3}{kg \cdot K} \right]$$

At 12 bar:

$$\left(\frac{\partial v}{\partial T} \right)_P \cong \left(\frac{\Delta v}{\Delta T} \right)_P = 4.80 \times 10^{-4} \left[\frac{m^3}{kg \cdot K} \right]$$

To integrate the above entropy equation, we need an expression that relates $\left(\frac{\partial v}{\partial T} \right)_P$ to

pressure. Thus, we will fit a line to the data. We obtain

---

[8] Koresky M.D., Engineering and Chemical Thermodynamics, Wiley, 2004, pg. 245

$$\left(\frac{\partial v}{\partial T}\right)_P = \left(-4.0\times10^{-10}\left[\frac{m^3}{kg\cdot K\cdot Pa}\right]\right)P + 9.6\times10^{-4}\left[\frac{m^3}{kg\cdot K}\right]$$

Now integrate the equation to find the entropy:

$$s_2 = s_1 + \int_{1.0\times10^6\ Pa}^{1.2\times10^6\ Pa}\left[\left(4.0\times10^{-10}\right)P - 9.6\times10^{-4}\right]dP = 5.4960 - 0.104\left[\frac{kJ}{kg\cdot K}\right] = 5.392\left[\frac{kJ}{kg\cdot K}\right]$$

Example 2.4-4.[9] --
You need to design a heater to preheat a gas flowing into a chemical reactor. The inlet temperature is 27°C and the inlet pressure is 50 bar. You desire to heat the gas to 227°C and 50 bar. You are provided with an equation of state for the gas.

$$Z = = \frac{Pv}{RT} = 1 + \frac{aP}{T^{0.5}},\ \text{with } a = -0.070\ [^\circ K^{1/2}/bar]$$

and with ideal gas heat capacity data:

$$\frac{c_P}{R} = 3.58 + 3.02\times10^{-3}T \text{ where } T \text{ is in } [^\circ K]$$

As accurately as you can, calculate, in [J/mol], the amount of heat required.

Solution ---
Energy balance: $\qquad h_2 - h_1 = q$

Because the gas is not ideal under these conditions, we have to create a hypothetical path that connects the initial and final states through three steps. One hypothetical path is shown below:
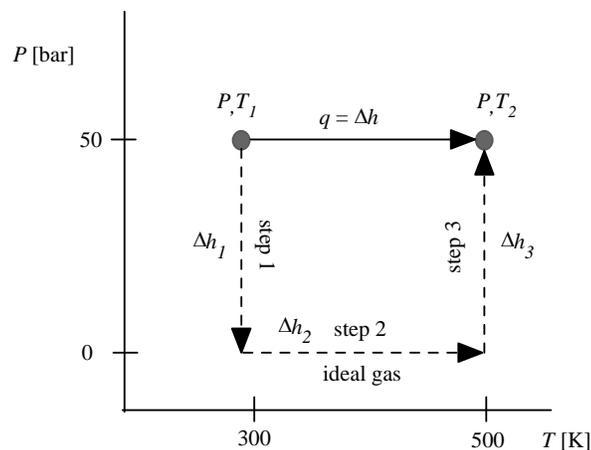
[9] Koresky M.D., Engineering and Chemical Thermodynamics, Wiley, 2004, pg. 245

Choosing T and P as the independent properties:

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP$$

Using Equation $\left(\dfrac{\partial h}{\partial P}\right)_T = -T\left(\dfrac{\partial v}{\partial T}\right)_P + v$ yields

$$dh = c_P dT + \left[-T\left(\frac{\partial v}{\partial T}\right)_P + v\right]dP$$

The given EOS can be rewritten as

$$v = R\left(\frac{1}{P} + aT^{1/2}\right)$$

Taking the derivative gives: $\left(\dfrac{\partial v}{\partial T}\right)_P = \dfrac{R}{P} + 0.5aRT^{-0.5}$

Hence

$$dh = c_P dT + \left(0.5aRT^{0.5}\right)dP$$

For step 1

$$\Delta h_1 = \int\limits_{50\,\text{bar}}^{0}\left(0.5aRT_1^{0.5}\right)dP = -0.5aRT_1^{0.5}P = 252\left[\frac{J}{\text{mol}}\right]$$

For step 2

$$\Delta h_2 = R\int\limits_{300\,\text{K}}^{500\,\text{K}}\left(3.58 + 3.02\times10^{-3}T - 0.875T^{-0.5}\right)dT = 7961\left[\frac{J}{\text{mol}}\right]$$

For step 3:

$$\Delta h_3 = \int\limits_{0}^{50\,\text{bar}}\left(0.5aRT_2^{0.5}\right)dP = 0.5aRT_2^{0.5}P = -323\left[\frac{J}{\text{mol}}\right]$$

Finally summing up the three terms, we get, $q = \Delta h_1 + \Delta h_2 + \Delta h_3 = 7888\left[\dfrac{J}{\text{mol}}\right]$

Chapter 3

Principles of Phase Equilibrium

3.1 Phase and Pure Substance

A *phase* is a quantity of matter characterized by both uniform physical structure and uniform chemical composition. A phase can be solid, liquid, vapor or gas. The atoms in a solid phase are fixed relative to other atoms in the solid. They are however can vibrate about this fixed position. Like a solid, molecules within the liquid phase are in close proximity to one another due to intermolecular forces. However, the molecules in a liquid are not fixed relative to other molecules in the liquid. They are constantly in motion, free to move relative to one another. More than one liquid phase can coexist such as oil and water. They are considered separate liquid phases since they are not miscible. Similarly, solids can coexist in different phases. For example, solid carbon can exist in the diamond phase or the graphite phase. Gas molecules move randomly to fill the entire volume of the container in which they are housed. The molecules continuously change direction as they colide with each other and bounce off the container surface creating the measurable pressure p.

A substance that has a fixed chemical composition throughout the system is called a *pure substance*. Water, hydrogen, nitrogen, and carbon monoxide, for example, are all pure substance. A pure substance can also be a mixture of various chemical elements or compounds as long as the mixture is homogeneous. Air, a mixture of several compounds, is often considered to be a pure substance because it has a uniform chemical composition. "A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same. A mixture of ice and liquid water, for example, is a pure substance because both phases have the same chemical composition."[1]

The state of a system at equilibrium is defined by the values of its thermodynamic properties. System of pure substances or *simple compressible systems* are defined by two intensive properties such as temperature and pressure. For any homogeneous, pure substance, all thermodynamic functions or properties may be expressed in terms of any two given independent properties.

$$v = f(T, p) \text{ or } \qquad v = v(T, p)$$

$$u = u(T, p) \text{ or } \qquad u = u(T, v)$$

$$s = s(T, p) \text{ or } \qquad s = s(T, v)$$

The functional relations for these properties must be developed from experimental data and are dependent on the particular chemical molecules making up the system. Only expansion or compression works given by $\int p\,dV$ are permissible in simple compressible systems undergoes quasiequilibrium processes.

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[1] Cengel Y. A., Boles M. A., <u>Thermodynamics: An Engineering Approach</u>, Mc-Graw Hill, 1998, pg. 48.

Pressure can be expressed as a function of temperature and specific volume: $p = p(T, v)$. The plot of $p = p(T, v)$ is a surface called *p-v-T* surface. Figure 3.1 shows the *p-v-T* surface of a substance such as water that expands on freezing.
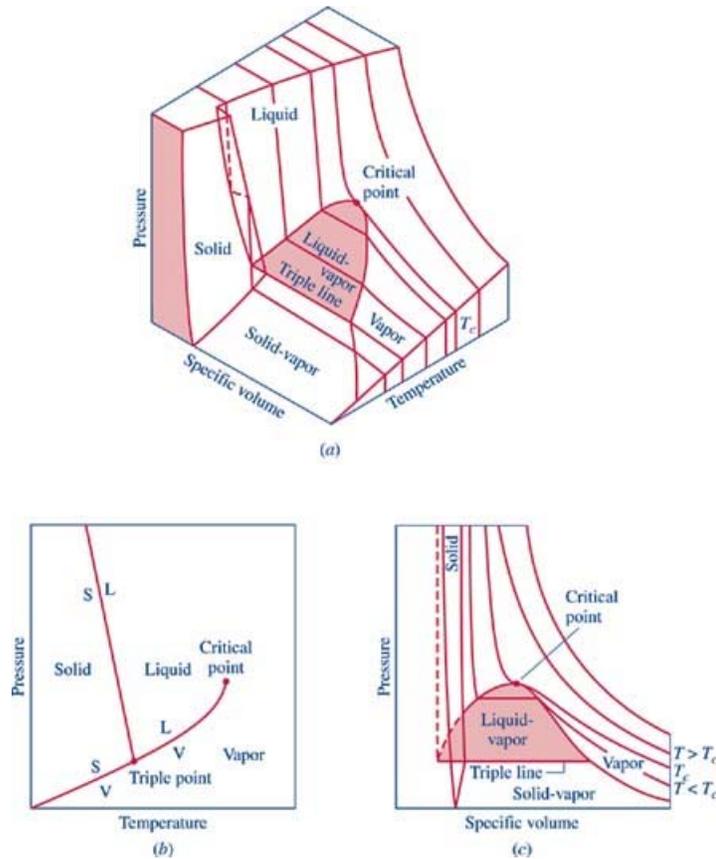
Figure 3.1-1 *p-v-T* surface and projections for a substance that expands on freezing.
(a) 3-D view (b) *p-T* diagram (c) *p-v* diagram[2].

The location of a point on the *p-v-T* surface gives the values of pressure, specific volume, and temperature at equilibrium. The regions on the *p-v-T* surface labeled *solid*, *liquid*, and *vapor* are single-phase regions. The state of a single phase is determined by any two of the properties: pressure, temperature, and specific volume. The two-phase regions where two phases exist in equilibrium separate the single-phase regions. The two-phase regions are: liquid-vapor, solid-liquid, and solid-vapor. Temperature and pressure are dependent within the two-phase regions. Once the temperature is specified, the pressure is determined and vice versa. The states within the two-phase regions can be fixed by specific volume and either temperature or pressure.

The projection of the *p-v-T* surface onto the *p-T* plane is known as the phase diagram as shown in Figure 3.1 (b). The two-phase regions of the *p-v-T* surface reduce to lines in the phase diagram. A point on any of these lines can represent any two-phase mixture at that particular temperature and pressure. The triple line of the *p-v-T* surface projects onto a point on the phase diagram called the triple point. Three phases coexist on the triple line or the triple point.

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[2] Moran, M. J. and Shapiro H. N., Fundamentals of Engineering Thermodynamics, Wiley, 2008, p. 83

The constant temperature lines of the *p-v* diagram are called the isotherms. For any specified temperature less than the critical temperature, the pressure remains constant within the two-phase region even though specific volume changes. In the single-phase liquid and vapor regions the pressure decreases at fixed temperature as specific volume increases. For temperature greater than or equal to the critical temperature, there is no passage across the two-phase liquid-vapor region.
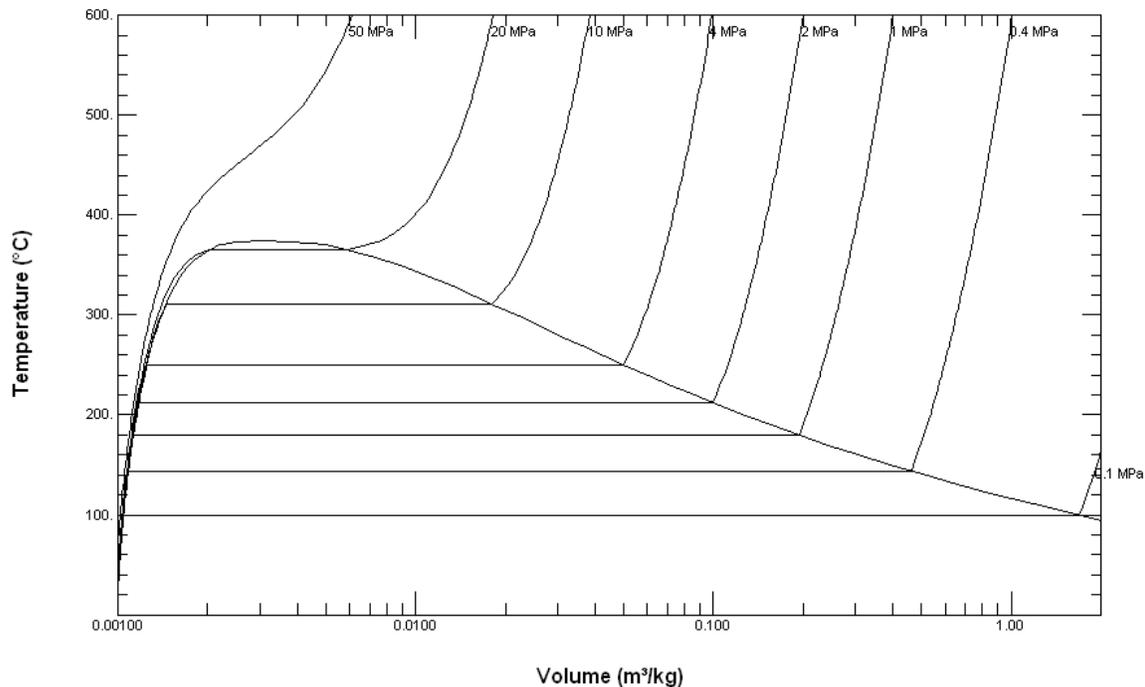
Figure 3.1-2 *T-v* diagram for water (to scale).

Figure 3.1-2 is a *T-v* diagram for water. For pressure greater than or equal to the critical pressure, temperature increases continously at fixed pressure as the specific volume increases and there is no passage across the two-phase liquid-vapor region. The isobaric curve marked 50 MPa in Figure 3.1-2 shows this behavior. For pressure less than the critical value, there is a two-phase region where the temperature remains constant at a fixed pressure as the two-phase region is traversed. The isobaric curve with values of 20 MPa or less in Figure 3.1-2 shows the constant temperature during the phase change.

At 100°C, the saturated volumes of liquid and vapor water are 1.0434 cm^3/g and 1,673.6 cm^3/g, respectively. The *quality* of steam is the mass fraction of water vapor in a mixture of liquid and vapor water. The specific volume of 100°C steam with a quality of 0.65 is given by

$$v = (1 - 0.65)v^{\mathrm{L}} + 0.65\ v^{\mathrm{V}} = (0.35)(1.0434) + (0.65)(1,673.6) = 1088.2\ \mathrm{cm}^3/\mathrm{g}$$

3-3

3.2 Phase Behavior

We will consider a phase change of 1 kg of liquid water contained within a piston-cycinder assembly as shown in Figure 3.2-1a. The water is at 20°C and 1.014 bar (or 1 atm) as indicated by point (1) on Figure 3.2-2.
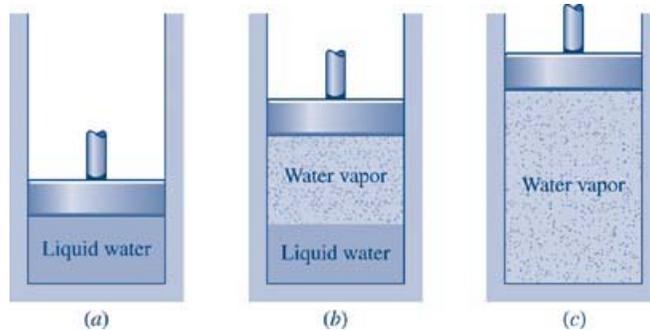
Figure 3.2-1 Phase change at constant pressure for water[3]
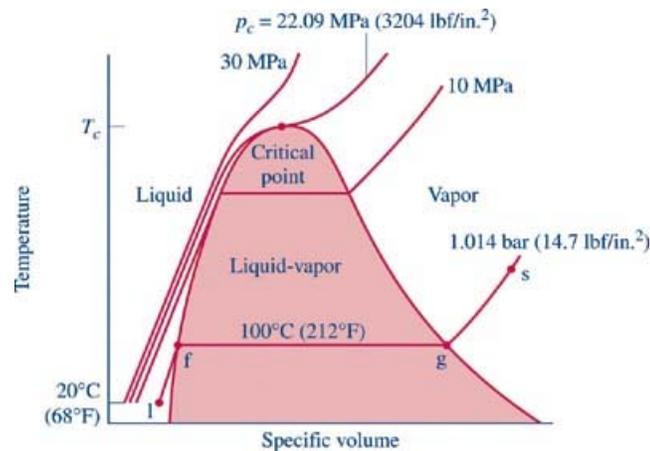
Figure 3.2-2 Sketch of *T-v* diagram for water[4]

As the water is heated at constant pressure, the temperature increases with a slight increase in specific volume until the system reaches point (f). This is the saturated liquid state corresponding to 1.014 bar. The saturation temperature for water at 1.014 bar is 100°C. The liquid states along the line segment 1-f are called *subcooled* or *compressed* liquid states. When the system is at the saturated liquid state (point f in Figure 3.2-2) any additional heat will cause the liquid to evaporate at constant pressure as shown in Figure 3.2-1b. When a mixture of liquid and vapor exists in equilibrium, the liquid phase is a saturated liquid and the vapor phase is a saturated vapor. Liquid water continues to evaporate with additional heat until it becomes all saturated vapor at point (g). Any further heating will cause an increase in both temperature and specific volume and the saturated vapor becomes superheated vapor denoted by point (s) in Figure 3.2-2. For a two-phase liquid-vapor mixture, the quality *x* is defined as the mass fraction of vapor in the mixture

$$x = \frac{m_{vapor}}{m_{vapor} + m_{liquid}} \qquad (3.2-1)$$

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[3] Moran, M. J. and Shapiro H. N., <u>Fundamentals of Engineering Thermodynamics</u>, Wiley, 2008, p. 87
[4] Moran, M. J. and Shapiro H. N., <u>Fundamentals of Engineering Thermodynamics</u>, Wiley, 2008, p. 86

The properties of pure subtances can be obtained from tables such as Table 3.2-1 for saturated properties of water and Table 3.2-2 for properties of superheated water vapor. Thermodynamic properties can also be obtained from softwares, which are more convenient since interpolations for values not directly available in the tables are not necessary.

Table 3.2-1 Thermodynamic properties of saturated water[5].

| Temp. °C | Press. bar | Specific Volume m³/kg | | Internal Energy kJ/kg | | Enthalpy kJ/kg | | | Entropy kJ/kg·K | | Temp. °C |
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Sat. Vapor s_g	
.01	0.00611	1.0002	206.136	0.00	2375.3	0.01	2501.3	2501.4	0.0000	9.1562	.01
4	0.00813	1.0001	157.232	16.77	2380.9	16.78	2491.9	2508.7	0.0610	9.0514	4
5	0.00872	1.0001	147.120	20.97	2382.3	20.98	2489.6	2510.6	0.0761	9.0257	5
6	0.00935	1.0001	137.734	25.19	2383.6	25.20	2487.2	2512.4	0.0912	9.0003	6
8	0.01072	1.0002	120.917	33.59	2386.4	33.60	2482.5	2516.1	0.1212	8.9501	8
10	0.01228	1.0004	106.379	42.00	2389.2	42.01	2477.7	2519.8	0.1510	8.9008	10
11	0.01312	1.0004	99.857	46.20	2390.5	46.20	2475.4	2521.6	0.1658	8.8765	11
12	0.01402	1.0005	93.784	50.41	2391.9	50.41	2473.0	2523.4	0.1806	8.8524	12
13	0.01497	1.0007	88.124	54.60	2393.3	54.60	2470.7	2525.3	0.1953	8.8285	13
14	0.01598	1.0008	82.848	58.79	2394.7	58.80	2468.3	2527.1	0.2099	8.8048	14
15	0.01705	1.0009	77.926	62.99	2396.1	62.99	2465.9	2528.9	0.2245	8.7814	15
16	0.01818	1.0011	73.333	67.18	2397.4	67.19	2463.6	2530.8	0.2390	8.7582	16
17	0.01938	1.0012	69.044	71.38	2398.8	71.38	2461.2	2532.6	0.2535	8.7351	17
18	0.02064	1.0014	65.038	75.57	2400.2	75.58	2458.8	2534.4	0.2679	8.7123	18
19	0.02198	1.0016	61.293	79.76	2401.6	79.77	2456.5	2536.2	0.2823	8.6897	19
20	0.02339	1.0018	57.791	83.95	2402.9	83.96	2454.1	2538.1	0.2966	8.6672	20
21	0.02487	1.0020	54.514	88.14	2404.3	88.14	2451.8	2539.9	0.3109	8.6450	21
22	0.02645	1.0022	51.447	92.32	2405.7	92.33	2449.4	2541.7	0.3251	8.6229	22
23	0.02810	1.0024	48.574	96.51	2407.0	96.52	2447.0	2543.5	0.3393	8.6011	23
24	0.02985	1.0027	45.883	100.70	2408.4	100.70	2444.7	2545.4	0.3534	8.5794	24
25	0.03169	1.0029	43.360	104.88	2409.8	104.89	2442.3	2547.2	0.3674	8.5580	25

---

[5] Moran, M. J. and Shapiro H. N., <u>Fundamentals of Engineering Thermodynamics</u>, Wiley, 2008, p. 817

Table 3.2-2 Thermodynamic properties of superheated water vapor[6].

T °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	p = 0.06 bar = 0.006 MPa (T_{sat} = 36.16°C)				p = 0.35 bar = 0.035 MPa (T_{sat} = 72.69°C)			
Sat.	23.739	2425.0	2567.4	8.3304	4.526	2473.0	2631.4	7.7158
80	27.132	2487.3	2650.1	8.5804	4.625	2483.7	2645.6	7.7564
120	30.219	2544.7	2726.0	8.7840	5.163	2542.4	2723.1	7.9644
160	33.302	2602.7	2802.5	8.9693	5.696	2601.2	2800.6	8.1519
200	36.383	2661.4	2879.7	9.1398	6.228	2660.4	2878.4	8.3237
240	39.462	2721.0	2957.8	9.2982	6.758	2720.3	2956.8	8.4828
280	42.540	2781.5	3036.8	9.4464	7.287	2780.9	3036.0	8.6314
320	45.618	2843.0	3116.7	9.5859	7.815	2842.5	3116.1	8.7712
360	48.696	2905.5	3197.7	9.7180	8.344	2905.1	3197.1	8.9034
400	51.774	2969.0	3279.6	9.8435	8.872	2968.6	3279.2	9.0291
440	54.851	3033.5	3362.6	9.9633	9.400	3033.2	3362.2	9.1490
500	59.467	3132.3	3489.1	10.1336	10.192	3132.1	3488.8	9.3194
	p = 0.70 bar = 0.07 MPa (T_{sat} = 89.95°C)				p = 1.0 bar = 0.10 MPa (T_{sat} = 99.63°C)			
Sat.	2.365	2494.5	2660.0	7.4797	1.694	2506.1	2675.5	7.3594
100	2.434	2509.7	2680.0	7.5341	1.696	2506.7	2676.2	7.3614
120	2.571	2539.7	2719.6	7.6375	1.793	2537.3	2716.6	7.4668
160	2.841	2599.4	2798.2	7.8279	1.984	2597.8	2796.2	7.6597
200	3.108	2659.1	2876.7	8.0012	2.172	2658.1	2875.3	7.8343
240	3.374	2719.3	2955.5	8.1611	2.359	2718.5	2954.5	7.9949
280	3.640	2780.2	3035.0	8.3162	2.546	2779.6	3034.2	8.1445
320	3.905	2842.0	3115.3	8.4504	2.732	2841.5	3114.6	8.2849
360	4.170	2904.6	3196.5	8.5828	2.917	2904.2	3195.9	8.4175
400	4.434	2968.2	3278.6	8.7086	3.103	2967.9	3278.2	8.5435
440	4.698	3032.9	3361.8	8.8286	3.288	3032.6	3361.4	8.6636
500	5.095	3131.8	3488.5	8.9991	3.565	3131.6	3488.1	8.8342

[6] Moran, M. J. and Shapiro H. N., Fundamentals of Engineering Thermodynamics, Wiley, 2008, p. 821

Example 3.2-1 ---.

(a) Determine the specific volume for saturated water vapor and internal energy for saturated liquid at 4.4°C from the following data

Temp. °C	Press. bar	Specific Volume m³/kg		Internal Energy kJ/kg		Temp. °C
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	
4	0.00813	1.0001	157.232	16.77	2380.9	4
5	0.00872	1.0001	147.120	20.97	2382.3	5

(b) Determine the specific volume and the internal energy for superheated water vapor at 90°C and 0.20 bar from the following data

T °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	$p = 0.06$ bar $= 0.006$ MPa ($T_{sat} = 36.16$°C)				$p = 0.35$ bar $= 0.035$ MPa ($T_{sat} = 72.69$°C)			
80	27.132	2487.3	2650.1	8.5804	4.625	2483.7	2645.6	7.7564
120	30.219	2544.7	2726.0	8.7840	5.163	2542.4	2723.1	7.9644

Solution --
   (a) Determine the specific volume for saturated water vapor at 4.4°C.
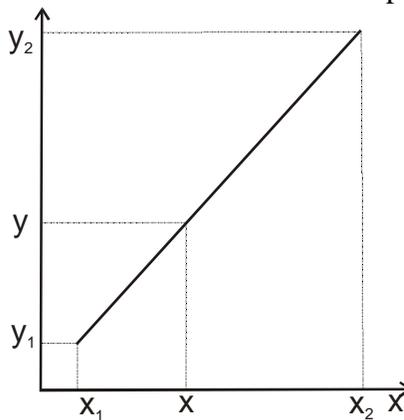
$$\frac{y - y_1}{x - x_1} = \frac{y_2 - y_1}{x_2 - x_1}$$

Using linear interpolation we have

$$\frac{v_g - 157.232}{4.4 - 4} = \frac{147.120 - 157.232}{5 - 4}$$

$$v_g = 157.232 + (0.4)(147.120 - 157.232) = \textbf{153.187 m}^3\textbf{/kg}$$

We can also use Matlab interpolation command interp1.

>> vg=interp1([4 5],[157.232 147.12],4.4)

vg =

  153.1872

Determine the internal energy for saturated liquid at 4.4°C

$$\frac{u_l - 16.77}{4.4 - 4} = \frac{20.97 - 16.77}{5 - 4}$$

$$u_1 = 16.77 + (0.4)(20.97 - 16.77) = \textbf{19.29 kJ/kg}$$

We can also use Matlab interpolation command interp1.

>> ul=interp1([4 5],[20.97 16.77],4.4)

ul =

  19.2900

Properties of water can also be obtained from the Steam4 program written by T.K. Nguyen. You should note that the values from the software might be different than the values obtained from linear interpolation since the software does not assume linear relation between the variables. The values calculated from software are in general more accurate.

Figure 3.2-3 Propterties of saturated liquid and vapor water.

The Catt2 program (Computer-Aided Thermodynamic Table 2) produced by Sonntag contains properties of other compounds beside water.
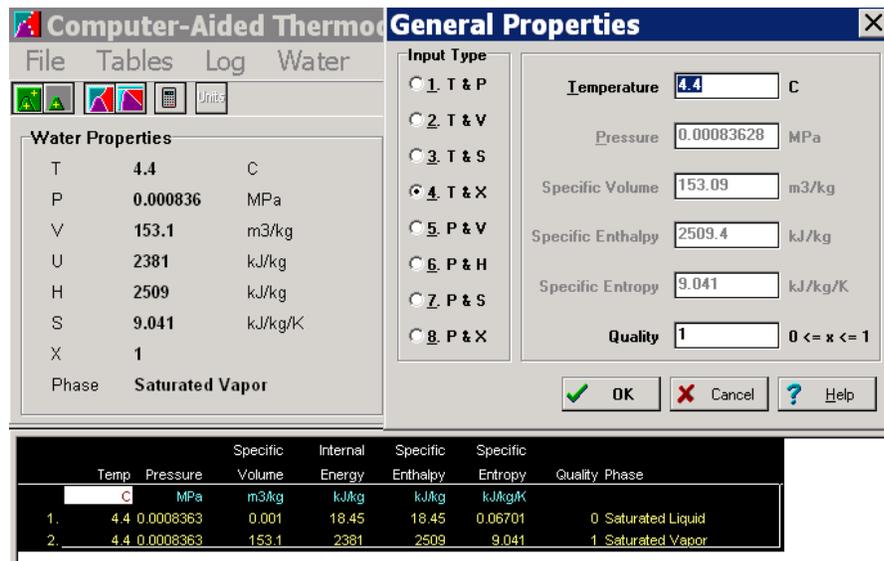
Figure 3.2-4 Propterties of saturated liquid and vapor water from Catt2.

(b) Determine the specific volume for superheated water vapor at 90°C and 0.20 bar

T °C	v m^3/kg	v m^3/kg
	0.06 bar	0.35 bar
80	27.132	4.625
120	30.219	5.163

We first need to determine v_1(90°C, 0.06 bar) and v_2(90°C, 0.35 bar)

$$\frac{v_1 - 27.132}{90 - 80} = \frac{30.219 - 27.132}{120 - 80}$$

$v_1 = 27.132 + (10)(30.219 - 27.132)/30 = \mathbf{27.90\ m^3/kg}$

$$\frac{v_2 - 4.625}{90 - 80} = \frac{5.163 - 4.625}{120 - 80}$$

$v_2 = 4.625 + (10)(5.163 - 4.625)/30 = \mathbf{4.760\ m^3/kg}$

We now determine v(90°C, 0.20 bar) from v_1(90°C, 0.06 bar) and v_2(90°C, 0.35 bar)

$$\frac{v - 27.9}{0.20 - 0.06} = \frac{4.76 - 27.9}{0.35 - 0.06}$$

$$v = 27.9 + (0.14)(4.76 - 27.9)/0.29 = \textbf{16.73 m}^3\textbf{/kg}$$

We can also use the following Matlab commands.

```
>> v1=interp1([80 120],[27.132 30.219],90);
>> v2=interp1([80 120],[4.625 5.163],90);
>> v=interp1([.06 .35],[v1 v2],.2)
```

v = 16.7307

Determine the internal energy for superheated water vapor at 90°C and 0.20 bar

T	u	u
°C	kJ/kg	kJ/kg
	0.06 bar	0.35 bar
80	2487.3	2483.7
120	2544.7	2542.4

Use the following Matlab commands, we obtain u = **2500.1 kJ/kg**

```
>> u1=interp1([80 120],[2487.3 2544.7],90);
>> u2=interp1([80 120],[2483.7 2542.4],90);
>> u=interp1([.06 .35],[u1 u2],.2)
```

u = 2.5001e+003

The internal energy for superheated water vapor at 90°C and 0.20 bar can also be obtained directly from thermodynamic property software.

Chapter 3

Principles of Phase Equilibrium

3.3 Introduction to Phase Equilibrium

A system is said to be in equilibrium when its properties are uniform over the system and are independent with time.
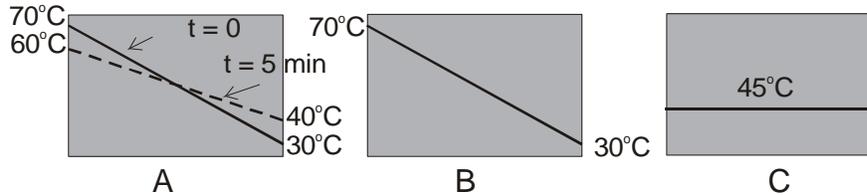
Figure 3.3 Example of equilibrium and non-equilibrium systems.

System A shown in Figure 3.3 is not at equilibrium since its temperature is a function of both position and time. It is an unsteady state system. System B is not at equilibrium since its temperature is a function of position. It is a steady state system. System C is at equilibrium since its temperature is uniform and independent of time.

We can use thermodynamics to form relationships between the states of a system that undergoes certain processes. From the first and second law we can calculate the work or heat required for the change of states or the value of an unknown property of a given state. We can also use thermodynamics to determine the composition of a mixture when it reaches equilibrium between coexisting phases with or without chemical reactions.

The criterion for equilibrium can be based on the energy or entropy of the system. For a spontaneous process, the system is at equilibrium if its energy is a minimum or its entropy is at a maximum. At equilibrium we have

$$\Delta G_{T,P} \leq 0 \tag{3.3-1a}$$

Equation (3.3-1a) says that in a closed system at constant temperature and pressure, spontaneous processes produce negative changes in Gibbs free energy, and at equilibrium the Gibbs free energy is at its minimum value.
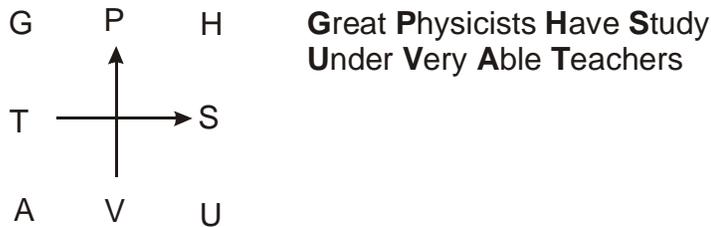
From the above diagram, we can see that equation (3.3-1) involves three variables in a group. We can use variables belong to different groups for the equilibrium criterion.

$$\Delta H_{P,S} \leq 0, \ \Delta U_{S,V} \leq 0, \ \text{or} \ \Delta A_{V,T} \leq 0. \qquad\qquad (3.3\text{-}1b,c,d)$$

The criterion based on entropy is given as

$$\Delta S_{U,V} \geq 0, \ \text{or} \ \Delta S_{H,P} \geq 0. \qquad\qquad (3.3\text{-}2a,b)$$

Equation (3.3-2a) says that in a closed system at constant internal energy and volume, spontaneous processes produce positive changes in entropy, and at equilibrium the entropy is at its maximum value.

3.4 Pure Species Phase Equilibrium

3.4-1 Gibbs Free Energy as a Criterion for Chemical Equilibrium

Consider a closed system of a pure component in mechanical and thermal equilibrium and, therefore, at constant T and P. The system can absorb energy Q at constant T. Therefore the surroundings will have a reduction in the entropy given by

$$\Delta S_{\text{sur}} = -\frac{Q}{T} \qquad\qquad (3.4\text{-}1)$$

From the second law we have

$$\Delta S_{\text{sur}} + \Delta S_{\text{sys}} \geq 0 \qquad\qquad (3.4\text{-}2)$$

In this expression, the equal sign applies for reversible processes and the unequal sign applies for irreversible processes. Combining equations (3.4-1) and (3.4-2) gives

$$\Delta S_{\text{sys}} \geq \frac{Q}{T}$$

We will now drop the subscript *sys* for the entropy of a system ($\Delta S = \Delta S_{\text{sys}}$), the above equation becomes

$$T\Delta S \geq Q \qquad\qquad (3.4\text{-}3)$$

The first law for a closed system with only PV work is given by

$$Q = \Delta U - W = \Delta U + P\Delta V$$

Substituting $Q = \Delta U + P\Delta V$ into equation (3.4-3) gives

$$\Delta U + P\Delta V - T\Delta S \leq 0 \qquad\qquad (3.4\text{-}4)$$

The Gibbs free energy is related to other properties by the following equation

$$G = H - TS = U + PV - TS$$

The change in Gibbs free energy is then

$$\Delta G = \Delta U + P\Delta V + V\Delta P - T\Delta S - S\Delta T$$

At constant T and P, $\Delta T = \Delta P = 0$, the above equation becomes

$$\Delta G = \Delta U + P\Delta V - T\Delta S \leq 0 \tag{3.4-5}$$

The above equation is essentially equation (3.3-1a), $\Delta G_{T,P} \leq 0$. Therefore in a closed system at constant temperature and pressure, spontaneous processes produce negative changes in Gibbs free energy, and at equilibrium the Gibbs free energy is at its minimum value. It should be noted that the specification of two intensive properties fixes the values of all other state properties only in the uniform equilibrium state of a single-component, single-phase system. Thus, the equilibrium criterion specified by Eq. (3.3-1a) or (3.4-5) can be used for identifying the final equilibrium state in an isolated system that is initially nonuniform, or in which several phases or components are present.

3.4-2 The Chemical Potential

G	P	H	**G**reat **P**hysicists **H**ave **S**tudy
	↑		**U**nder **V**ery **A**ble **T**eachers
T	→	S	
A	V	U	

Consider the fundamental grouping $\{U, S, V\}$, we have

$$U = U(S, V)$$

For a system with C component, the internal energy U also depends on the number of moles, n_i, of each component. Let $C = 3$, we have

$$U = U(S, V, n_1, n_3, n_3)$$

The differential change in U is given by

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_1,n_2,n_3} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_1,n_2,n_3} dV + \left(\frac{\partial U}{\partial n_1}\right)_{S,V,n_2,n_3} dn_1 + \left(\frac{\partial U}{\partial n_2}\right)_{S,V,n_1,n_3} dn_2 + \left(\frac{\partial U}{\partial n_3}\right)_{S,V,n_1,n_2} dn_3$$

In general, we have

$$U = U(S, V, n_1, \ldots, n_i, \ldots, n_C) \tag{3.4-6}$$

and

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} dV + \sum_{i=1}^{C} \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} dn_i \tag{3.4-7}$$

The subscript j denotes a component different than i. The first two coefficient of Eq. (3.4-7) refer to conditions of constant composition. This refers to the same conditions as $\left(\dfrac{\partial U}{\partial S}\right)_V$ and $\left(\dfrac{\partial U}{\partial V}\right)_S$.
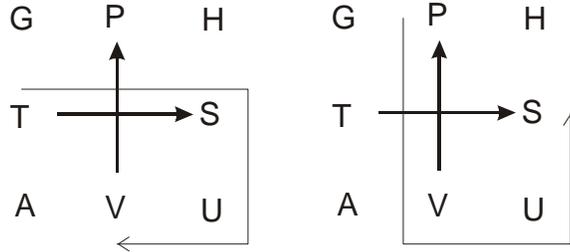
Therefore

$$\left(\frac{\partial U}{\partial S}\right)_{V,n_i} = T \text{ and } \left(\frac{\partial U}{\partial V}\right)_{S,n_i} = -P$$

We can simplify Eq. (3.4-7) by defining the chemical potential μ_i:

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j}$$

Equation (3.4-7) now becomes

$$dU = TdS - PdV + \sum_{i=1}^{C} \mu_i \, dn_i \tag{3.4-8}$$

Adding $d(PV)$ to each side of this equation, we obtain

$$dH = dU + d(PV) = VdP + TdS + \sum_{i=1}^{C} \mu_i \, dn_i \tag{3.4-9}$$

Subtracting $d(TS)$ from each side of Eq. (3.4-8) yields

$$dA = dU - d(TS) = -SdT - PdV + \sum_{i=1}^{C} \mu_i \, dn_i \tag{3.4-10}$$

Similarly, subtracting $d(TS)$ from each side of Eq. (3.4-9) yields

$$dG = dH - d(TS) = VdP - SdT + \sum_{i=1}^{C} \mu_i \, dn_i \tag{3.4-11}$$

Equations (3.4-8)-(3.4-11) are applicable to closed systems where the change in the number of moles of one or more components is caused by a chemical reaction. They are also applicable to open systems where the change is from a transfer of matter.

G P H **G**reat **P**hysicists **H**ave **S**tudy
        Under **V**ery **A**ble **T**eachers
T   → S

A V U
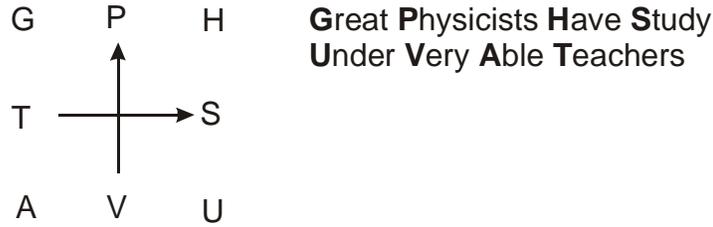
We defined the chemical potential as

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j}$$

From equations (3.4-9)-(3.4-11), we can also define the chemical potential in terms of H, A, and G

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i} \right)_{P,S,n_j} = \left(\frac{\partial S}{\partial n_i} \right)_{T,V,n_j} = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \tag{3.4-12}$$

These definitions involve the 3 properties at each corner of the diagram. They can be considered as alternative ways of determining a thermodynamic property. The last term in equation (3.4-12) is the more useful definition since a process of constant temperature and pressure is experimentally the most convenient. For a single component system $G = Ng$, and

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} = \left(\frac{\partial (Ng)}{\partial N} \right)_{T,P} = g$$

A physical meaning of the chemical potential may be obtained when Eq. (3.4-8) is applied to a process.

$$dU = TdS - PdV + \sum_{i=1}^{C} \mu_i \, dn_i \tag{3.4-8}$$

From the first law, we have $dU = \delta Q + \delta W$. Therefore

$$\delta Q + \delta W = TdS - PdV + \sum_{i=1}^{C} \mu_i \, dn_i \tag{3.4-13}$$

Since this equation applies only to changes between equilibrium states, $\delta Q = TdS$. Equation (3.4-13) becomes

$$\delta W = -PdV + \sum_{i=1}^{C} \mu_i \, dn_i \tag{3.4-14}$$

Eq. (3.4-14) is the work interaction of a system. It contains a Pv work and a work involved a change in mole numbers due to chemical reaction or mass transfer.

3.4-3 Vapor Liquid Phase Equilibrium

Consider an isolated system of a single component shown in Figure 3.4-1. The equilibrium system consists of a vapor phase (*I*) and a liquid phase (*II*). For the entire system, the total moles, internal energy, volume, and entropy, all of which are extensive variables, are the sums of these quantities in the two phases, that is,

$$N = N^{\mathrm{I}} + N^{\mathrm{II}}$$

$$U = U^{\mathrm{I}} + U^{\mathrm{II}}$$

$$V = V^{\mathrm{I}} + V^{\mathrm{II}}$$

and
$$S = S^{\mathrm{I}} + S^{\mathrm{II}}$$
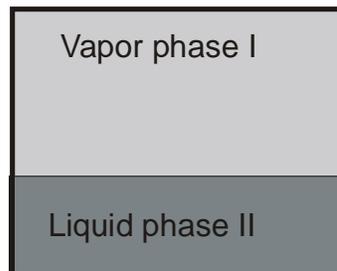
Figure 3.4-1 An isolated equilibrium system.

We now consider the internal energy to be a function of volume, entropy, and mole number.

$$U^{\mathrm{I}} = U^{\mathrm{I}}(S^{\mathrm{I}}, V^{\mathrm{I}}, N^{\mathrm{I}})$$

We can calculate the change in the internal energy for the vapor phase *I* due to changes in S^{I}, V^{I}, and N^{I}.

$$dU^{\mathrm{I}} = \left(\frac{\partial U^{I}}{\partial S^{I}}\right)_{V^{I},N^{I}} dS^{\mathrm{I}} + \left(\frac{\partial U^{I}}{\partial V^{I}}\right)_{S^{I},N^{I}} dV^{\mathrm{I}} + \left(\frac{\partial U^{I}}{\partial N^{I}}\right)_{S^{I},V^{I}} dN^{\mathrm{I}} \tag{3.4-15}$$

The partial derivatives can be written in terms of thermodynamic properties.

$$dU^{\mathrm{I}} = T^{\mathrm{I}}dS^{\mathrm{I}} - P^{\mathrm{I}}dV^{\mathrm{I}} + g^{\mathrm{I}}dN^{\mathrm{I}} \tag{3.4-16}$$

Solving the above equation for dS^{I} yields

$$dS^{\mathrm{I}} = \frac{1}{T^{\mathrm{I}}} dU^{\mathrm{I}} + \frac{P^{\mathrm{I}}}{T^{\mathrm{I}}} dV^{\mathrm{I}} - \frac{g^{\mathrm{I}}}{T^{\mathrm{I}}} dN^{\mathrm{I}} \tag{3.4-17a}$$

Similarly, for the liquid phase we have

$$dS^{\mathrm{II}} = \frac{1}{T^{\mathrm{II}}} dU^{\mathrm{II}} + \frac{P^{\mathrm{II}}}{T^{\mathrm{II}}} dV^{\mathrm{II}} - \frac{g^{\mathrm{II}}}{T^{\mathrm{II}}} dN^{\mathrm{II}} \tag{3.4-17b}$$

The entropy change of the entire system is

$$dS = dS^{\mathrm{I}} + dS^{\mathrm{II}} = \frac{1}{T^{\mathrm{I}}} dU^{\mathrm{I}} + \frac{1}{T^{\mathrm{II}}} dU^{\mathrm{II}} + \frac{P^{\mathrm{I}}}{T^{\mathrm{I}}} dV^{\mathrm{I}} + \frac{P^{\mathrm{II}}}{T^{\mathrm{II}}} dV^{\mathrm{II}} - \frac{g^{\mathrm{I}}}{T^{\mathrm{I}}} dN^{\mathrm{I}} - \frac{g^{\mathrm{II}}}{T^{\mathrm{II}}} dN^{\mathrm{II}}$$

Since the system is isolated, the total number of moles, total internal energy, and total volume are constant.

$$dN = dN^{\mathrm{I}} + dN^{\mathrm{II}} = 0 \Rightarrow dN^{\mathrm{I}} = -dN^{\mathrm{II}}$$

$$dU = dU^{\mathrm{I}} + dU^{\mathrm{II}} = 0 \Rightarrow dU^{\mathrm{I}} = -dU^{\mathrm{II}}$$

$$dV = dV^{\mathrm{I}} + dV^{\mathrm{II}} = 0 \Rightarrow dV^{\mathrm{I}} = -dV^{\mathrm{II}}$$

Therefore

$$dS = \left(\frac{1}{T^{\mathrm{I}}} - \frac{1}{T^{\mathrm{II}}} \right) dU^{\mathrm{I}} + \left(\frac{P^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{P^{\mathrm{II}}}{T^{\mathrm{II}}} \right) dV^{\mathrm{I}} - \left(\frac{g^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{g^{\mathrm{II}}}{T^{\mathrm{II}}} \right) dN^{\mathrm{I}} \tag{3.4-18}$$

At equilibrium, the value of S is at a maximum. Hence $dS = 0$. Since U^{I}, V^{I}, and N^{I} are independent, dS can be equal to zero only if the coefficients of dU^{I}, dV^{I}, and dN^{I} must all equal to zero.

$$\left(\frac{1}{T^{\mathrm{I}}} - \frac{1}{T^{\mathrm{II}}} \right) \Rightarrow T^{\mathrm{I}} = T^{\mathrm{II}}$$

$$\left(\frac{P^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{P^{\mathrm{II}}}{T^{\mathrm{II}}} \right) \Rightarrow P^{\mathrm{I}} = P^{\mathrm{II}}$$

$$\left(\frac{g^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{g^{\mathrm{II}}}{T^{\mathrm{II}}} \right) \Rightarrow g^{\mathrm{I}} = g^{\mathrm{II}}$$

Therefore, the equilibrium condition for the two phases system shown in Figure 3.4-1 is satisfied if both phases have the same temperature, the same pressure, and the same chemical potential or Gibbs free energy.

Example 3.4-1[7] --

Calculate the horsepower for compressing 5,000 lbs/hr of ethylene from 100 psia, -40°F to 200 psia. The adiabatic efficiency of the compressor is 75%. Include your calculations and Mollier chart.

Solution ---

The Mollier chart (Pressure-Enthalpy diagram) for ethylene can be obtained from the text by Darby, R., Chemical Engineering Fluid Mechanics, Marcel Dekker, 2001, p. 511.
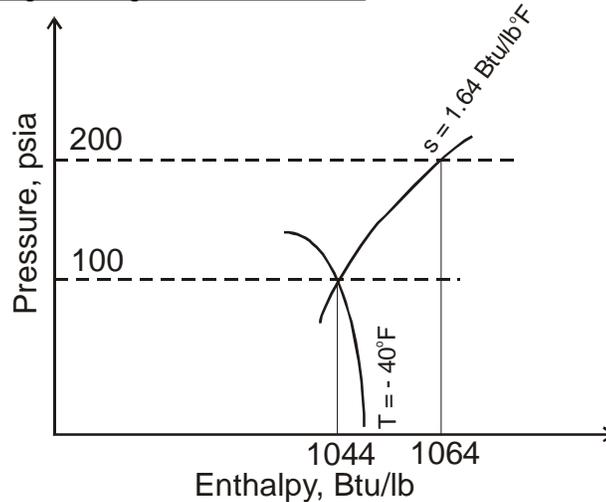
The enthalpy of ethylene at 100 psia and -40°F can be located from the diagram to give

$$h_1 = 1044 \text{ Btu/lb}$$

For isentropic compression, $\Delta s = 0$, we follow the curve where s is a constant until it reaches the line where $P = 200$ psia to locate a value for the enthalpy

$$h_2 = 1064 \text{ Btu/lb}$$

Therefore $(h_2 - h_1)_{\text{isentropic}} = 1064 - 1044 = 20$ Btu/lb.

The actual increase in enthalpy of the gas is obtained from the adiabatic efficiency

$$(h_2 - h_1)_{\text{actual}} = \frac{1}{0.75}(h_2 - h_1)_{\text{isentropic}} = 26.7 \text{ Btu/lb}$$

The horesepower supplied by the compressor to compress 5000 lb/hr of ethylene is

$$Power = 5000 \times 26.7 = 133,500 \text{ Btu/hr}$$

Power $= (133,500 \text{ Btu/hr})(3.9301 \times 10^{-4} \text{ hp/(Btu/hr)}) = $ **52.5 hp**

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[7] Dr. Pang's Notes

Chapter 3

Example 3.4-2 --
Design a refrigeration system, which supplies two levels of ammonia refrigerant at 10^oC and at -10^oC to two exchangers requiring duties of 850 and 2,500 kW, respectively. Draw a process flow diagram (PFD) showing major equipment, flow rates in kg/s of refrigerant, duty of each heat exchanger, duty, and horsepower of each compressor. Also, show temperatures and pressures of all streams. There are no inter-coolers between compressors. The compressed gas from the last stage compressor can be cooled to saturated liquid at 30^oC. Use 75% adiabatic efficiency for all compressors.

Solution --

Figure 3.4-2 A two level refrigeration system.

A design of a two level refrigeration system is shown in Figure 3.4-2. Saturated liquid ammonia at T_i is partially vaporized through a let-down valve V1 to T_1 and P_1. Part of the liquid separated by the flash drum F1 is used to provide the first level refrigeration through the heat exchanger E1. The remaining liquid passes through a second valve where its temperature and pressure is reduced to T_2 and P_2. The liquid stream from the second flash drum F2 is used for the second level refrigeration through the heat exchanger E2 where it

3-19

becomes saturated vapor. This stream is combined with the saturated vapor from the second flash drum and compressed back to pressure P_1.
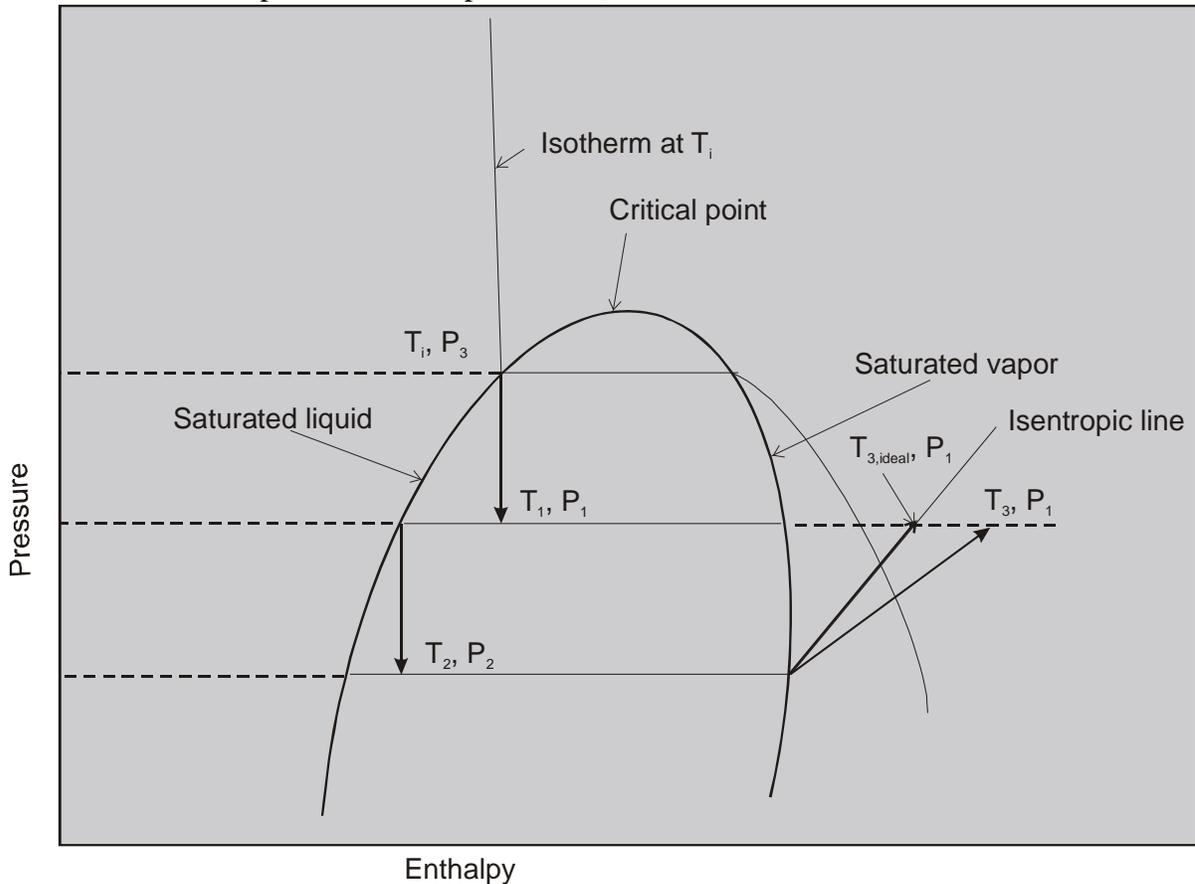
Figure 3.4-3 Pressure-Enthalpy diagram.

The problem can be solved either with a Pressure-Enthalpy diagram of ammonia as shown in Figure 3.4-3 or with a program solving an equation of state to obtain thermodynamic properties of a pure substance given any two other properties (for example, temperature and pressure or saturation temperature). We will use the computer program CATT2 to obtain thermodynamic values listed in Table 3.4-1. For this example the pressure drop across the heat exchangers and across the flash drums will be neglected.

Saturated liquid ammonia at $T_i = 30^oC$ is a defined state at $P_3 = 1.167$ MPa with enthalpy equal to 322.4 kJ/kg as shown in the first line of the property table 3.4-1. Similarly, the saturated properties of ammonia at 10^oC and -10^oC can be obtained. The mass flow rated of saturated liquid ammonia, $\dot{m}_{L,2}$, required to remove 2,500 kW in heat exchanger E2 is given by

$$\dot{m}_{L,2} = \frac{2500 kW}{h_{V,2} - h_{L,2}}$$

In this equation, $h_{V,2}$ and $h_{L,2}$ are the enthalpy of saturated vapor and liquid ammonia at -10^oC, respectively. Therefore

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$$\dot{m}_{L,2} = \frac{2500kW}{h_{V,2} - h_{L,2}} = \frac{2500}{1431 - 134.4} = 1.9281 \text{ kg/s}$$

Table 3.4-1 Thermodynamic properties of ammonia.

Type	Temp C	Pressure MPa	Specific Volume m3/kg	Specific Enthalpy kJ/kg	Specific Entropy kJ/kg/K	Quality	Phase
1 Ammonia	30	1.167	0.00168	322.4	1.2	0	Saturated Liquid
2 Ammonia	30	1.167	0.1105	1466	4.974	1	Saturated Vapor
3 Ammonia	10	0.6152	0.0016	227	0.8779	0	Saturated Liquid
4 Ammonia	10	0.6152	0.2054	1452	5.204	1	Saturated Vapor
5 Ammonia	-10	0.2909	0.001534	134.4	0.5408	0	Saturated Liquid
6 Ammonia	-10	0.2909	0.4181	1431	5.467	1	Saturated Vapor
7 Ammonia	39.43	0.6152	0.2343	1530	5.467		Superheated Vapor
8 Ammonia	52.64	0.6152	0.2465	1563	5.57		Superheated Vapor
9 Ammonia	38.85	0.6152	0.2338	1529	5.463		Superheated Vapor
10 Ammonia	87.57	1.167	0.1417	1628	5.463		Superheated Vapor
11 Ammonia	100.8	1.167	0.1482	1661	5.554		Superheated Vapor

$\dot{m}_{L,2}$ is also the liquid flow rate leaving flash drum F2. The vapor flow rate, $\dot{m}_{V,2}$, leaving the second flash drum F2 can be determined from the mass and energy balance around valve V2 and flash drum F2.

$$\dot{m}_2 = \dot{m}_{L,2} + \dot{m}_{V,2}$$

In this equation $\dot{m}_2$ is the saturated liquid ammonia flow rate at T_1 and P_1 entering valve V2. The energy balance is given by

$$(\dot{m}_{L,2} + \dot{m}_{V,2})h_{L,1} = \dot{m}_{L,2} h_{L,2} + \dot{m}_{V,2} h_{V,2}$$

Solving for $\dot{m}_{V,2}$ we have

$$\dot{m}_{V,2} = \dot{m}_{L,2} \frac{h_{L,1} - h_{L,2}}{h_{V,2} - h_{L,1}} = 1.9281 \frac{227 - 134.4}{1431 - 227} = \mathbf{0.1483 \text{ kg/s}}$$

The liquid flow rate through valve V2 is then

$$\dot{m}_2 = 1.9281 + 0.1483 = 2.0764 \text{ kg/s}$$

The mass flow rated of saturated liquid ammonia, $\dot{m}_{E,1}$, required to remove 850 kW in heat exchanger E1 is given by

$$\dot{m}_{E,1} = \frac{850kW}{h_{V,1} - h_{L,1}}$$

In this equation, $h_{V,1}$ and $h_{L,1}$ are the enthalpy of saturated vapor and liquid ammonia at 10°C, respectively. Therefore

$$\dot{m}_{E,1} = \frac{850kW}{h_{V,1} - h_{L,1}} = \frac{850}{1452 - 227} = \mathbf{0.6939 \ kg/s}$$

The liquid flow rate, $\dot{m}_{L,1}$, leaving flash drum F1 is the sum of the liquid flow rate through the heat exchanger E1 and the liquid flow rate through the valve V2

$$\dot{m}_{L,1} = \dot{m}_{E,1} + \dot{m}_2 = 0.6939 + 2.0764 = 2.7703 \ kg/s$$

Similarly, the vapor flow rate, $\dot{m}_{V,1}$, leaving the first flash drum F1 can be determined from the mass and energy balance around valve V1 and flash drum F1.

$$\dot{m}_{V,1} = \dot{m}_{L,1} \frac{h_i - h_{L,1}}{h_{V,1} - h_{i1}} = 2.7703 \frac{322.4 - 227}{1466 - 322.4} = 0.2340 \ kg/s$$

The total mass flow rate $\dot{m}_i$ of ammonia required for the system is then

$$\dot{m}_i = \dot{m}_{L,1} + \dot{m}_{V,1} = 2.7703 + 0.2340 = \mathbf{3.0043 \ kg/s}$$

The vapor flow rate $\dot{m}_{1,vap}$ from both the exchanger E1 and the flash drum F1 is given by

$$\dot{m}_{1,vap} = \dot{m}_{E,1} + \dot{m}_{V,1} = 0.6939 + 0.2340 = 0.9279 \ kg/s$$

We now determine the horsepower of the second compressor. The saturated vapor leaving the second exchanger E2 and the flash drum F2 must be compressed from 0.2909 MPa to 0.6152 MPa. For isentropic work, the gas entering and exiting the compressor will have the same entropy at 5.467 kJ/kg·°K. The enthalpy of the gas leaving the second compressor C2 due to isentropic compression is 1530 kJ/kg. For 75% adiabatic efficiency, the actual enthalpy of the exiting gas is given by

$$h_{3,\text{actual}} = 1431 + (1530 - 1431)/0.75 = 1563 \ kJ/kg$$

The horsepower required of the second compressor C2 is

$$HP_2 = 2.0764 \times (1530 - 1431)/0.75 = \mathbf{274.1 \ kW = 368 \ hp}$$

The actual temperature T_3 of the exiting gas is obtained from $P_1 = 0.6152$ MPa and $h_{3,\text{actual}} = 1563$ kJ/kg. We have the gas leaving the second compressor at $T_3 = 52.64$°C that must be mixed with the saturated gas leaving the first heat exchanger E1 and the first flash drum F1 at 10°C. The enthalpy of the gas entering the first compressor C1 is then

$$h_4 = \frac{2.0764 \times 1563 + 0.9279 \times 1452}{2.0764 + 0.9279} = 1528.7 \text{ kJ/kg}$$

At these conditions (P_1 = 0.6152 MPa, h_4 = 1528.7 kJ/kg) T_4 = 38.85°C and entropy s_4 = 5.463 kJ/kg·°K, the gas will be compressed to 1.167 MPa. The enthalpy of the gas leaving the first compressor C1 due to isentropic compression is 1628 kJ/kg. For 75% adiabatic efficiency, the actual enthalpy of the exiting gas is given by

$$h_{5,\text{actual}} = 1528.7 + (1628 - 1528.7)/0.75 = 1661.1 \text{ kJ/kg}$$

The horsepower required of the first compressor C1 is

$$HP_1 = 3.0043 \times (1628 - 1528.7)/0.75 = \textbf{398 kW} = \textbf{534 hp}$$

The gas leaving the first compressor C1 at P_3 = 1.167 MPa, $h_{5,\text{actual}}$ = 1661.1 kJ/kg, its temperature T_5 is 100.8°C. The gas will be condensed to saturated liquid at 30°C (1.167 MPa). The duty of the heat exchanger E3 is given by

$$Q_3 = 3.0043 \times (1661.1 - 322.4) = \textbf{4022 kW}$$

3.4-4 The Clapeyron Equation

Temperature and pressure are not independent for a pure species that exists in two phases at equilibrium. We now wish to derive an expression relating the pressure at which two phases can coexist to the temperature of the system. At equilibrium between α and β phases, where α and β can represent the vapor, liquid, or solid phases, we have

$$T^\alpha = T^\beta, P^\alpha = P^\beta, \text{ and } g^\alpha = g^\beta \tag{3.4-19}$$

Hence, the differential changes in Gibbs free energy of each phase must be equal

$$dg^\alpha = dg^\beta$$

$$\left(\frac{\partial g^\alpha}{\partial T}\right)_P dT + \left(\frac{\partial g^\alpha}{\partial P}\right)_T dP = \left(\frac{\partial g^\beta}{\partial T}\right)_P dT + \left(\frac{\partial g^\beta}{\partial P}\right)_T dP \tag{3.4-20}$$

Equation (3.4-20) shows the displacement of the system from its original equilibrium state described by Eqs. (3.4-19) to another equilibrium state. This change will move the system along one of the coexistence lines shown in Figure 3.4-5 to a new T and P where

$$T \rightarrow T + dT \text{ and } P \rightarrow P + dP$$
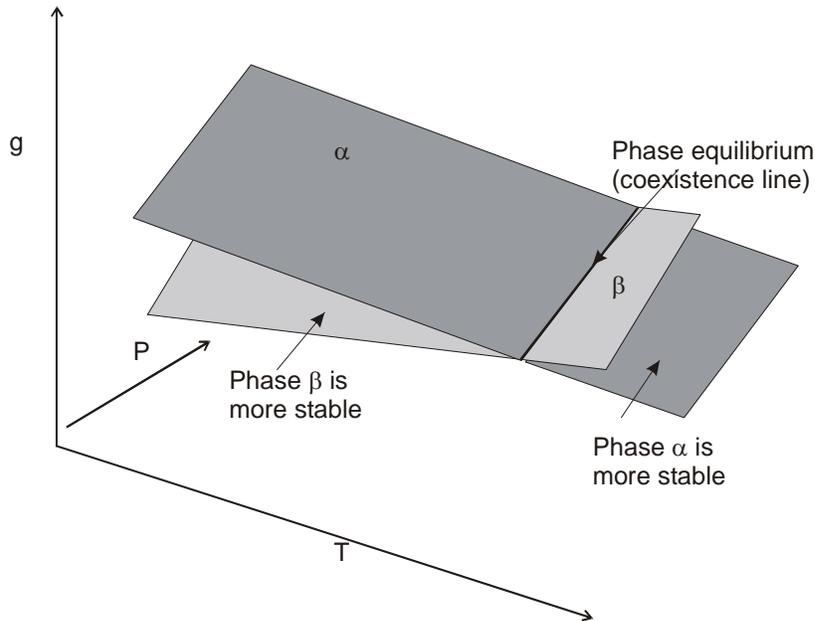
Figure 3.4-5 Surfaces of Gibbs surfaces for two phases α and β.

Applying the fundamental property relation for g to each phase yields

$$- s^\alpha dT + v^\alpha dP = - s^\beta dT + v^\beta dP \qquad (3.4\text{-}20)$$

Rearrangement gives

$$\frac{dP}{dT} = \frac{s^\alpha - s^\beta}{v^\alpha - v^\beta} \qquad (3.4\text{-}21)$$

We have $\qquad g^\alpha = g^\beta \Rightarrow h^\alpha - Ts^\alpha = h^\beta - Ts^\beta$

Solving for the difference in entropy yields

$$s^\alpha - s^\beta = \frac{h^\alpha - h^\beta}{T}$$

Substituting the expression for entropy into equation (3.4-21) gives

$$\frac{dP}{dT} = \frac{h^\alpha - h^\beta}{\left(v^\alpha - v^\beta\right)T} \qquad (3.4\text{-}22)$$

Equation (3.4-22), called the Clapeyron equation, is a general relationship among pressure, temperature, volume change, and enthalpy change for a single component, two-phase system at equilibrium. This equation can be applied to any kind of phase equilibrium including solid-vapor and solid-liquid equilibria by substituting the alternative sublimation or fusion properties into the equation.

For solid-liquid equilibrium, we are usually interested in the change of freezing point with pressure dT/dP. We can invert Eq. (3.4-22) to obtain

$$\frac{dT}{dP} = \frac{(v^l - v^s)T}{h^l - h^s}$$
(3.4-23)

For most substances dT/dP is small and positive; however for water dT/dP is negative since ice is less dense than liquid water. This unusual behavior for water means that ice will melt when pressure is applied to it isothermally as shown in Figure 3.4-6. Due to this phenomenon, you can skate on ice.
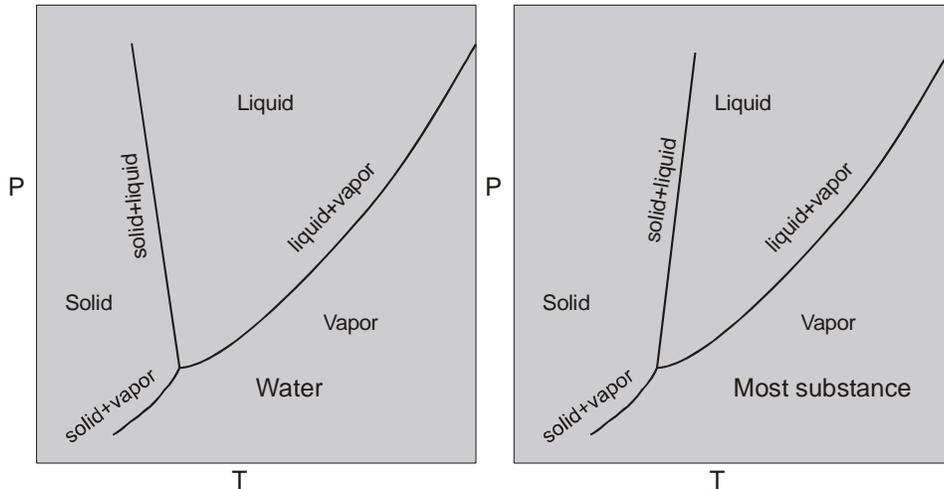
Figure 3.4-6 *P-T* behavior of real fluid.

For vapor-liquid equilibrium, we have

$$\frac{dP^{sat}}{dT} = \frac{h^v - h^l}{(v^v - v^l)T}$$
(3.4-24)

When applied to equilibrium involving a vapor phase, the pressure is referred to as the vapor or saturation pressure and will be denoted by P^{sat}. In the region far from the critical point, $v^l \ll v^v$, the volume of the liquid is negligible compared to the volume of the vapor. If the vapor obeys ideal gas law, Eq. (3.4-24) becomes

$$\frac{dP^{sat}}{dT} = \frac{P^{sat}\Delta h_{vap}}{RT^2}$$
(3.4-25)

In this equation, $\Delta h_{vap} = h^v - h^l$ is the enthalpy of vaporization of the substance at temperature T. Equation (3.4-25) can be rewritten in the form

$$d \ln P^{sat} = -\frac{\Delta h_{vap}}{R} d\left(\frac{1}{T}\right)$$
(3.4-26)

Integrating Eq.(3.4-26) between state 1 and state 2 yields

$$\ln\left(\frac{P_2^{sat}}{P_1^{sat}}\right) = -\frac{\Delta h_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \tag{3.4-27}$$

We can also integrate Eq. (3.4-26) using a constant of integration C_1

$$\ln P^{sat} = C_1 - \frac{\Delta h_{vap}}{RT} \tag{3.4-28}$$

Equations (3.4-27) and (3.4-28) are often called the Clausius-Clapeyron equation. They can be used to correlate, interpolate, and extrapolate of vapor data or to estimate latent heats from vapor pressure data. Equation (3.4-28) suggests that a plot of $\ln P^{sat}$ vs. $(1/T)$ should be a straight line over the region where Δh_{vap} is a constant. Actually, it has been found that Eq. (3.4-28) is valid over a surprisingly wide range of temperature due to a cancellation of errors introduced by the various assumptions.

Saturation pressure data are commonly correlated in terms of the Antoine equation

$$\ln P^{sat} = A - \frac{B}{C+T} \tag{3.4-29}$$

The Antoine equation can be regarded as an empirical version of the Clausius-Clapeyron equation. Values for the Antoine constants, A, B, and C can be found for various substances in Koretsky's text[8]. There are several more complex correlations[9] available for saturation data that are accurate over a wider range of temperature. For example, the water vapor pressure can be obtained accurately from the following equation[10]

$$P^{sat} = P_{crit}\exp\left[\tau 10^{-5}(T_{cri}-T)\sum_{i=1}^{8}F_i(0.65-0.01T)^{i-1}\right] \tag{3.4-30}$$

In this equation, T denotes saturation temperature (^oC), P_{crit} critical pressure (220.88 bars), T_{cri} critical temperature (374.136^oC), $\tau = 1000/T(^oK)$, and F_i is given by

F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8
-741.9242	-29.7210	-11.55286	-.8685635	.1094098	.439993	.02520658	.05218684

[8] Koretsky M.D., Engineering and Chemical Thermodynamics, Wiley, 2004, pg. 499
[9] Reid R. C., Praunits J. M., Poling B. E., The Properties of Gases & Liquids, McGraw-Hill, 1987
[10] Keenan J. H., Steam Tables, Wiley, pg. 141

Chapter 3

Example 3.4-3[16] --
The heat of fusion of ice is 80 cal/g at 0°C and 1 atm, and the ratio of the specific volume of water to that of ice is 1.000:1.091. The saturated vapor pressure and the heat of vaporization of water at 0°C are 4.58 mmHg and 600 cal/g, respectively. Estimate the triple point using these data.

Solution --
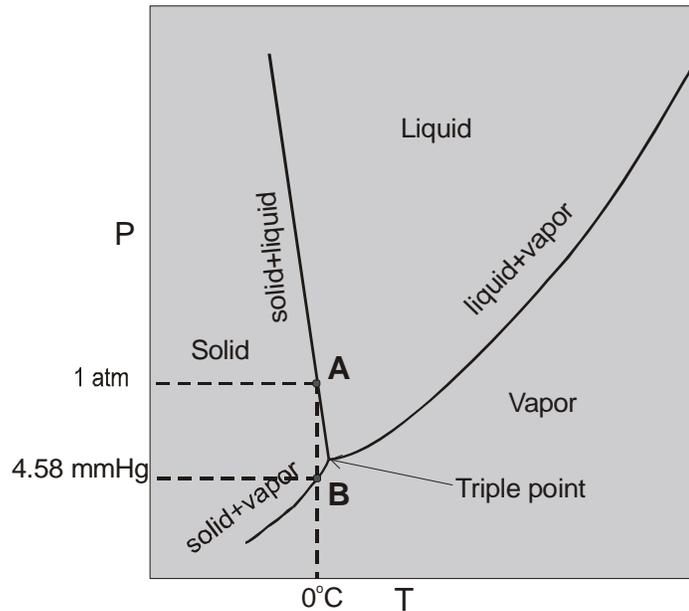
Figure E3.4-3 *P-T* behavior of water.

The coordinates of point A and B are (0°C, 1 atm) and (0°C, 4.58 mmHg), respectively. The coexistence line through A will intersect the coexistence line through B at the triple point. For equilibrium between the solid and liquid phase we have

$$\mathrm{d}g^{\mathrm{s}} = \mathrm{d}g^{\mathrm{l}}$$

$$\left(\frac{\partial g^{s}}{\partial T} \right)_{P} \mathrm{d}T + \left(\frac{\partial g^{s}}{\partial P} \right)_{T} \mathrm{d}P = \left(\frac{\partial g^{l}}{\partial T} \right)_{P} \mathrm{d}T + \left(\frac{\partial g^{l}}{\partial P} \right)_{T} \mathrm{d}P$$

Applying the fundamental property relation for *g* to each phase yields

$$- s^{\mathrm{s}}\mathrm{d}T + v^{\mathrm{s}}\mathrm{d}P = - s^{\mathrm{l}}\mathrm{d}T + v^{\mathrm{l}}\mathrm{d}P$$

Rearrangement gives

$$\frac{dP}{dT} = \frac{s^{l} - s^{s}}{v^{l} - v^{s}}$$

---

[16] Kyle, B.G., <u>Chemical and Process Thermodynamics</u>, Prentice Hall, 1999, pg. 234

We have $\qquad g^s = g^l \Rightarrow h^s - Ts^s = h^l - Ts^l$

Solving for the difference in entropy yields

$$s^l - s^s = \frac{h^l - h^s}{T}$$

Substituting the expression for entropy into dP/dT yields

$$\frac{dP}{dT} = \frac{h^l - h^s}{\left(v^l - v^s\right)T}$$

$$\frac{dP}{dT} = \frac{80}{(-0.091)(273.15)} = -3.2185 \text{ cal/cm}^{3}.{}^{o}\text{K}$$

We need to change the unit from cal/cm$^3 \cdot {}^{o}$K to mmHg/^{o}K.

$$1 \text{ cal} = 4.184 \text{ J} = 4.184 \text{ kg} \cdot \text{m}^2/\text{s}^2 = 4.184 \times 10^4 \text{ kg} \cdot \text{cm}^2/\text{s}^2$$

$$1 \text{ cal/cm}^3 = 4.184 \times 10^4 \text{ kg/s}^2 \cdot \text{cm} = 4.184 \times 10^6 \text{ kg/s}^2 \cdot \text{m}$$

$$1 \text{ mmHg} = \frac{1.013 \times 10^5}{760} \text{ kg/s}^2 \cdot \text{m} \Rightarrow \text{kg/s}^2 \cdot \text{m} = 7.502 \times 10^{-3} \text{ mmHg}$$

Therefore

$$\frac{dP}{dT} = (-3.2185)(4.184 \times 10^6)(7.502 \times 10^{-3}) = -1.01 \times 10^5 \text{ mmHg/}^{o}\text{K}$$

The equation for the straight line through A(0°C, 760 mmHg) with slope $dP/dT = -1.012 \times 10^5$ mmHg/^{o}K is given by

$$\frac{P - 760}{T - 0} = -1.01 \times 10^5 \text{ mmHg/}^{o}\text{K} \qquad\qquad\qquad \text{(E-1)}$$

Similarly for equilibrium between the solid and vapor phase we have

$$\frac{dP}{dT} = \frac{h^v - h^s}{\left(v^v - v^s\right)T}$$

Neglecting the solid volume compared to the volume of the vapor and using ideal gas law we obtain

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$$\frac{dP}{dT} = \frac{P(h^v - h^s)}{RT^2} = \frac{(4.58)(600)(18)}{(1.987)(273.15^2)} = 0.33365 \text{ mmHg/}^o\text{K}$$

The equation for the straight line through B(0°C, 4.58 mmHg) with slope dP/dT = 0.33365 mmHg/^{o}K is given by

$$\frac{P - 4.58}{T - 0} = 0.33365 \text{ mmHg/}^o\text{K} \qquad\qquad\qquad \text{(E-2)}$$

At the triple point $P = P_t$ and $T = T_t$, Equations (E-1) and (E-2) become, respectively

$$P_t - 760 = -1.01 \times 10^5 \, T_t \qquad\qquad\qquad \text{(E-3)}$$

$$P_t - 4.58 = 0.33365 \, T_t \qquad\qquad\qquad \text{(E-4)}$$

Solving the two linear equations (E-3) and (E-4) gives

$$T_t = 7.5 \times 10^{-3\,o}\text{C}$$

$$P_t = 4.5825 \text{ mmHg}$$

3.5 Refrigeration

The most common refrigeration cycle is the vapor compression cycle shown in Figure 3.5-1. In step $4 \rightarrow 1$, heat is removed at the temperature T_L from the system being refrigerated by the evaporation of a liquid under the pressure P_L. In step $1 \rightarrow 2$, saturated vapor at P_L is compress isentropically to P_H where it becomes superheated vapor. In step $2 \rightarrow 3$, heat Q_H is transferred to the surrounding by condensation at T_H. In step $3 \rightarrow 4$, the cycle is closed by throttling the liquid to the lower pressure P_L.
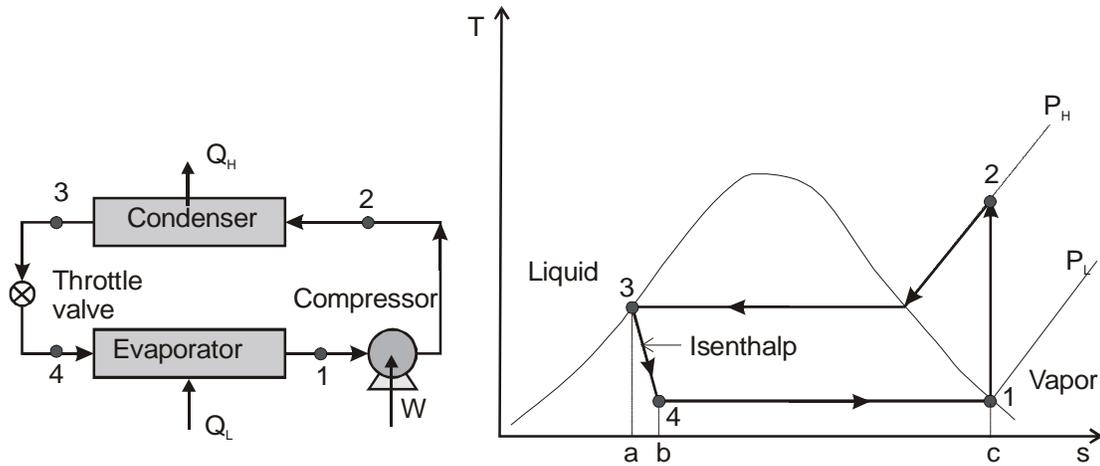
Figure 3.5-1 A vapor-compression refrigeration cycle and its Ts diagram.

The heat transfer between the system and the surroundings can be obtained from the Ts diagram. Since $Q = \int Tds$, the heat effect is the area under the curve representing the path. In Figure 3.5-1 the heat Q_H transferred from the refrigerator to the high temperature environment is the area 2-3-a-c, which is negative. The heat Q_L removed from the low temperature system is the area 4-1-c-b and is positive. For the cyclic process

$$\Delta U = Q_L + W - Q_H = 0 \Rightarrow W = Q_H - Q_L \qquad (3.5\text{-}1)$$

The efficiency of the refrigeration cycle, called the coefficient of performance COP, is given by

$$\text{COP} = \frac{Q_L}{W} \qquad (3.5\text{-}2)$$

The work required for the refrigeration cycle can be obtained from the Ts diagram

$$W = Q_H - Q_L = (\text{Area 2-3-a-c}) - (\text{Area 4-1-c-b})$$

$$W = Q_H - Q_L = (\text{Area 1-2-3-4}) + (\text{Area 3-4-b-a})$$

The refrigeration cycle shown in Figure 3.5-1 is a semi-reversible cycle since all steps except throttling are reversible.

Example 3.5-1[17]--
A vapor compression refrigeration process using NH_3 as the working fluid is to operate between 20 and 80°F. Determine the coefficient of performance for the semi-reversible operation.

Solution --
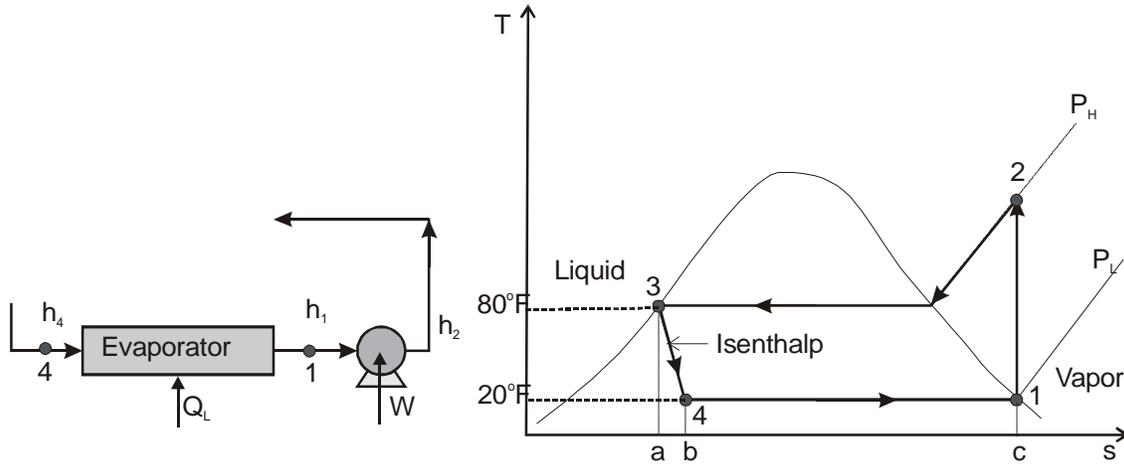
	Type	Temp	Pressure	Specific Volume	Internal Energy	Specific Enthalpy	Specific Entropy	Quality	Phase
		F	psia	ft3/lbm	Btu/lbm	Btu/lbm	Btu/lbm/R		
1.	Ammonia	80	153.1	0.02668	130.9	131.7	0.2741	0	Saturated Liquid
2.	Ammonia	20	48.22	5.904	564.2	616.8	1.295	1	Saturated Vapor
3.	Ammonia	20	48.22	0.7415	125.1	131.7	0.2833	0.1219	Liquid Vapor Mixture
4.	Ammonia	165.1	153.1	2.407	618.4	686.6	1.295		Superheated Vapor

We will first locate the four states of the refrigeration cycle:

State 3: Saturated liquid at 80°F, $h_3 = h_4 = 131.7$ Btu/lb.
State 1: Saturated vapor at 20°F, $h_1 = 616.8$ Btu/lb.
State 4: Liquid and vapor mixture at $h_4 = 131.7$ Btu/lb and 20°C
State 2: Superheated vapor at $s_2 = s_1 = 1.295$ Btu/lb·°R, $P_H = P_2 = 153.1$ psia

Making energy balance around the evaporator yields

$$0 = h_4 - h_1 + Q_L \Rightarrow Q_L = h_1 - h_4 = 616.8 - 131.7 = 485.1 \text{ Btu/lb}$$

Making energy balance around the compressor yields

$$0 = h_1 - h_2 + W \Rightarrow W = h_2 - h_1 = 686.6 - 616.8 = 69.8 \text{ Btu/lb}$$

The coefficient of performance is then

$$\text{COP} = \frac{Q_L}{W} = \frac{485.1}{69.8} = \textbf{6.95}$$

---

[17] Kyle, B.G., <u>Chemical and Process Thermodynamics</u>, Prentice Hall, 1999, pg. 656

Example 3.5-2[13]--

Refrigerant 134a is the working fluid in an ideal vapor-compression refrigeration cycle that communicates thermally with a cold region at 0°C and a warm region at 26°C. Saturated vapor enters the compressor at 0°C and saturated liquid leaves the condenser at 26°C. The mass flow rate of the refrigerant is 0.08 kg/s. Determine **(a)** the compressor power, in kW, **(b)** the refrigeration capacity, in tons, **(c)** the coefficient of performance, and **(d)** the coefficient of performance of a Carnot refrigeration cycle operating between warm and cold regions at 26 and 0°C, respectively.

Solution --
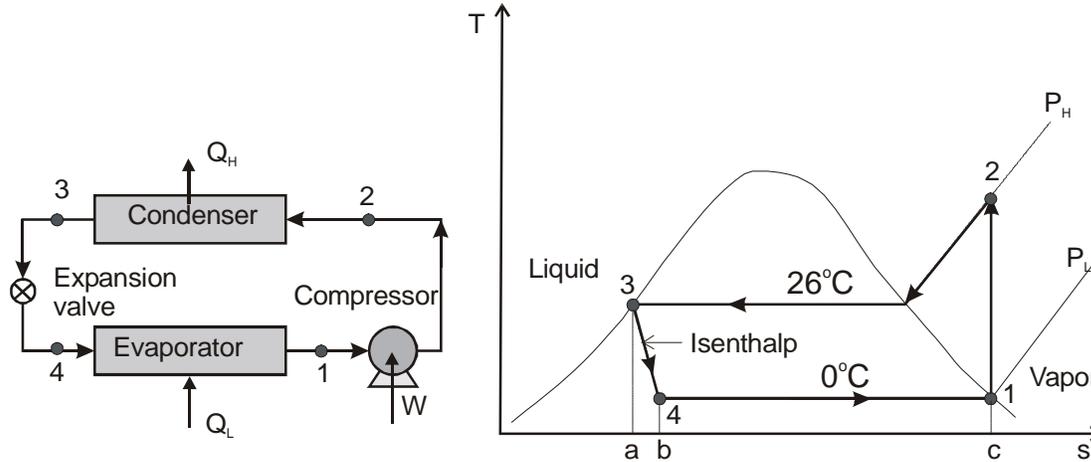
	Type	Temp	Pressure	Specific Volume	Internal Energy	Specific Enthalpy	Specific Entropy	Quality	Phase
		C	MPa	m3/kg	kJ/kg	kJ/kg	kJ/kg/K		
1	R-134a	**0**	0.2928	0.06931	378.3	398.6	1.727	**1**	Saturated Vapor
3	R-134a	**26**	0.6854	0.000831	235.4	236	1.125	**0**	Saturated Liquid
2	R-134a	29.25	**0.6854**	0.0306	395.2	416.2	**1.727**		Superheated Vapor

(a) The compressor work is give by

$$\dot{W}_c = \dot{m}\,(h_2 - h_1) = (0.08 \text{ kg/s})(416.2 - 398.6)\text{ kJ/kg} = \textbf{1.408 kW}$$

(b) The refrigeration capacity, in tons, is

$$\dot{Q}_L = \dot{m}\,(h_1 - h_4) = (0.08 \text{ kg/s})(398.6 - 236)\text{ kJ/kg} = 13.0 \text{ kW}$$

$$\dot{Q}_L = (13.0 \text{ kJ/s})(60 \text{ s/min})\left(\frac{1 \text{ ton}}{211 \text{ kJ/min}}\right) = \textbf{3.7 ton}$$

(c) Tthe coefficient of performance is

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[13] Moran, M. J. and Shapiro H. N., Fundamentals of Engineering Thermodynamics, Wiley, 2008, pg. 539

$$\beta = \frac{\dot{Q}_L}{\dot{W}_c} = \frac{13.0}{1.408} = \mathbf{9.23}$$

(d) The coefficient of performance of a Carnot refrigeration cycle operating between warm and cold regions at 26 and 0°C, respectively

$$\beta = \frac{\dot{Q}_L}{\dot{W}_c} = \frac{\dot{Q}_L}{\dot{Q}_H - \dot{Q}_L} = \frac{T_L}{T_H - T_L} = \frac{273}{299 - 273} = \mathbf{10.5}$$
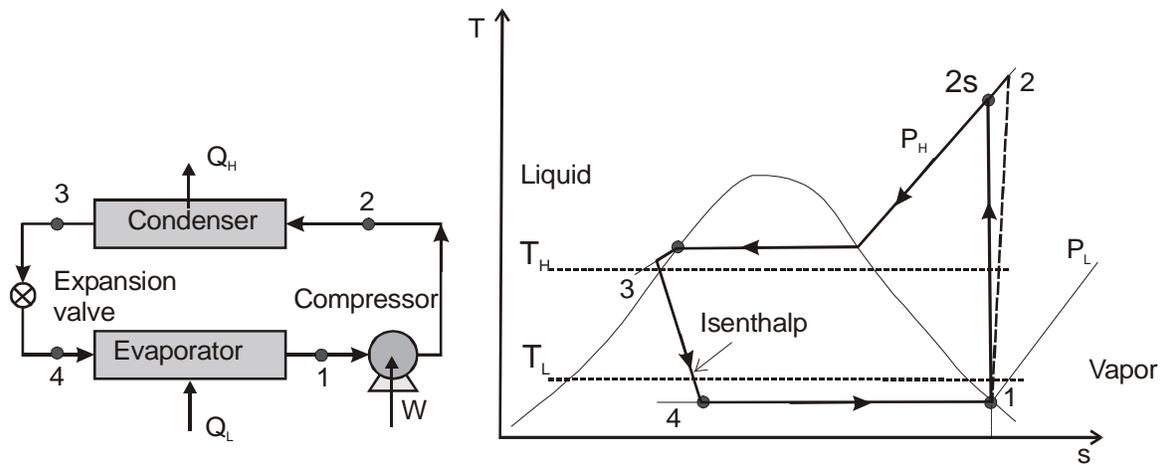
Figure 3.5-2 A vapor-compression refrigeration with irreversibilities.

Figure 3.5-2 shows several features existed in actual vapor compression systems. The heat transfers between the refrigerant and the warm and cold regions are not accomplished reversibly: the refrigerant temperature in the evaporator is less than the low reservoir temperature, T_L, and the refrigerant temperature in the condenser is greater than the high reservoir temperature, T_H. The compressor will not have 100% efficiency so that the fluid leaving the compressor will be at state (2), which is at higher entropy than the isentropic compression state (2s). The coefficient of performance decreases as the average temperature of the refrigerant in the evaporator decreases and as the average temperature of the refrigerant in the condenser increases. If the thermal efficiency of the compressor is known, the enthapy h_2 at state (2) can be determined from the following expression:

$$\eta_c = \frac{\left(\dot{W}_c / \dot{m}\right)_s}{\left(\dot{W}_c / \dot{m}\right)} = \frac{h_{2s} - h_1}{h_2 - h_1}$$

Due to frictions, there will be pressure drops as the refrigerant flows through the evaporator, condenser, and piping connecting the various components. The pressure drops are ignored in subsequent calcualtions for simplicity.

Example 3.5-3[14]--
Refrigerant 134a is the working fluid in an ideal vapor-compression refrigeration cycle that communicates thermally with a cold region at − 10°C. Saturated vapor enters the compressor at − 10°C and saturated liquid leaves the condenser at 9 bar. The mass flow rate of the refrigerant is 0.08 kg/s. Determine **(a)** the compressor power, in kW, **(b)** the refrigeration capacity, in tons, **(c)** the coefficient of performance.
Solution ---

Type	Temp	Pressure	Specific Volume	Internal Energy	Specific Enthalpy	Specific Entropy	Quality	Phase
	C	MPa	m3/kg	kJ/kg	kJ/kg	kJ/kg/K		
1 R-134a	-10	0.2006	0.09959	372.7	392.7	1.733	1	Saturated Vapor
2 R-134a	41.47	0.9	0.02359	402.7	423.9	1.733		Superheated Vapor
3 R-134a	35.53	0.9	0.000858	249	249.8	1.169	0	Saturated Liquid

(a) The compressor work is give by

$$\dot{W}_c = \dot{m}\,(h_2 - h_1) = (0.08 \text{ kg/s})(423 - 392.7) \text{ kJ/kg} = \textbf{2.424 kW}$$

(b) The refrigeration capacity, in tons, is

$$\dot{Q}_L = \dot{m}\,(h_1 - h_4) = (0.08 \text{ kg/s})(392.7 - 249.8) \text{ kJ/kg} = 11.432 \text{ kW}$$

$$\dot{Q}_L = (11.432 \text{ kJ/s})(60 \text{ s/min})\left(\frac{1 \text{ ton}}{211 \text{ kJ/min}}\right) = \textbf{3.25 ton}$$

(c) The coefficient of performance is
$$\beta = \frac{\dot{Q}_L}{\dot{W}_c} = \frac{11.432}{2.424} = \textbf{4.72}$$

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[14] Moran, M. J. and Shapiro H. N., <u>Fundamentals of Engineering Thermodynamics</u>, Wiley, 2008, pg. 541

Example 3.5-4[15]--
Refrigerant 134a is the working fluid in an ideal vapor-compression refrigeration cycle that communicates thermally with a cold region at − 10°C. Saturated vapor enters the compressor at − 10°C and liquid leaves the condenser at 9 bar and 30°C. The compressor has an efficiency of 80%. The mass flow rate of the refrigerant is 0.08 kg/s. Determine **(a)** the compressor power, in kW, **(b)** the refrigeration capacity, in tons, **(c)** the coefficient of performance.

Solution ---

	Type	Temp	Pressure	Specific Volume	Specific Enthalpy	Specific Entropy	Quality	Phase
		C	MPa	m3/kg	kJ/kg	kJ/kg/K		
1	R-134a	-10	0.2006	0.09959	392.7	1.733	1	Saturated Vapor
2s	R-134a	41.47	0.9	0.02359	423.9	1.733		Superheated Vapor
3	R-134a	30	0.9	0.000842	241.7	1.143		Compressed Liquid
4	R-134a	-10	0.2006	0.02716	241.7	1.16	0.2671	Liquid Vapor Mixture

(a) The compressor work is give by

$$\dot{W}_c = \dot{m}\,(h_2 - h_1) = \dot{m}\,\frac{h_{2s} - h_1}{\eta} = (0.08 \text{ kg/s})\frac{423.9 - 392.7}{.8} \text{ kJ/kg} = \textbf{3.12 kW}$$

(b) The refrigeration capacity, in tons, is

$$\dot{Q}_L = \dot{m}\,(h_1 - h_4) = (0.08 \text{ kg/s})(\,392.7 - 241.7)\text{ kJ/kg} = 12.08 \text{ kW}$$

$$\dot{Q}_L = (12.08 \text{ kJ/s})(60 \text{ s/min})\left(\frac{1 \text{ ton}}{211 \text{ kJ/min}}\right) = \textbf{3.44 ton}$$

(c) Tthe coefficient of performance is

$$\beta = \frac{\dot{Q}_L}{\dot{W}_c} = \frac{12.08}{3.12} = \textbf{3.87}$$

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[15] Moran, M. J. and Shapiro H. N., <u>Fundamentals of Engineering Thermodynamics</u>, Wiley, 2008, pg. 543

3.6 Partial Molar Properties

If we mix 50 cm^3 of ethanol with 20 cm^3 of water at 25°C we will obtain 67 cm^3 of the resulting solution[16]. The difference in the solution volume and the sum of the pure volumes is due to the nature of the unlike ethanol-water interactions and the fact that they are different from the water-water or ethanol-ethanol pure species interactions. When a species becomes part of a mixture, its properties change; however it still contributes to the properties of the mixture, since the total solution properties of the mixture depend on the amount present of each species and its resultant interactions. We can define a partial molar property to account for the contribution of a species to the mixture property.

We will first consider the volume of the mixture V, an extensive property, which at a specified temperature and pressure will depend on the number of moles of each species in the mixture. The partial molar volume of species i, $\overline{V}_i$, in a mixture is defined as

$$\overline{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_j} \tag{3.6-1}$$

We use the notation n_j to specify that we are holding the number of moles of all species except species i constant when we take the partial derivative with respect to n_i. A partial molar property is always defined at constant temperature and pressure, two of the criteria for phase equilibrium. In general, the solution property K is a function of T, P, and the number of moles of m different species:

$$K = K(T, P, n_1, n_2, ..., n_i, ..., n_m) \tag{3.6-2}$$

The differential of K can then be written as the sum of partial derivatives of each of these independent variables, as follows:

$$dK = \left(\frac{\partial K}{\partial T} \right)_{P,n_i} dT + \left(\frac{\partial K}{\partial P} \right)_{T,n_i} dP + \sum_{i=1}^{m} \left(\frac{\partial K}{\partial n_i} \right)_{T,P,n_j} dn_i \tag{3.6-3}$$

If we multiply the number of moles in a system by an arbitrary amount α at a given T and P, the extensive property K should also increased by that amount:

$$\alpha K = K(T, P, \alpha n_1, \alpha n_2, ..., \alpha n_i, ..., \alpha n_m) \tag{3.6-4}$$

According to Euler's theorem, the above equation is a first-order, homogeneous function of n_i. Differentiating Eq. (3.6-4) with respect to α yields

$$\left(\frac{\partial (\alpha K)}{\partial \alpha} \right)_{T,P} = K = n_1 \left(\frac{\partial K}{\partial (\alpha n_1)} \right)_{T,P,n_j} + n_2 \left(\frac{\partial K}{\partial (\alpha n_2)} \right)_{T,P,n_j} + ...$$

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[16] Koretsky M.D., <u>Engineering and Chemical Thermodynamics</u>, Wiley, 2004, pg. 263

$$+ n_i \left(\frac{\partial K}{\partial (\alpha n_i)} \right)_{T,P,n_j} + \dots + n_m \left(\frac{\partial K}{\partial (\alpha n_m)} \right)_{T,P,n_j} \qquad (3.6\text{-}5)$$

Equation (3.6-5) must be valid for any value of α, so at $\alpha = 1$, we get

$$K = \sum_{i=1}^{m} n_i \left(\frac{\partial K}{\partial n_i} \right)_{T,P,n_j} \qquad (3.6\text{-}6)$$

The total solution volume is then given by

$$V = \sum_{i=1}^{m} n_i \left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_j} = \sum_{i=1}^{m} n_i \overline{V}_i \qquad (3.6\text{-}7)$$

Example 3.6-1[17]---
We need 2,000 cm^3 of an antifreeze solution consisting of 30-mol% methanol in water. What volumes of pure methanol and of pure water at 25°C must be mixed to form the 2,000 cm^3 antifreeze, also at 25°C? Partial molar volumes for methanol and water in a 30-mol% methanol solution and their pure-species molar volumes, both at 25°C, are:

Methanol (1): $\overline{V}_1 = 38.632$ cm^3 mol^{-1} $v_1 = 40.727$ cm^3 mol^{-1}

Water (2): $\overline{V}_2 = 17.765$ cm^3 mol^{-1} $v_2 = 18.068$ cm^3 mol^{-1}

Solution --

The molar solution volume at 30-mol% methanol is given as

$$v = \frac{V}{n_T} = \frac{\sum_{i=1}^{m} n_i \overline{V}_i}{n_T} = \sum_{i=1}^{m} x_i \overline{V}_i = x_1 \overline{V}_1 + x_2 \overline{V}_2$$

$$v = (0.3)(38.632) + (0.7)(17.765) = 24.025 \text{ cm}^3 \text{ mol}^{-1}$$

The total number of mole required is

$$n_T = \frac{V}{v} = \frac{2000}{24.025} = 83.246 \text{ mol}$$

Volume of pure methanol is $V_1 = x_1 n_T v_1 = (0.3)(83.246)(40.727) = 1,017$ cm^3

Volume of pure methanol is $V_2 = x_2 n_T v_2 = (0.7)(83.246)(18.068) = 1,053$ cm^3

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[17] Smith J. M., Van Ness H. C., and Abbott M. M., <u>Introduction to Chemical Engineering Thermodynamics</u>, Mc Graw Hill, 2001, pg. 377

Example 3.6-2--
A 20 wt% chloroform solution is obtained by mixing chloroform, $CHCl_3$, with acetone, C_3H_6O, in an insulated mixer at steady state. For every gram of solution, 9.83 J is removed to keep the system temperature constant at 14^oC. Determine the enthalpy of mixing for this solution.

Solution --
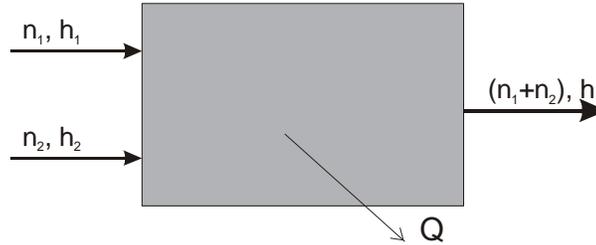
Chloroform (1), $CHCl_3$ $Mw_1 = 119.39$
Acetone (2), C_3H_6O $Mw_2 = 58.08$

For 100 g of solution, we have

$$n_1 = 20/119.39 = 0.1675 \text{ mol } CHCl_3$$

$$n_2 = 80/58.08 = 1.3774 \text{ mol } C_3H_6O$$

Therefore $n_T = n_1 + n_2 = 0.1675 + 1.3774 = 1.5449 \text{ mol}$

A first law over the system gives

$$n_1h_1 + n_2h_2 - (n_1 + n_2)h - Q = 0 \Rightarrow -Q/(n_1 + n_2) = h - (x_1h_1 + x_2h_2)$$

$$\Delta h_{mix} = -Q/n_T = h - (x_1h_1 + x_2h_2)$$

$$x_1 = 0.1675/1.5449 = 0.1084$$

$$x_1 = 1.3774/1.5449 = 0.8916$$

The heat of mixing is equal to the heat removed per mole of solution

$$\Delta h_{mix} = -Q/n_T = -q = -\hat{q}(x_1Mw_1 + x_2Mw_2)$$

$$\Delta h_{mix} = -(9.83)(0.1084 \times 119.39 + 0.8916 \times 58.08) = \textbf{636.3 J/mol}$$

Chapter 3

Example 3.6-3[18] --

A 5.0 wt% H_2SO_4 solution at 60°F is to be concentrated to 45 wt% by evaporation of water. The concentrated solution and water vapor leaving the evaporator at 180°F and 1 atm. Calculate the rate at which heat must be supplied to the evaporator to process 500 lb/hr of the feed solution. The enthalpy-concentration chart for H_2SO_4-H_2O is given in Figure E-1 where the reference states pure liquid water at 32°F and pure liquid H_2SO_4 at 77°F.
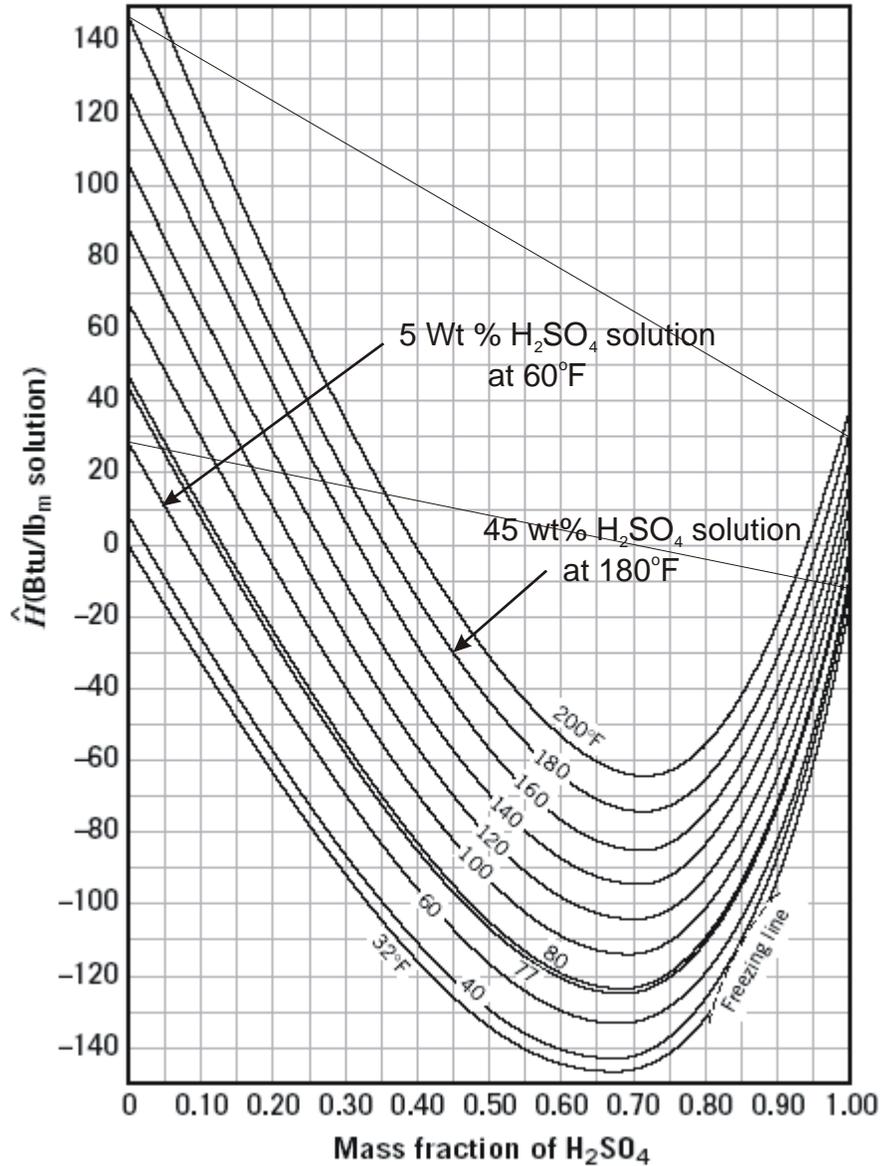
Figure E-1 Enthalpy-concentration chart for H_2SO_4-H_2O.

[18] Felder R. M., Rousseau R. W., <u>Elementary Principles of Chemical Processes</u>, Wiley, 2000
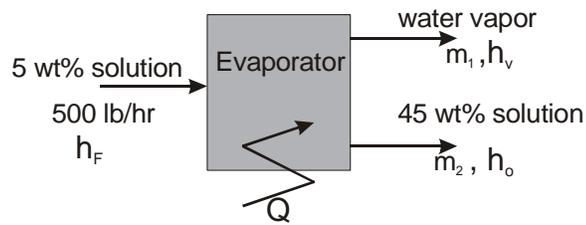
Solution --

Making an acid balance around the evaporator yields

$$(0.05)(500) = (0.45)(m_2) \Rightarrow m_2 = 55.56 \text{ lb/hr}$$

The rate of water vapor leaving the evaporator is then

$$m_1 = 500 - 55.56 = 444.44 \text{ lb/hr}$$

Enthalpy of the 5 wt% feed solution at 60°F is obtained from the chart

$$h_F = 10 \text{ Btu/lb}$$

Similarly, the enthalpy of 45 wt% solution at 180°F from the chart is

$$h_o = -30 \text{ Btu/lb}$$

You should note that the solution enthalpy could not be obtained from the pure properties. If it were the value would be on the straight line connecting the enthalpies of pure water and pure acid as shown in Figure E-1.

The enthalpy of water vapor, h_v, at 180°F, 1 atm can be approximated by the enthalpy of saturated water vapor at 180°F using steam table.

$$h_v = 1138 \text{ Btu/lb}$$

Making an energy balance over the evaporator gives

$$Q = 444.44 h_v + 55.56 h_o - 500 h_F$$

$$Q = (444.44)(1138) + (55.56)(-30) - (500)(10) = \mathbf{5.0 \times 10^5 \text{ lb/hr}}$$

Chapter 4
Principle of Phase Equilibrium II

4.1 The Phase Rule

We want to determine the number of intensive variables that must be specified to define a system consisting of m non-reacting components distributed among π phases. To describe each phase we need $m-1$ independent compositions, T, and P to a total of $m+1$ intensive variables. The total number of variables required to specify π phases is $\pi(m+1)$. For phase equilibrium we have the following set of equations:

$$T^{\alpha} = T^{\beta} = \ldots = T^{\pi}$$

$$P^{\alpha} = P^{\beta} = \ldots = P^{\pi}$$

$$\mu_1^{\alpha} = \mu_1^{\beta} = \ldots = \mu_1^{\pi}$$

$$\mu_2^{\alpha} = \mu_2^{\beta} = \ldots = \mu_2^{\pi}$$

$$\vdots$$

$$\mu_m^{\alpha} = \mu_m^{\beta} = \ldots = \mu_m^{\pi}$$

Each row in the set of equations above contains $(\pi-1)$ independent equations. Thus there are a total of $(\pi-1)(m+2)$ independent equations between the variables. The number of variables we can independently pick (the so-called degree of freedom, F) is obtained by subtracting the total $\pi(m+1)$ variables we need to specify by the $(\pi-1)(m+2)$ independent equations.

$$F = \pi(m+1) - (\pi-1)(m+2) = m - \pi + 2$$

We can independently specify $(m - \pi + 2)$ to complete define a system with m components and π phases.

Example 4.1-1 --
Determine the degree of freedom for the following system:

$$2x_1 - x_2 + 3x_3 = 0$$
$$x_1 + x_2 + 3x_3 = 5$$

Solution ---

There are three variables and two independent equations. Hence, the system has one degree of freedom.

Example 4.1-2 --

Determine the degree of freedom for the following vapor liquid equilibrium system with three species A, B, and C.

(a) A, B, and C are present in both gas and one single liquid phase.
(b) A, B, and C are present in gas phase but only A and B are present in the single liquid phase.
(c) A, B, and C are present in both gas and liquid phase (I) but only A and B are present in the liquid phase (II).

Solution --

(a) <u>A, B, and C are present in both gas and one single liquid phase.</u>

Number of intensive variables to specify the system is

$$\pi(m+1) = 2(3 + 1) = 8$$

For phase equilibrium we have the following set of independent equations:

$$T^L = T^G, P^L = P^G$$

$$\mu_A^L = \mu_A^G, \; \mu_B^L = \mu_B^G, \text{ and } \mu_C^L = \mu_C^G$$

The degree of freedom is then

$$f = \text{\# of variables} - \text{\# independent equations} = 8 - 5 = \mathbf{3}$$

(b) <u>A, B, and C are present in gas phase but only A and B are present in the single liquid phase.</u>

Number of intensive variables to specify the system:

Gas phase: $2 + 2 = 4$
Liquid phase: $1 + 2 = 3$

For phase equilibrium we have the following set of independent equations:

$$T^L = T^G, P^L = P^G$$

$$\mu_A^L = \mu_A^G, \text{ and } \mu_B^L = \mu_B^G$$

The degree of freedom is then

$$f = \text{\# of variables} - \text{\# independent equations} = 7 - 4 = \mathbf{3}$$

(c) *A, B,* and *C* are present in both gas and liquid phase (I) but only *A* and *B* are present in the liquid phase (II).

Number of intensive variables to specify the system:

> Gas phase: $2 + 2 = 4$
> Liquid phase (I): $2 + 2 = 4$
> Liquid phase (II): $1 + 2 = 3$

For phase equilibrium we have the following set of independent equations:

$$T^{L1} = T^{G},\ P^{L1} = P^{G},\ T^{L2} = T^{G},\ \text{and}\ P^{L2} = P^{G}$$

$$\mu_A^{L1} = \mu_A^{L2} = \mu_A^{G},\ \mu_B^{L1} = \mu_B^{L2} = \mu_B^{G},\ \text{and}\ \mu_C^{L1} = \mu_C^{G}$$

The degree of freedom is then

$$f\ =\ \#\ \text{of variables} - \#\ \text{independent equations} = 11 - 9 = \mathbf{2}$$

4.2 The Fugacity

Fugacity is a derived thermodynamic property that has the units of pressure. Fugacity is an abstract concept defined to facilitate certain calculations involved with phase and chemical equilibrium. For a pure substance at given T and P, we have

$$d\mu = vdP - sdT$$

At constant temperature

$$d\mu = vdP \tag{4.2-1}$$

If the gas is ideal, $v = RT/P$, Eq. (4.2-1) becomes

$$d\mu = RT\frac{dP}{P} \Rightarrow d\mu = RTd(\ln P) \tag{4.2-2}$$

For a real gas, $v \neq RT/P$. However we define a function f called fugacity so that the change in chemical potential with respect to P is given by an expression similar to equation (4.2-2)

$$d\mu = RTd(\ln f) \tag{4.2-3}$$

In the limit as $P \to 0$, $f \to P$ or $f/P \to 1$ since ideal gas law applies as $P \to 0$. Integrating Eq. (4.2-3) between a reference state and the state of the system yields

$$\mu - \mu^{o} = RT\ln\left(\frac{f}{f^{o}}\right) \tag{4.2-4}$$

In this equation μ^o is the chemical potential at the reference pressure, P^o, and at the same temperature as the chemical potential μ of interest. Similarly, the fugacity, $\hat{f}_i$, of a species in solution is defined as

$$\mu_i - \mu_i^o = RT\ln\left(\frac{\hat{f}_i}{\hat{f}_i^o}\right)$$

(4.2-5)

We now derive the criteria for phase equilibrium using fugacity. For phases α and β in equilibrium we have

$$\mu_i^\alpha = \mu_i^\beta$$

Substituting Eq. (4.2-5) into the above equation yields

$$\mu_i^{o,\alpha} + RT\ln\left(\frac{\hat{f}_i^\alpha}{\hat{f}_i^{\alpha,o}}\right) = \mu_i^{o,\beta} + RT\ln\left(\frac{\hat{f}_i^\beta}{\hat{f}_i^{\beta,o}}\right)$$

(4.2-6)

Rearranging Eq. (4.2-6) gives

$$\mu_i^{o,\alpha} - \mu_i^{o,\beta} = RT\ln\left(\frac{\hat{f}_i^{\alpha,o}}{\hat{f}_i^{\beta,o}}\right) + RT\ln\left(\frac{\hat{f}_i^\beta}{\hat{f}_i^\alpha}\right)$$

(4.2-7)

The first three terms of the equation are parts of the definition of fugacity given by Eq. (4.2-5).

$$\mu_i^{o,\alpha} - \mu_i^{o,\beta} = RT\ln\left(\frac{\hat{f}_i^{\alpha,o}}{\hat{f}_i^{\beta,o}}\right)$$

Therefore

$$0 = RT\ln\left(\frac{\hat{f}_i^\beta}{\hat{f}_i^\alpha}\right) \Rightarrow \hat{f}_i^\alpha = \hat{f}_i^\beta$$

(4.2-8)

Equation (4.2-8) forms the criterion for phase equilibrium in terms of fugacity.

Example 4.2-1[1] ---
Determine the fugacity of liquid water at 30°C and at the saturation pressure, 10 bar, and 100 bar.

Solution ---

At 30°C, $P^{\text{sat}} = 0.0424$ bar. In the limit as $P \to 0, f \to P$, therefore $f^{\text{sat}} = P^{\text{sat}} = 0.0424$ bar. From the definition of fugacity, we have

$$d\mu = RT d(\ln f) = v dP$$

Integrating the above equation from P^{sat} to P yields

$$RT\ln\left(\frac{f^L}{f^{sat}}\right) = v(P - P^{\text{sat}}) \Rightarrow f^L = f^{\text{sat}}\exp\left\{\frac{v(P - P^{sat})}{RT}\right\}$$

We have assumed the volume of liquid water remains constant at the saturation temperature of 30°C.

$$v = 0.001004 \text{ m}^3/\text{kg} = (0.001004)(18.02) = 0.01809 \text{ m}^3/\text{kmol}$$

The fugacity of liquid water at 30°C and 10 bar is then

$$f^L = 0.0424\exp\left\{\frac{0.01809(10 - 0.0424)\times 10^5}{(8314.3)(303.15)}\right\} = \textbf{0.0427 bar}$$

The fugacity of liquid water at 30°C and 100 bar is

$$f^L = 0.0424\exp\left\{\frac{0.01809(100 - 0.0424)\times 10^5}{(8314.3)(303.15)}\right\} = \textbf{0.0455 bar}$$

Hence the fugacity of a pure liquid varies little over a moderate pressure range.

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[1] Kyle, B.G., <u>Chemical and Process Thermodynamics</u>, Prentice Hall, 1999, pg. 257

Example 4.2-2 ---
Determine the fugacity of CO_2 at $310^\circ K$ and 1.4×10^6 Pa using the Van der Waals equation of state (EOS).

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

Data: $a = 0.3658$ Pa·m^6/mol^2, $b = 4.286\times10^{-5}$ m^3/mol

Solution --

From the definition of fugacity, we have

$$d\mu = RTd(\ln f) = vdP \tag{E-1}$$

Since the equation of state is given explicitly in terms of pressure P, we need to rearrange the above equation so that the term vdP can be easily integrated. For an ideal gas we have

$$RTd(\ln P) = vdP = \frac{RT}{P}dP \tag{E-2}$$

Subtracting Eq. (E-1) from Eq. (E-2) gives

$$RTd(\ln f/P) = \left(v - \frac{RT}{P} \right)dP$$

Integrating the equation from 0 to P gives

$$RT\int_1^{f/P} d\,(\ln f/P) = \int_0^P \left(v - \frac{RT}{P} \right)dP$$

$$\ln\left(\frac{f}{P} \right) = \frac{1}{RT}\int_0^P \left(v - \frac{RT}{P} \right)dP \tag{E-3}$$

We now want to change the integrating variable from P to v using the product rule

$$d(Pv) = Pdv + vdP \Rightarrow dP = \frac{1}{v}d(Pv) - \frac{P}{v}dv$$

Using the definition of the compressibility factor, $Z = \dfrac{Pv}{RT}$, we have

$$d(Pv) = RTdZ \Rightarrow dP = \frac{RT}{v}dZ - \frac{P}{v}dv = \frac{P}{Z}dZ - \frac{P}{v}dv$$

Substituting dP from the above equation to Eq. (E-3) gives

$$\ln\left(\frac{f}{P}\right) = \frac{1}{RT} \int_{v=\infty}^{v} \left(v - \frac{RT}{P}\right)\left(\frac{P}{Z}dZ - \frac{P}{v}dv\right) \tag{E-4}$$

Expanding the right hand side of the equation yields

$$\ln\left(\frac{f}{P}\right) = \frac{1}{RT} \int_{v=\infty}^{v} \left(\frac{RT}{v} - P\right)dv + \frac{1}{RT} \int_{Z=1}^{Z} \left(\frac{Pv}{Z} - \frac{RT}{Z}\right)dZ \tag{E-5}$$

We can integrate the second integral on the RHS of Eq. (E-5).

$$\frac{1}{RT} \int_{Z=1}^{Z} \left(\frac{Pv}{Z}Z - \frac{RT}{Z}\right)dZ = \int_{1}^{Z} \left(\frac{Pv}{RT}\frac{1}{Z} - \frac{1}{Z}\right)dZ = \int_{1}^{Z} \left(1 - \frac{1}{Z}\right)dZ$$

$$\frac{1}{RT} \int_{Z=1}^{Z} \left(\frac{Pv}{Z}Z - \frac{RT}{Z}\right)dZ = (Z - \ln Z)\Big|_{1}^{Z} = Z - \ln Z - 1$$

Hence

$$\ln\left(\frac{f}{P}\right) = \frac{1}{RT} \int_{v=\infty}^{v} \left(\frac{RT}{v} - P\right)dv - \ln Z + (Z - 1)$$

We will now integrate the integral with respect to v using the Van der Waals equation of state.

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\frac{RT}{v} - P = \frac{RT}{v} - \frac{RT}{v-b} + \frac{a}{v^2}$$

$$\frac{1}{RT} \int_{v=\infty}^{v} \left(\frac{RT}{v} - P\right)dv = \int_{v=\infty}^{v} \frac{dv}{v} - \int_{v=\infty}^{v} \frac{dv}{v-b} + \int_{v=\infty}^{v} \frac{adv}{RTv^2}$$

$$\frac{1}{RT} \int_{v=\infty}^{v} \left(\frac{RT}{v} - P\right)dv = \ln\frac{v}{v-b}\Big|_{v^{\infty}}^{v} - \frac{a}{RTv}\Big|_{v^{\infty}}^{v} = \ln\frac{v}{v-b} - \ln\frac{v^{\infty}}{v^{\infty}-b}$$

$$\frac{1}{RT} \int_{v=\infty}^{v} \left(\frac{RT}{v} - P\right)dv = \ln\frac{v}{v-b} - \ln\frac{v^{\infty}}{v^{\infty}-b} - \frac{a}{RTv}$$

$$\frac{1}{RT} \int_{v=\infty}^{v} \left(\frac{RT}{v} - P\right)dv = -\ln\frac{v-b}{v} - \frac{a}{RTv} = -\ln\left(1 - \frac{b}{v}\right) - \frac{a}{RTv}$$

Therefore

$$\ln\left(\frac{f}{P}\right) = -\ln\left(1 - \frac{b}{v}\right) - \frac{a}{RTv} - \ln Z + (Z - 1) \tag{E-6}$$

We need to evaluate the compressibility factor Z from the Van der Waals equation of state.

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \Rightarrow \frac{Pv}{RT} = \frac{v}{v - b} - \frac{a}{RTv}$$

$$Z = \frac{1}{1 - b/v} - \frac{a}{RTv}$$

Since $v = \dfrac{ZRT}{P} \Rightarrow Z = \dfrac{1}{1 - \dfrac{bP}{ZRT}} - \dfrac{aP}{Z(RT)^2}$ \hfill (E-7)

Let $B = \dfrac{bP}{RT}$ and $A = \dfrac{aP}{(RT)^2}$, equation (E-7) becomes

$$Z = \frac{1}{1 - \dfrac{B}{Z}} - \frac{A}{Z}$$

We now will rearrange the equation into the polynomial form

$$Z\left(1 - \frac{B}{Z}\right)Z = Z - A\left(1 - \frac{B}{Z}\right)$$

$$Z^2 - BZ = Z - A + \frac{AB}{Z}$$

$$Z^3 - (1 + B)Z^2 + AZ - AB = 0 \tag{E-8}$$

In terms of A and B, equation (E-6) becomes

$$\ln\left(\frac{f}{P}\right) = -\ln\left(1 - \frac{B}{Z}\right) - \frac{A}{Z} - \ln Z + (Z - 1)$$

$$\ln\left(\frac{f}{P}\right) = (Z - 1) - \frac{A}{Z} - \ln (Z - B) \tag{E-9}$$

The fugacity can be determined from Eq. (E-9) with the values of Z obtained from the solution of Eq. (E-8). Table 4.2-1 lists the Matlab program and the results for the fugacity calculation. From the program, we have

$$f = 1.325 \times 10^6 \text{ Pa}$$

4-8

Chapter 4

Table 4.2-1 --

```
% Example 4.2-2, compressibility using Van der Waals EQS
%
R = 8.314; % Pa.m3/(mol.K)
a=0.3658; % Pa.m6/mol2
b=4.286e-5; % m3/mol
%
P=1.4e6; % Pa
T=310; % K
%
A=a*P/(R*T)^2;B=b*P/(R*T);
fprintf('A = %8.5e, B = %8.5e\n',A,B)
b2=-(1+B);b1=A;b0=-A*B;
fprintf('b2 = %8.5e, b1 = %8.5e, b0 = %8.5e\n',b2,b1,b0)
%
%  Solve for the compressibility factor Z using Newton method
%
Z=1;
for i=1:20
   fz=((Z+b2)*Z+b1)*Z+b0;
   dfz=(3*Z+2*b2)*Z+b1;
   eZ=fz/dfz;Z=Z-eZ;
   if abs(eZ)<.00001; break; end
end
foP=exp((Z-1)-A/Z-log(Z-B));
f=P*foP;
fprintf('Z = %8.5f, f/P = %8.5f\n',Z,foP)
fprintf('f(Pa) = %8.5e\n',f)

>> e4d2d2
A = 7.70954e-002, B = 2.32814e-002
b2 = -1.02328e+000, b1 = 7.70954e-002, b0 = -1.79489e-003
Z =  0.94359, f/P =  0.94642
f(Pa) = 1.32499e+006
```

Example 4.2-3 ---

Use data from the steam table to calculate the fugacity of steam at $300^\circ C$ and 8×10^6 Pa.

Solution --

From the definition of fugacity for pure component we have

$$d\mu = dg = RT d(\ln f)$$

We integrate this equation from the pressure low enough so that the fugacity is essentially the same as the pressure.

$$\int_{g^{IG}}^{g} dg = RT \int_{P}^{f} d(\ln f)$$

$$f = P\exp\left(\frac{g - g^{IG}}{RT}\right) \qquad\qquad\qquad\qquad (E\text{-}1)$$

From the steam table, at $300^\circ C$ or $573.15^\circ K$ and $P = 10^4$ Pa, the pressure is low enough so that ideal gas law applies, we have

$$h^{IG} = 3077 \text{ kJ/kg and } s^{IG} = 9.281 \text{ kJ/kg·}^\circ K$$

Therefore $\quad g^{IG} = h^{IG} - Ts^{IG} = 3077 - (573.15)(9.281) = -2243 \text{ kJ/kg}$

$$g^{IG} = -(2243)(18) = -40,409 \text{ J/mol}$$

At $573.15^\circ K$ and $P = 8\times10^6$ Pa, we have

$$h = 2785 \text{ kJ/kg and } s = 5.791 \text{ kJ/kg·}^\circ K$$

$$g = h - Ts = -534 \text{ kJ/kg} = -9,618 \text{ J/mol}$$

Substituting the values of Gibbs free energy into equation (E-1) yields

$$f = P\exp\left(\frac{g - g^{IG}}{RT}\right) = 10^4 \exp\left(\frac{-9,618 - (-40,409)}{8.314 \times 573.15}\right) = \mathbf{6.401\times10^6 \, Pa}$$

Example 4.2-4 ---

Determine the change in Gibbs energy, Δg, of CO_2 at 310°K, 1.4×10^6 Pa and at 310°K, 1.4×10^7 Pa using the Van der Waals equation of state (EOS).

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

Data: $a = 0.3658$ Pa·m^6/mol^2, $b = 4.286\times10^{-5}$ m^3/mol

(a) Evaluate Δg using the fugacity, $\Delta g = RT\ln(f_2/f_1)$.
(b) Evaluate Δg using direct integration, $\Delta g = \int v \, dP$.

Solution ---

(a) Evaluate Δg using the fugacity, $\Delta g = RT\ln(f_2/f_1)$.

The fugacity using Van der Waals EOS is given by

$$\ln\left(\frac{f}{P}\right) = (Z-1) - \frac{A}{Z} - \ln(Z-B)$$

The compressibility Z is the largest root of the equation $Z^3 - (1+B)Z^2 + AZ - AB = 0$ where

$$A = \frac{aP}{(RT)^2} = 7.70954\times10^{-2} \text{ (at } 310^\circ\text{K, } 1.4\times10^6 \text{ Pa)}$$

$$B = \frac{bP}{RT} = 2.32814\times10^{-2} \text{ (at } 310^\circ\text{K, } 1.4\times10^6 \text{ Pa)}$$

Table 4.2-2 lists the Matlab program to determine Z, f, and Δg with the following results at 310°K:

P(Pa)	Z	f(Pa)
1.4×10^6	0.94359	1.325×10^6
1.4×10^7	0.41648	6.680×10^6

The change in Gibbs energy is then given by

$$\Delta g = RT\ln(f_2/f_1) = (8.314)(310)\ln(6.680/1.325) = 4169.23 \text{ J}$$

(b) Evaluate Δg using direct integration, $\Delta g = \int v \, dP$.

We can use 5 points Simpson's rule to evaluate the integral where

$$\Delta g = \frac{\Delta P}{3}(v_1 + 4v_2 + 2v_3 + 4v_4 + v_5)$$

$$\Delta P = \frac{1.4 \times 10^7 - 1.4 \times 10^6}{4} = 3.15 \times 10^6 \text{ Pa}$$

The specific volume can be determined from $v = \dfrac{ZRT}{P}$ using the following values for P and Z.

P(Pa)	Z	v(m^3/mol)
1.40×10^6	0.94359	1.737×10^{-3}
4.55×10^6	0.78834	4.466×10^{-4}
7.70×10^6	0.48223	1.614×10^{-4}
1.085×10^7	0.35298	8.385×10^{-5}
1.40×10^7	0.41648	7.667×10^{-5}

The change in Gibbs energy is then

$$\Delta g = \frac{\Delta P}{3}(v_1 + 4v_2 + 2v_3 + 4v_4 + v_5) = 4471.12 \text{ J}$$

The result of the integral $\int v \, dP$ can be improved by using more points for the Simpson's rule as shown in the following table

n	5	9	13	17	35
Δg(J)	4471.12	4226.39	4187.28	4175.95	4170.54

At $n = 35$, the value of $\int v \, dP$ is almost the same as the value obtained from the expression:
$\Delta g = RT\ln(f_2/f_1) = 4169.23$ J.

Table 4.2-1 ---

```matlab
% Example 4.2-4, change in Gibbs energy using Van der Waals EOS
%
R = 8.314; % Pa.m3/(mol.K)
a=0.3658; % Pa.m6/mol2
b=4.286e-5; % m3/mol
%
ns=input('Odd number of data point, ns = ');
T=310; RT = R*T; % K
v=zeros(ns,1);
%
Pv=linspace(1.4e6,1.4e7,ns);; % Pa
Z=1;
fv=zeros(ns,1);
for ni=1:ns
   P=Pv(ni);
   A=a*P/(RT)^2;B=b*P/(RT);
   b2=-(1+B);b1=A;b0=-A*B;
for i=1:20
   fz=((Z+b2)*Z+b1)*Z+b0;
   dfz=(3*Z+2*b2)*Z+b1;
   eZ=fz/dfz;Z=Z-eZ;
   if abs(eZ)<.00001; break; end
end
   v(ni)=Z*RT/P;
   f=P*exp((Z-1)-A/Z-log(Z-B));
   fprintf('Z = %8.5f, f(Pa) = %8.3e\n',Z,f)
   fv(ni)=f;
end
dg=R*T*log(fv(ns)/fv(1));
fprintf('From fugacity, dg(J) = %8.2f\n',dg)
con=(Pv(2)-Pv(1))/3;
sum=v(1)+v(ns);
for i=2:2:ns
   sum=sum+4*v(i);
end
for i=3:2:ns-1
   sum=sum+2*v(i);
end
dg=sum*con;
fprintf('From integration of vdP, dg(J) = %8.2f\n',dg)
```

```
>> e4d2d4
Odd number of data point, ns = 35
Z =  0.94359, f(Pa) = 1.325e+006, v(m3/mol) = 1.737e-003
Z =  0.92768, f(Pa) = 1.651e+006, v(m3/mol) = 1.350e-003
Z =  0.91127, f(Pa) = 1.966e+006, v(m3/mol) = 1.097e-003
Z =  0.89433, f(Pa) = 2.271e+006, v(m3/mol) = 9.177e-004
Z =  0.87680, f(Pa) = 2.565e+006, v(m3/mol) = 7.840e-004
Z =  0.85861, f(Pa) = 2.849e+006, v(m3/mol) = 6.803e-004
Z =  0.83967, f(Pa) = 3.123e+006, v(m3/mol) = 5.972e-004
Z =  0.81989, f(Pa) = 3.386e+006, v(m3/mol) = 5.291e-004
Z =  0.79913, f(Pa) = 3.638e+006, v(m3/mol) = 4.719e-004
Z =  0.77724, f(Pa) = 3.879e+006, v(m3/mol) = 4.230e-004
Z =  0.75399, f(Pa) = 4.110e+006, v(m3/mol) = 3.806e-004
Z =  0.72911, f(Pa) = 4.329e+006, v(m3/mol) = 3.431e-004
Z =  0.70218, f(Pa) = 4.537e+006, v(m3/mol) = 3.095e-004
Z =  0.67258, f(Pa) = 4.732e+006, v(m3/mol) = 2.788e-004
Z =  0.63934, f(Pa) = 4.916e+006, v(m3/mol) = 2.501e-004
Z =  0.60064, f(Pa) = 5.086e+006, v(m3/mol) = 2.225e-004
Z =  0.55256, f(Pa) = 5.240e+006, v(m3/mol) = 1.943e-004
Z =  0.48223, f(Pa) = 5.377e+006, v(m3/mol) = 1.614e-004
Z =  0.35936, f(Pa) = 5.484e+006, v(m3/mol) = 1.148e-004
Z =  0.33269, f(Pa) = 5.569e+006, v(m3/mol) = 1.016e-004
Z =  0.32811, f(Pa) = 5.648e+006, v(m3/mol) = 9.597e-005
Z =  0.32914, f(Pa) = 5.725e+006, v(m3/mol) = 9.238e-005
Z =  0.33267, f(Pa) = 5.801e+006, v(m3/mol) = 8.975e-005
Z =  0.33757, f(Pa) = 5.875e+006, v(m3/mol) = 8.767e-005
Z =  0.34333, f(Pa) = 5.949e+006, v(m3/mol) = 8.596e-005
Z =  0.34966, f(Pa) = 6.022e+006, v(m3/mol) = 8.450e-005
Z =  0.35638, f(Pa) = 6.095e+006, v(m3/mol) = 8.324e-005
Z =  0.36340, f(Pa) = 6.168e+006, v(m3/mol) = 8.212e-005
Z =  0.37064, f(Pa) = 6.241e+006, v(m3/mol) = 8.112e-005
Z =  0.37804, f(Pa) = 6.314e+006, v(m3/mol) = 8.021e-005
Z =  0.38557, f(Pa) = 6.387e+006, v(m3/mol) = 7.939e-005
Z =  0.39319, f(Pa) = 6.460e+006, v(m3/mol) = 7.863e-005
Z =  0.40090, f(Pa) = 6.533e+006, v(m3/mol) = 7.793e-005
Z =  0.40866, f(Pa) = 6.606e+006, v(m3/mol) = 7.728e-005
Z =  0.41648, f(Pa) = 6.680e+006, v(m3/mol) = 7.667e-005
From fugacity, dg(J) =  4169.23
From integration of vdP, dg(J) =  4170.54
>>
```

Chapter 4

4.3 Fugacity of Species i in a Gas Mixture

The fugacity, $\hat{f}_i^v$, of species i in a gas mixture depends on temperature, pressure, and composition of the mixture.

$$\hat{f}_i^v(T, P, n_1, n_2, \ldots n_m) = y_i \hat{\varphi}_i^v(T, P, n_1, n_2, \ldots n_m)P \qquad (4.3\text{-}1)$$

In this equation, $\hat{\varphi}_i^v$ is the fugacity coefficient and m is the number of component. To completely specify the reference state for a mixture, we need to know T, P, and composition. The reference pressure is a low enough pressure, P_{low}, so that the mixture behaves as an ideal gas. The reference temperature is that of the system of interest, T_{sys} and the reference composition is that of the system $n_{i,sys}$. The fugacity, $\hat{f}_i$, of a species in solution is defined as

$$\mu_i - \mu_i^o = RT\ln\left(\frac{\hat{f}_i}{\hat{f}_i^o}\right) \qquad (4.3\text{-}2)$$

At constant temperature

$$d\mu_i = \overline{V}_i \, dP \implies \mu_i - \mu_i^o = \int_{P_{low}}^{P} \overline{V}_i \, dP = RT\ln\left(\frac{\hat{f}_i}{\hat{f}_i^o}\right) \qquad (4.3\text{-}3)$$

Many equations of state are explicit in P but not V, so it is convenient to express the partial molar volume in terms of derivative in P.

$$\overline{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j \neq i}} \qquad (4.3\text{-}4)$$

Using the cyclic rule at constant T, we have

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P}\left(\frac{\partial P}{\partial V}\right)_{T,n_i}\left(\frac{\partial n_i}{\partial P}\right)_{T,V} = -1 \qquad (4.3\text{-}4)$$

Since the reference state and the system have the same composition, the integral in equation (4.3-3) is carried out with both n_i and T constant. Therefore the second partial derivative in equation (4.3-4) is replaced with a total derivative.

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P}\frac{dP}{dV}\left(\frac{\partial n_i}{\partial P}\right)_{T,V} = -1$$

Rearranging the equation yields

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P} dP = -\left(\frac{\partial P}{\partial n_i}\right)_{T,V} dV \tag{4.3-5}$$

Equation (4.3-3) becomes

$$RT\ln\left(\frac{\hat{f}_i}{\hat{f}_i^o}\right) = RT\ln\left(\frac{\hat{f}_i}{y_i P_{low}}\right) = -\int_{V^{IG}}^{V}\left(\frac{\partial P}{\partial n_i}\right)_{T,P,n_j} dV \tag{4.3-6}$$

Equation (4.3-6) can be evaluated with an equation of state such as the Peng-Robinson equation:

$$P = \frac{RT}{v-b} - \frac{a\alpha}{v^2 + 2bv - b^2} \tag{4.3-7}$$

In this equation, $a = 0.45724\dfrac{(RT_c)^2}{P_c}$, $b = 0.0778\dfrac{RT_c}{P_c}$, and

$$\alpha = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)\left(1 - \sqrt{T_r}\right)\right]^2$$

ω is the acentric factor. The Peng-Robinson equation of state can be expressed in terms of the compressibility Z as

$$Z^3 + (B-1)Z^2 + (A - 3B^2 - 2B)Z + (B^3 + B^2 - AB) = 0 \tag{4.3-8}$$

In this equation, $Z = \dfrac{Pv}{RT}$, $A = \displaystyle\sum_{i=1}^{m}\sum_{j=1}^{m} x_i x_j A_{ij}$, $B = \displaystyle\sum_{i=1}^{m} x_i B_i$, where

$$A_{ii} = 0.45724\frac{P_{r,i}}{T_{r,i}^2}\left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)\left(1 - \sqrt{T_r}\right)\right]^2$$

$$A_{ij} = A_{ji} = (1 - k_{ij})(A_{ii}A_{jj})^{1/2}, \quad k_{ij} = \text{binary interaction parameter}$$

$$B_i = 0.0778\frac{P_{r,i}}{T_{r,i}}$$

The smallest root of equation (4.3-8), Z^L, is identified with the liquid phase while the largest root, Z^V, is identified with the vapor phase. Using the Peng-Robinson equation, the fugacity coefficient of species i in a mixture is given by

$$\ln \hat{\varphi}_i = \frac{1}{2\sqrt{2}B}\left(\frac{AB_i}{B} - 2\sum_{j=1}^{m} \chi_j A_{ij}\right)\ln\left(\frac{Z + \left(1 + \sqrt{2}\right)B}{Z + \left(1 - \sqrt{2}\right)B}\right) + \frac{B_i}{B}(Z-1) - \ln(Z-B) \tag{4.3-9}$$

For the liquid $Z = Z^L$, $\hat{\varphi}_i = \hat{\varphi}_i^L$, and $\chi = x$ = mole fraction of species i in the liquid phase. For the vapor $Z = Z^V$, $\hat{\varphi}_i = \hat{\varphi}_i^v$, and $\chi = y$ = mole fraction of species i in the vapor phase.

Example 4.3-1 ---
Determine the fugacity coefficient of each species in a gas mixture of 20% ethane in propane at a pressure of 50 bar and a temperature of 25°C using the Peng-Robinson EOS.

Solution --

The fugacity coefficient of each species in a gas mixture might be obtained from the free T.K. Nguyen's program VLE. The results are displayed as follows

The program *Thermosolver* by Koretsky can also determine the fugacity coefficient as shown

Table 4.3-1 lists the Matlab program and the results for the fugacity coefficient calculation. **Note:** In this program A = am, B = bm, A_{ij} = aij, and B_i = b.

Table 4.3-1 --

```
% Example 4.3-1, Fugacity coefficient using Peng-Robinson EOS
% Binary mixture of 20 mole % ethane (1) in propane at 50 bar and 25 C
%
Tc=[305.43 369.9]; % Degree K
Pc=[48.84 42.57]; % bar
w=[0.0986 0.1524];
m=2; P=50; T=25+273.15;y=[.2 .8];
Tr=T./Tc;Pr=P./Pc;
 b= .0778 * Pr ./ Tr;
  xk = .37464 + (1.54226 - .26992 * w) .* w;
  alfa = 1 + xk .* (1 - sqrt(Tr));
  a= .45724 * alfa .* alfa .* Pr ./ (Tr.* Tr);
for i = 1:m
   aij(i, i) = a(i);
end
for i = 1 : m - 1
  for j = 1 + i : m
    aij(i, j) = sqrt(a(i) * a(j));aij(j, i) = aij(i, j);
  end
end
am=0;bm=0;
for i = 1 : m
  bm = bm + y(i) * b(i);
  for j = 1 : m
    am = am + y(i) * y(j) * aij(i, j);
  end
end
b2 = bm - 1; b1 = am - 3 * bm * bm - 2 * bm;
b0 = bm * (bm * bm + bm - am);
Z=1;
for i=1:20
   fz=((Z+b2)*Z+b1)*Z+b0;
   dfz=(3*Z+2*b2)*Z+b1;
   eZ=fz/dfz;Z=Z-eZ;
   if abs(eZ)<.00001; break; end
end
fprintf('Z = %8.5f\n',Z)
s2=sqrt(2);
Tem = (Z + (1+s2 )* bm) / (Z + (1-s2 ) * bm);
ag = log(Tem)/(2*s2*bm);
for i = 1 : m
  suma = 0;
  for j = 1 : m
    suma = suma + y(j) * aij(i, j);
  end
```

```
   fuco(i) = exp(ag * (am*b(i) / bm - 2 * suma)  + b(i) * (Z - 1) / bm - log(Z - bm));
 fprintf('Species %g, fugacity coef. = %8.5f\n',i,fuco(i))
end
>> e4d3d1
Z =  0.16436
Species 1, fugacity coef. =  0.61165
Species 2, fugacity coef. =  0.18551
```

4.4 Fugacity in the Liquid Phase

In the liquid phase we also need to choose a suitable reference state with a corresponding reference chemical potential and reference fugacity to complete the definition defined by

$$\mu_i - \mu_i^o = RT\ln\left(\frac{\hat{f}_i}{\hat{f}_i^o}\right) \tag{4.4-1}$$

For an ideal solution, we have

$$\mu_i^{ideal} - g_i^{ideal} = RT\ln x_i = RT\ln\left(\frac{\hat{f}_i^{ideal}}{f_i^{ideal}}\right) \tag{4.4-2}$$

Equation (4.4-2) indicates that the fugacity of an ideal solution is linear in mole fraction to the pure species fugacity

$$\hat{f}_i^{ideal} = x_i f_i^{ideal} \tag{4.4-3}$$

If the reference state is the pure fugacity of species i, we have the **Lewis/Randall rule**:

$$f_i^{ideal} = f_i^o = f_i \tag{4.4-4}$$

The activity coefficient, γ_i, is defined as the ratio of the fugacity in the actual solution to the fugacity in the ideal solution at the composition of the mixture.

$$\gamma_i = \frac{\hat{f}_i^l}{\hat{f}_i^{ideal}} = \frac{\hat{f}_i^l}{x_i f_i^o} \tag{4.4-5}$$

The activity coefficient, γ_i, is similar to the fugacity coefficient, $\hat{\varphi}_i^v$, defined for the vapor phase

$$\hat{\varphi}_i^v = \frac{\hat{f}_i^v}{p_{i,sys}} = \frac{\hat{f}_i^v}{y_i P_{sys}} \tag{4.4-6}$$

The fugacity coefficient is a dimensionless quantity expressing how the fugacity in the vapor phase compares to how it would hypothetically behave as an ideal gas while the activity coefficient represents a dimensionless quantity of how the fugacity in the liquid phase compares relative to the ideal reference state. Both of these coefficients tell us how far the system is deviating from ideal behavior. For gases, the ideal state is a unique state where the intermolecular interactions are zero. For liquids, on the other hand, the reference state is a state where all the intermolecular interactions are the same.

The activity of species i in the liquid, a_i, is often used for system in chemical equilibrium. It is defined as follows:

$$a_i = \frac{\hat{f}_i^l}{f_i^o} \tag{4.4-7}$$
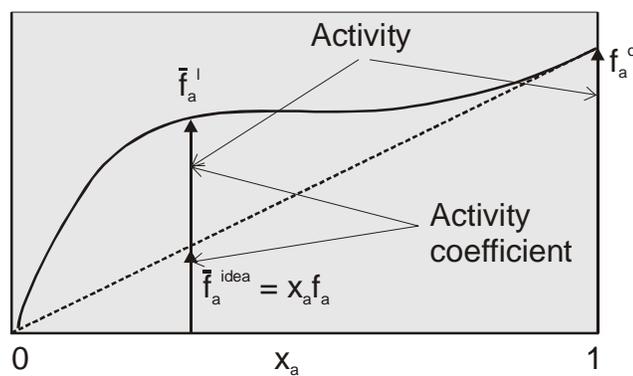
Figure 4.4-1 Fugacity of a binary liquid mixture.

The activity compares the fugacity of species i in the solution to the fugacity of the pure species in its reference state. On the other hand, the activity coefficient compares the fugacity of species i in the solution to the fugacity of species i in an ideal solution as shown in Figure 4.4-1. Comparison of Equations (4.4-5) and (4.4-7) gives a relation between the activity and the activity coefficient.

$$a_i = x_i \gamma_i \tag{4.4-8}$$

We will normally use activity coefficients to describe non-ideal solution in phase equilibrium. However activity will be more convenient to use when we encounter chemical equilibrium.

In summary, the reference state for species i in the liquid (or solid) phase is just a defined state, real or hypothetical, at a given P and x_i (usually that of the system) and at the temperature of the system. Some text will define the reference state that has the temperature of the system as a *standard state* to distinguish from the reference state that is not at the system temperature. A pure gas can be a non-ideal gas, while a pure liquid must be an ideal solution since all intermolecular forces in a pure liquid are the same. An increase in pressure will lead to deviation from ideal gas law, whereas deviations form ideal solution can occur at low pressure since non-ideal behavior is mainly due to dissimilar intermolecular forces between species in a mixture.

Chapter 5

Applied Phase Equilibrium

5.1 Vapor-Liquid Equilibrium for Ideal Systems

The most common problems requiring contact between phases chemical engineers encounter in the chemical, petroleum, and related industries involve vapor-liquid equilibrium. At equilibrium, the fugacity of species i in the vapor phase is equal to that in the liquid phase

$$\hat{f}_i^v = \hat{f}_i^l \tag{5.1-1}$$

The fugacity of species i in the vapor phase can be expressed in terms of the mole fraction, y_i, fugacity coefficient, $\hat{\varphi}_i^v$, and total pressure, P, as

$$\hat{f}_i^v = y_i \hat{\varphi}_i^v P \tag{5.1-2}$$

The fugacity of species i in the liquid phase can be expressed in terms of the mole fraction, x_i, activity coefficient, $\hat{\varphi}_i^v$, and fugacity of pure component, P, as

$$\hat{f}_i^l = x_i \gamma_i f_i \tag{5.1-3}$$

Therefore

$$y_i \hat{\varphi}_i^v P = x_i \gamma_i f_i \tag{5.1-4}$$

If the vapor phase obeys ideal gas law, $\hat{\varphi}_i^v = 1$, and the liquid solution is ideal, $\gamma_i = 1$, Eq. (5.1-4) becomes

$$y_i P = x_i f_i \tag{5.1-5}$$

At low pressure, $f_i = P_i^{sat}$, Eq. (5.1-5) becomes Raoult's law

$$y_i P = x_i P_i^{sat} \tag{5.1-6}$$

The equilibrium ratio or K-value is defined as

$$K_i = \frac{y_i}{x_i} \tag{5.1-7}$$

When Raoult's law applies we have

$$K_i = \frac{P_i^{sat}}{P} \tag{5.1-8}$$

In general, the K-values depend on temperature, pressure, and the composition in both phases. For light hydrocarbon system (methane to decane), the K-values have been determined semi-empirically and can be evaluated from the equations given in **Table 5.1-1**[1]. In general, K is a function of temperature, pressure, and composition.

Table 5.1-1 Equilibrium K values for light hydrocarbon systems

==

(1) $\ln K = -A/T^2 + B - C \ln(P) + D/P^2$

(2) $\ln K = -A/T^2 + B - C \ln(P) + D/P$

(3) $\ln K = -A/T + B - C \ln(P)$, where P is in psia, T is in ^oR

Compound	A	B	C	D	Form
Methane	292860	8.2445	.8951	59.8465	(1)
Ethylene	600076.9	7.90595	.84677	42.94594	(1)
Ethane	687248.2	7.90694	.866	49.02654	(1)
Propylene	923484.7	7.71725	.87871	47.67624	(1)
Propane	970688.6	7.15059	.76984	6.90224	(2)
i-Butane	1166846	7.72668	.92213	0	(1)
n-Butane	1280557	7.94986	.96455	0	(1)
i-Pentane	1481583	7.58071	.93159	0	(1)
n-Pentane	1524891	7.33129	.89143	0	(1)
n-Hexane	1778901	6.96783	.84634	0	(1)
n-Heptane	2013803	6.52914	.79543	0	(1)
n-Octane	7646.816	12.48457	.73152		(3)
n-Nonane	2551040	5.69313	.67818	0	(1)
n-Decane	9760.457	13.80354	.7147		(3)

==

In flash distillation, a liquid mixture is partially vaporized and the vapor is allowed to come to equilibrium with the liquid. The process flow diagram is shown in **Figure 5.1-1**. The vapor and liquid phases are then separated.
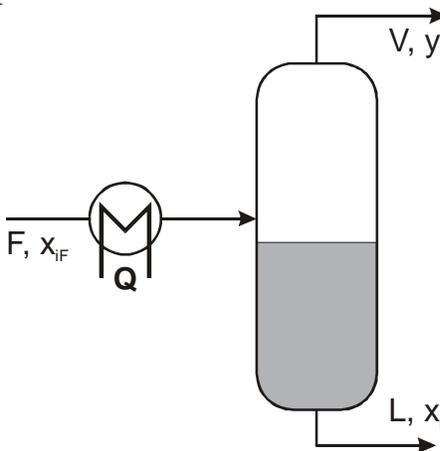
Figure 5.1-1 Flash distillation.

[1] Wankat, P. C., Equilibrium Staged Separations, Elsevier, 1988

Besides flash calculation, which will be discussed later, there are four types of vapor-liquid equilibrium calculations: (1) Bubble point temperature calculation, (2) Bubble point pressure calculation, (3) Dew point temperature calculation, and (4) Dew point pressure calculation.

Bubble point temperature calculation

In a bubble point temperature calculation, the pressure and liquid phase composition are specified. We will solve for the temperature and the vapor composition. The solution provides the composition of the first bubble of vapor that forms when heat is supplied to a saturated liquid. Since the vapor mole fractions are unknown, we start with the equation

$$\sum_{i=1}^{m} y_i = 1 \tag{5.1-9}$$

Using the K-values: $K_i = \dfrac{y_i}{x_i}$, Eq. (5.1-9) becomes

$$\sum_{i=1}^{m} K_i x_i = 1 \tag{5.1-10}$$

If the system contains more than two components, we might want to solve the log form of equation (5.1-10) for better convergence

$$\ln\left(\sum_{i=1}^{m} K_i x_i\right) = 0 \tag{5.1-11}$$

Example 5.1-1 ---
Determine the temperature and composition of the first bubble created from a saturated liquid mixture of benzene and toluene containing 45 mole percent benzene at 200 kPa. Benzene and toluene mixtures may be considered as ideal.

Data: Vapor pressure, P^{sat}, data: $\ln P^{sat} = A - B/(T + C)$, where P^{sat} is in kPa and T is in °K.

Compound	A	B	C
Benzene (1)	14.1603	2948.78	− 44.5633
Toluene (2)	14.2515	3242.38	− 47.1806

Solution --

We start with the equation

$$y_1 + y_2 = 1 \tag{E-1}$$

Substituting $y_i = x_i P_i^{sat}/P$ into equation (E-1) yields

$$x_1 P_1^{sat} + x_2 P_2^{sat} = P \tag{E-2}$$

With the numerical values for mole fractions and pressure, equation (E-2) becomes

$$0.45\exp(14.1603 - 2948.78/(T - 44.5633))$$
$$+ 0.55\exp(14.2515 - 3242.38/(T - 47.1806)) = 200 \qquad \text{(E-3)}$$

The bubble point temperature should be between the boiling points of benzene and toluene given by

$$T_1{}^{\text{boil}} = \frac{2948.78}{14.1603 - \log(200)} + 44.5633 = 377.31^{\circ}\text{K}$$

$$T_2{}^{\text{boil}} = \frac{3242.38}{14.2515 - \log(200)} + 47.1806 = 409.33^{\circ}\text{K}$$

The solution of the nonlinear algebraic equation (E-3) can be determined using Matlab function fsolve with inline function as follows:

```
fun=inline('0.45*exp(14.1603  -  2948.78/(T  -  44.5633))+  0.55*exp(14.2515  -
3242.38/(T - 47.1806)) - 200');
>> T=fsolve(fun,400,optimset('Display','off'))
T =
 391.7925
```

The bubble point temperature of the benzene-toluene mixture is **391.8°K**. At this temperature, the vapor pressure of benzene is

$$P_1{}^{\text{sat}} = \exp(14.1603 - 2948.78/(391.7925 - 44.5633)) = 289.45 \text{ kPa}$$

The mole fraction of benzene in the vapor phase is then

$$y_1 = \frac{x_1 P_1{}^{sat}}{P} = \frac{(0.45)(289.45)}{200} = \mathbf{0.6513}$$

The mole fraction of toluene in the vapor phase is

$$y_2 = 1 - y_1 = \mathbf{0.3487}$$

Bubble point pressure calculation

In a bubble point pressure calculation, the temperature and liquid phase composition are specified. We will solve for the pressure and the vapor composition. Since the vapor mole fractions are unknown, we start with the equation

$$\sum_{i=1}^{m} y_i = 1 \qquad \text{(5.1-12)}$$

Using the K-values: $K_i = \dfrac{y_i}{x_i}$, Eq. (5.1-12) becomes

$$\sum_{i=1}^{m} K_i x_i - 1 = 0 \tag{5.1-13}$$

Example 5.1-2 ---

Determine the pressure and composition of the first bubble created from a saturated liquid mixture of benzene and toluene containing 45 mole percent benzene at 400°K. Benzene and toluene mixtures may be considered as ideal.

Data: Vapor pressure, P^{sat}, data: $\ln P^{sat} = A - B/(T + C)$, where P^{sat} is in kPa and T is in °K.

Compound	A	B	C
Benzene (1)	14.1603	2948.78	− 44.5633
Toluene (2)	14.2515	3242.38	− 47.1806

Solution --

We start with the equation

$$y_1 + y_2 = 1 \tag{E-1}$$

Substituting $y_i = x_i P_i^{sat}/P$ into equation (E-1) yields

$$x_1 P_1^{sat} + x_2 P_2^{sat} = P \tag{E-2}$$

With the numerical values for mole fractions and temperature, the bubble point pressure is

$$P = 0.45\exp(14.1603 - 2948.78/(400 - 44.5633))$$
$$+ 0.55\exp(14.2515 - 3242.38/(400 - 47.1806)) = \textbf{245.284 kPa}$$

At 400°K, the vapor pressure of benzene is

$$P_1^{sat} = \exp(14.1603 - 2948.78/(400 - 44.5633)) = 352.160 \text{ kPa}$$

The mole fraction of benzene in the vapor phase is then

$$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{(0.45)(352.160)}{245.284} = \textbf{0.6461}$$

The mole fraction of toluene in the vapor phase is

$$y_2 = 1 - y_1 = \textbf{0.3539}$$

Dew point temperature calculation

In a dew point temperature calculation, the pressure and vapor phase composition are specified. We will solve for the temperature and the liquid composition. The solution provides the composition of the first drop of dew that forms from a saturated vapor. Since the liquid mole fractions are unknown, we start with the equation

$$\sum_{i=1}^{m} x_i = 1 \tag{5.1-14}$$

Using the K-values: $K_i = \dfrac{y_i}{x_i}$, Eq. (5.1-14) becomes

$$\sum_{i=1}^{m} \frac{y_i}{K_i} = 1 \tag{5.1-15}$$

Example 5.1-3 --
Determine the temperature and composition of the first dew created from a saturated vapor mixture of benzene and toluene containing 45 mole percent benzene at 200 kPa. Benzene and toluene mixtures may be considered as ideal.

Data: Vapor pressure, P^{sat}, data: $\ln P^{\text{sat}} = A - B/(T + C)$, where P^{sat} is in kPa and T is in °K.

Compound	A	B	C
Benzene (1)	14.1603	2948.78	− 44.5633
Toluene (2)	14.2515	3242.38	− 47.1806

Solution ---

We start with the equation

$$x_1 + x_2 = 1 \tag{E-1}$$

Substituting $x_i = y_i P / P_i^{\text{sat}}$ into equation (E-1) yields

$$\frac{y_1 P}{P_1^{\,sat}} + \frac{y_2 P}{P_2^{\,sat}} = 1 \tag{E-2}$$

With the numerical values for mole fractions and pressure, equation (E-2) becomes

$$90/\exp(14.1603 - 2948.78/(T - 44.5633))$$
$$+ \, 110/\exp(14.2515 - 3242.38/(T - 47.1806)) = 1 \tag{E-3}$$

The dew point temperature should be between the boiling points of benzene and toluene given by

$$T_1^{\text{boil}} = \frac{2948.78}{14.1603 - \log(200)} + 44.5633 = 377.31^{\circ}\text{K}$$

$$T_2^{\text{boil}} = \frac{3242.38}{14.2515 - \log(200)} + 47.1806 = 409.33^{\circ}\text{K}$$

The solution of the nonlinear algebraic equation (E-3) can be determined using Matlab function fsolve with inline function as follows:

```
>> fun=inline('90/exp(14.1603 - 2948.78/(T - 44.5633))+ 110/exp(14.2515 - 3242.38/(T - 47.1806)) - 1');
>> T=fsolve(fun,400,optimset('Display','off'))
T =
 398.0874
```

The dew point temperature of the benzene-toluene mixture is **398.1°K**. At this temperature, the vapor pressure of benzene is

$$P_1^{\text{sat}} = \exp(14.1603 - 2948.78/(398.0874 - 44.5633)) = 336.70 \text{ kPa}$$

The mole fraction of benzene in the liquid phase is then

$$x_1 = \frac{y_1 P}{P_1^{sat}} = \frac{(0.45)(200)}{336.7} = \mathbf{0.2673}$$

The mole fraction of toluene in the liquid phase is

$$x_2 = 1 - x_1 = \mathbf{0.7327}$$

Dew point pressure calculation

In a dew point pressure calculation, the temperature and vapor phase composition are specified. We will solve for the pressure and the liquid composition. Since the liquid mole fractions are unknown, we start with the equation

$$\sum_{i=1}^{m} x_i = 1 \tag{5.1-16}$$

Using the *K*-values: $K_i = \dfrac{y_i}{x_i}$, Eq. (5.1-16) becomes

$$\sum_{i=1}^{m} \frac{y_i}{K_i} = 1 \tag{5.1-17}$$

If the system contains more than two components, we might want to solve the log form of equation (5.1-17) for better convergence

$$\ln\left(\sum_{i=1}^{m}\frac{y_i}{K_i}\right)=0 \qquad\qquad (5.1\text{-}18)$$

Example 5.1-4 ---
Determine the temperature and composition of the first dew created from a saturated vapor mixture of benzene and toluene containing 45 mole percent benzene at 400°K. Benzene and toluene mixtures may be considered as ideal.

Data: Vapor pressure, P^{sat}, data: $\ln P^{sat} = A - B/(T + C)$, where P^{sat} is in kPa and T is in °K.

Compound	A	B	C
Benzene (1)	14.1603	2948.78	− 44.5633
Toluene (2)	14.2515	3242.38	− 47.1806

Solution ---

We start with the equation

$$x_1 + x_2 = 1 \qquad\qquad (E\text{-}1)$$

Substituting $x_i = y_i P/P_i^{sat}$ into equation (E-1) yields

$$\frac{y_1 P}{P_1^{sat}} + \frac{y_2 P}{P_2^{sat}} = 1 \Rightarrow P = \frac{1}{\dfrac{y_1}{P_1^{sat}} + \dfrac{y_2}{P_2^{sat}}} \qquad\qquad (E\text{-}2)$$

With the numerical values for mole fractions and temperature, equation (E-2) becomes

$$P = \frac{1}{\dfrac{0.45}{\exp(14.1603 - 2948.78/(400 - 44.5633))} + \dfrac{0.55}{\exp(14.2515 - 3242.38/(400 - 47.1806))}}$$

$P = 209.98$ kPa

At 400°K, the vapor pressure of benzene is

$$P_1^{sat} = \exp(14.1603 - 2948.78/(400 - 44.5633)) = 352.160 \text{ kPa}$$

The mole fraction of benzene in the liquid phase is then

$$x_1 = \frac{y_1 P}{P_1^{sat}} = \frac{(0.45)(209.98)}{352.16} = \mathbf{0.2683}$$

Chapter 5

Example 5.1-5 --
Construct a *Txy* diagram for a mixture of benzene and toluene at 200 kPa. Benzene and toluene mixtures may be considered as ideal.

Data: Vapor pressure, P^{sat}, data: $\ln P^{sat} = A - B/(T + C)$, where P^{sat} is in kPa and *T* is in K.

Compound	A	B	C
Benzene (1)	14.1603	2948.78	− 44.5633
Toluene (2)	14.2515	3242.38	− 47.1806

Solution --

The temperature for the *Txy* diagram should be between the boiling points of benzene and toluene given by

$$T_1{}^{boil} = \frac{2948.78}{14.1603 - \log(200)} + 44.5633 = 377.31 \text{ K}$$

$$T_2{}^{boil} = \frac{3242.38}{14.2515 - \log(200)} + 47.1806 = 409.33 \text{ K}$$

The simplest procedure is to choose a temperature *T* between 377.31 K and 409.33 K, evaluate the vapor pressures, and solve for *x* and *y* from the following equations:

$$\frac{y_i}{x_i} = \frac{P_i{}^{sat}}{P} \tag{E-1}$$

At 400°K, the vapor pressure of benzene and toluene are given by

$$P_1{}^{sat} = \exp(14.1603 - 2948.78/(400 - 44.5633)) = 352.160 \text{ kPa}$$

$$P_2{}^{sat} = \exp(14.2515 - 3242.38/(400 - 47.1806)) = 157.8406 \text{ kPa}$$

Therefore

$$\frac{y_1}{x_1} = \frac{352.16}{200} \Rightarrow y_1 = K_1 x_1 = 1.7608 x_1 \tag{E-1}$$

$$\frac{1 - y_1}{1 - x_1} = \frac{157.841}{200} \Rightarrow 1 - y_1 = K_2 (1 - x_1) = 0.7892 (1 - x_1) \tag{E-1}$$

Substituting Eq. (E-2) into (E-1) yields

$$1 - K_1 x_1 = K_2 (1 - x_1)$$

Therefore

$$x_1 = \frac{1-K_2}{K_1-K_2} = \frac{1-0.7892}{1.7608-0.7892} = 0.2170$$

$$y_1 = K_1\, x_1 = 1.7608 x_1 = 0.3820$$

The Matlab program listed in **Table E5-1** plots the *Txy* diagram shown in **Figure E5-1**.
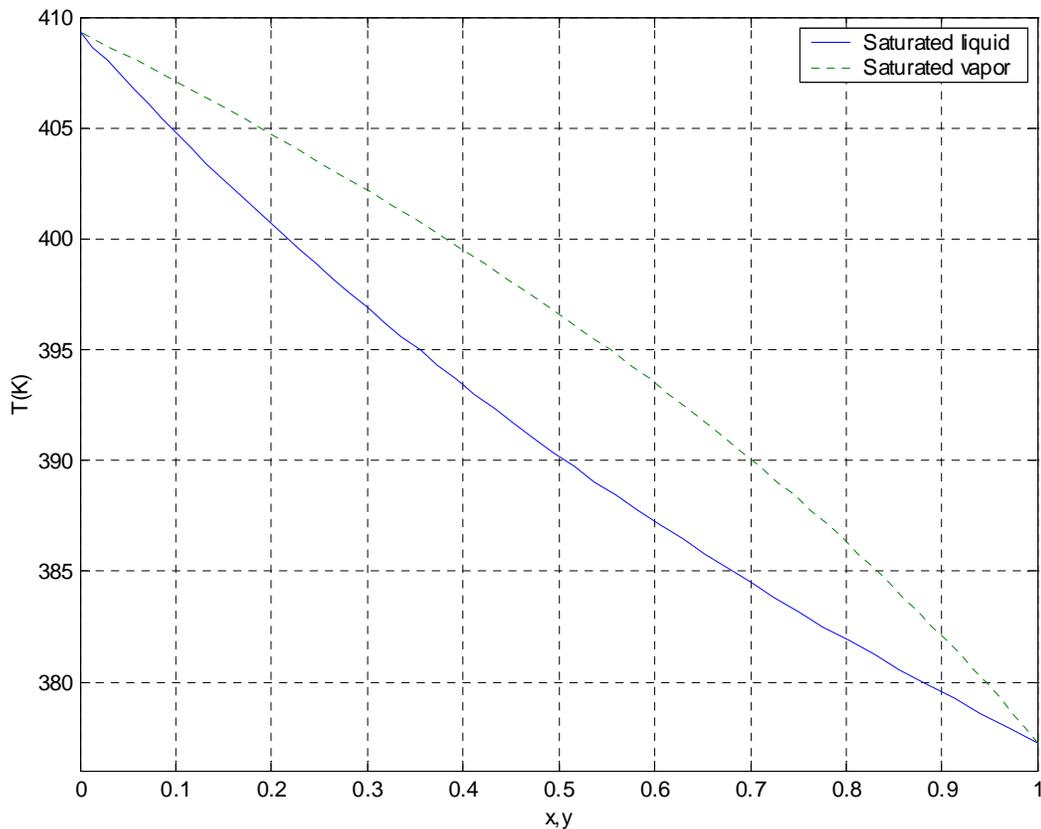
Figure E5-1 Calculated *Txy* diagram of benzene and toluene at 200 kPa.

Table E5-1---
```
% Example 5.1-5, Txy diagram for benzene-toluene mixture at 200 kPa
%
P=200; % kPa
A=[14.1603 14.2515]; B=[2948.78 3242.38]; C=[-44.5633  -47.1806];
% Boling point at 200 kPa
Tb=B./(A-log(P))-C;
fprintf('Boiling point of Benzene at P = %g, Tb = %6.2f C\n',P,Tb(1))
fprintf('Boiling point of Toluene at  P = %g, Tb = %6.2f C\n',P,Tb(2))
T=linspace(Tb(1),Tb(2),50);
K1=exp(A(1)-B(1)./(T+C(1)))/P;
K2=exp(A(2)-B(2)./(T+C(2)))/P;
x=(1-K2)./(K1-K2); y = K1.*x;
```

```
ymin=round(Tb(1)-1);ymax=round(Tb(2)+1);
plot(x,T,y,T,':')
axis([0 1 ymin ymax]);
grid on
xlabel('x,y');ylabel('T(K)')
legend('Saturated liquid','Saturated vapor')
```

Example 5.1-6[2] ---
We want to condense the following vapor mixture at 100^oF.

Ethylene C_2H_4: 20%	Ethane C_2H_6: 20%	Propane C_3H_8: 40%	n-Buane C_4H_{10}: 20%

Determine the dew point pressure and the pressure required to totally condense the vapor using the *K*-values.

Data:

Equilibrium K values for light hydrocarbon systems
==

$\ln K = -A/T^2 + B - C \ln(P) + D/P + E/P^2$, where *P* is in psia, *T* is in ^oR

Compound	A	B	C	D	E
Ethylene	600076.9	7.90595	.84677	0	42.94594
Ethane	687248.2	7.90694	.866	0	49.02654
Propane	970688.6	7.15059	.76984	6.90224	0
n-Butane	1280557	7.94986	.96455	0	0

==

Solution --
For dew point pressure calculation, the liquid mole fractions are unknown. We start with the equation

$$\sum_{i=1}^{m} x_i = 1 \tag{E-1}$$

Using the *K*-values: $K_i = \dfrac{y_i}{x_i}$, Eq. (E-1) becomes

$$\sum_{i=1}^{m} \frac{y_i}{K_i} = 1 \tag{E-2}$$

We will solve the log form of equation (E-2) for better convergence

$$\ln\left(\sum_{i=1}^{m} \frac{y_i}{K_i}\right) = 0 \tag{E-3}$$

---

[2] Kyle, B.G., Chemical and Process Thermodynamics, Prentice Hall, 1999, pg. 266

5-11

We will use Newton's method to solve Eq. (E-3). A review of Newton's method is given in Appendix A. The procedure for the calculation is as follows:

1) Estimate vapor pressure, P_i^{sat}, by setting $K_i = 1$ and solve for P_i^{sat} using only the three constants A, B, and C in the expression for the equilibrium ratio.

$$P_i^{sat} = \exp\left(\frac{1}{C}\left(B - \frac{A}{T^2}\right)\right)$$

2) Assume a pressure $P = 0.5\sum_{i=1}^{m} y_i P_i^{sat}$

3) Evaluate $K_i = K_i\,(T, P)$

4) Evaluate $f(P) = \ln\left(\sum_{i=1}^{m} \frac{y_i}{K_i}\right)$

5) Evaluate $K_i = K_i\,(T, P + dP)$ and $f(P + dP)$

6) Since the slope of the curve $f(P)$ versus P is approximated by

$$\text{Slope} = \frac{f(P + dP) - f(P)}{dP} = \frac{f(P)}{P - P_{cal}}$$

The calculated P_{cal} is given by

$$P_{cal} = P - \frac{f(P)dP}{f(P + dP) - f(P)}$$

Steps (3-6) are repeated until $|P_{cal} - P| \le$ error tolerance

In a bubble point pressure calculation, the temperature and liquid phase composition are specified. We will solve for the pressure and the vapor composition. Since the vapor mole fractions are unknown, we start with the equation

$$\sum_{i=1}^{m} y_i = 1 \qquad\qquad\qquad\qquad \text{(E-4)}$$

Using the K-values: $K_i = \dfrac{y_i}{x_i}$, Eq. (E-4) becomes

$$\sum_{i=1}^{m} K_i x_i - 1 = 0 \qquad\qquad\qquad\qquad \text{(E-5)}$$

We will also use Newton's method to solve Eq. (E-5). The procedure for the calculation is as follows:

1) Estimate vapor pressure, P_i^{sat}, by setting $K_i = 1$ and solve for P_i^{sat} using only the three constants A, B, and C in the expression for the equilibrium ratio.

$$P_i^{sat} = \exp\left(\frac{1}{C}\left(B - \frac{A}{T^2}\right)\right)$$

2) Assume a pressure $P = \sum_{i=1}^{m} x_i P_i^{sat}$

3) Evaluate $K_i = K_i\,(T, P)$

4) Evaluate $f(P) = \sum_{i=1}^{m} K_i x_i - 1$

5) Evaluate $K_i = K_i\,(T, P + dP)$ and $f(P + dP)$

6) Since the slope of the curve $f(P)$ versus P is approximated by

$$\text{Slope} = \frac{f(P + dP) - f(P)}{dP} = \frac{f(P)}{P - P_{cal}}$$

The calculated P_{cal} is given by

$$P_{cal} = P - \frac{f(P)dP}{f(P + dP) - f(P)}$$

Steps (3-6) are repeated until $|P_{cal} - P| \le$ error tolerance.

The following Matlab program can be used to determine the dew and bubble point pressure calculation:

```
--------------------------------------------------------------------------------
% Example 5.1-6,
% Dew point pressure calculation
%
T=100+460;
A=[600076.9 687248.2 970688.6 1280577];
B=[7.90595 7.90694 7.15059 7.94986];
C=[0.84677 0.866 0.76984 0.96455];
D=[0 0 6.90224 0];
E=[42.94594 49.02654 0 0];
% Estimate vapor pressure by setting Ki=1
Pisat=exp((B-A/(T*T))./C);
yi=[.2 .2 .4 .2];
```

```
Pe=yi*Pisat'; % Estimate pressure from vapor pressure and composition
P=.5*Pe;
fK='exp(-A/(T*T)+B-C*log(P)+D/P+E/(P*P))';
dP=1;eP=1;
while abs(eP)>.1
   Ki=eval(fK);fP=log(sum(yi./Ki));
   Psav=P;P=P+dP;
   Ki=eval(fK);fdP=log(sum(yi./Ki));
   eP=fP*dP/(fdP-fP);
   P=Psav-eP;
end
Ki=eval(fK);x=yi./(Ki);
fprintf('Dew point pressure, P(psia) = %8.2f\n',P)
disp('Species: Ethylene    Ethane    Propane    n-Butane')
fprintf('y =        ');disp(yi)
fprintf('x =        ');disp(x)
disp(' ')
% Bubble point pressure calculation
xi=yi;eP=1;P=Pe;
while abs(eP)>.1
   Ki=eval(fK);fP=xi*Ki'-1;
   Psav=P;P=P+dP;
   Ki=eval(fK);fdP=xi*Ki'-1;
   eP=fP*dP/(fdP-fP);
   P=Psav-eP;
end
Ki=eval(fK);y=xi.*Ki;
fprintf('Bubble point pressure, P(psia) = %8.2f\n',P)
disp('Species: Ethylene    Ethane    Propane    n-Butane')
fprintf('x =        ');disp(xi)
fprintf('y =        ');disp(y)

>> e5d1d6

Dew point pressure, P(psia) =    163.64
Species: Ethylene    Ethane    Propane    n-Butane
y =        0.2000    0.2000    0.4000    0.2000
x =        0.0374    0.0544    0.3364    0.5718

Bubble point pressure, P(psia) =    449.30
Species: Ethylene    Ethane    Propane    n-Butane
x =        0.2000    0.2000    0.4000    0.2000
y =        0.4545    0.3064    0.2128    0.0264
```

5.2 Isothermal Flash Calculation Using K-values

In flash distillation, a liquid mixture is partially vaporized and the vapor is allowed to come to equilibrium with the liquid. The process flow diagram is shown in **Figure 5.2-1**. The vapor and liquid phases are then separated.
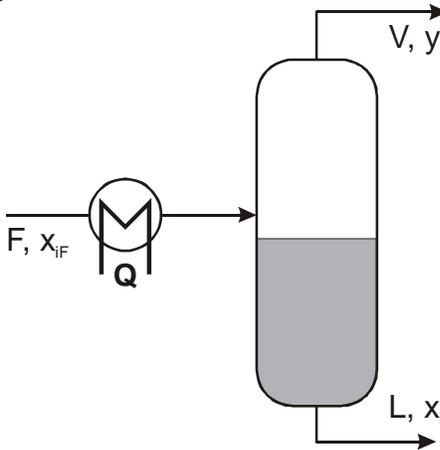
Figure 5.2-1 Flash distillation.

Making a component *i* balance gives

$$Fx_{iF} = Vy_i + Lx_i = Vy_i + (F - V)x_i \tag{5.2-1}$$

Defining $f = V/F$, Eq. (5.2-1) becomes

$$x_{iF} = fy_i + (1 - f)x_i \tag{5.2-2}$$

The above equation can be solved for y_i,

$$y_i = K_i x_i = \frac{f-1}{f}x_i + \frac{x_{iF}}{f} \tag{5.2-3}$$

or for x_i,

$$x_i = \frac{x_{iF}}{f(K_i - 1) + 1} \tag{5.2-4}$$

We will discuss the solution for two cases of isothermal flash calculation. In the first case, the fraction of the feed vaporized, f, is specified and in the second case f is determined.

Case 1: Fraction of the feed, *f*, vaporized is specified

The feed composition x_{iF} and the fraction f of the feed vaporized are given at a specified separator pressure P, the temperature T and compositions x_i and y_i can be calculated by solving the equation:

$$\sum_{i=1}^{m} x_i = \sum \frac{x_{iF}}{f(K_i(T,P)-1)+1} = 1$$

The procedure for the calculation is as follows:

1) Determine the bubble, T_b, and dew, T_d, point temperatures at the feed composition.

2) Assume a temperature $T = fT_d + (1-f)T_b$

3) Evaluate $K_i = K_i(T, P)$

4) Evaluate $f(T) = \sum \frac{x_{iF}}{f(K_i(T,P)-1)+1} - 1$

5) Evaluate $K_i = K_i(T + dT, P)$ and $f(T + dT)$

6) Since the slope of the curve $f(T)$ versus T is approximated by

$$\text{Slope} = \frac{f(T+dT)-f(T)}{dT} = \frac{f(T)}{T-T_{cal}}$$

The calculated T_{cal} is given by

$$T_{cal} = T - \frac{f(T)dT}{f(T+dT)-f(T)}$$

Steps (3-6) are repeated until $|T_{cal} - T| \le$ error tolerance

Chapter 5

Case 2: Fraction of the feed, *f*, vaporized is determined

If the feed composition x_{iF}, temperature T and pressure P of separator are given, then the fraction of the feed vaporized V/F and compositions x_i and y_i can be calculated. Eqs. (5.2-3) and (5.2-4) can be arranged so that $f = V/F$ is the only unknown.

$$\sum y_i - \sum x_i = 0 \tag{5.2-5}$$

$$\sum \frac{K_i x_{iF}}{f(K_i - 1) + 1} - \sum \frac{x_{iF}}{f(K_i - 1) + 1} = 0 \tag{5.2-6}$$

$$F = \sum \frac{(K_i - 1)x_{iF}}{f(K_i - 1) + 1} = 0 \tag{5.2-7}$$

Equation (5.2-7), which is known as the Rachford-Rice equation, has excellent convergent properties and can be solved by Newton's method. Take the derivative of the function F with respect to V/F (or f),

$$\frac{dF}{df} = -\sum \frac{(K_i - 1)^2 x_{iF}}{\left[f(K_i - 1) + 1\right]^2} \tag{5.2-8}$$

The following procedure can be used to solve for V/F:

1) Evaluate $K_i = K_i\,(T, P)$

2) Check to see if T is between T_b and T_d.

If all K-values are greater than 1, the feed is a superheated vapor above the dew point[3]. If all K-values are less than 1, the feed is a subcooled liquid below the bubble point. If one or more K-values are greater than 1 and one or more K-values are less than 1 we need to evaluate Eq. (5.2-7) at $f = 0$ and at $f = 1$.

2a) If $\sum (K_i - 1)x_{iF} < 0$, the feed is below its bubble point.

2b) $\sum \dfrac{(K_i - 1)x_{iF}}{K_i} > 0$ the feed is above its dew point.

3) Assume $f = 0.5$

---

[3] Seader J. D., and Henley E. J., <u>Separation Process Principles</u>, Wiley, 1998, pg. 180.

4) Evaluate $F = \sum \dfrac{(K_i - 1)x_{iF}}{f(K_i - 1) + 1}$

5) Evaluate $\dfrac{dF}{df} = -\sum \dfrac{(K_i - 1)^2 x_{iF}}{[f(K_i - 1) + 1]^2}$

6) Let $ER = F / \dfrac{dF}{df}$, and $\quad f = f - ER$

7) **If** abs(ER) > .001 go to step 4, otherwise

$$x_i = \dfrac{x_{iF}}{f(K_i - 1) + 1} \quad \text{and } y_i = K_i x_i$$

Example 5.2-1 ---
The following mixture is fed to a flash drum at 200 psia.

| Ethylene C_2H_4: 20% | Ethane C_2H_6: 20% | Propane C_3H_8: 40% | n-Buane C_4H_{10}: 20% |

Determine the temperature and the composition of the vapor and liquid streams leaving the flash drum if 40% of the feed is vaporized.

Data:
Equilibrium K values for light hydrocarbon systems
==
$\ln K = -A/T^2 + B - C \ln(P) + D/P + E/P^2$, where P is in psia, T is in $^\circ$R

Compound	A	B	C	D	E
Ethylene	600076.9	7.90595	.84677	0	42.94594
Ethane	687248.2	7.90694	.866	0	49.02654
Propane	970688.6	7.15059	.76984	6.90224	0
n-Butane	1280557	7.94986	.96455	0	0

==

Solution ---

% Example 5.2-1, Isothermal Flash with f=V/F specified
% Dew point temperature calculation
%
P=200; % psia
f=0.4;
A=[600076.9 687248.2 970688.6 1280577];
B=[7.90595 7.90694 7.15059 7.94986];
C=[0.84677 0.866 0.76984 0.96455];
D=[0 0 6.90224 0];
E=[42.94594 49.02654 0 0];
% Estimate the saturation temperature by setting Ki=1

```
Tsat=sqrt(A./(B-C*log(P)));
zi=[.2 .2 .4 .2];yi=zi;
Te=yi*Tsat'; % Estimate temperature from saturation temperature and composition
T=Te;
fK='exp(-A/(T*T)+B-C*log(P)+D/P+E/(P*P))';
dT=1;eT=1;
while abs(eT)>.1
   Ki=eval(fK);fT=sum(yi./Ki)-1;
   Tsav=T;T=T+dT;
   Ki=eval(fK);fdT=sum(yi./Ki)-1;
   eT=fT*dT/(fdT-fT);
   T=Tsav-eT;
end
Td=T;
fprintf('Dew point temperature, T(R) = %8.2f\n',T)
disp(' ')
% Bubble point temperature calculation
xi=zi;eT=1;T=Te;
while abs(eT)>.1
   Ki=eval(fK);fT=log(xi*Ki');
   Tsav=T;T=T+dT;
   Ki=eval(fK);fdT=log(xi*Ki');
   eT=fT*dT/(fdT-fT);
   T=Tsav-eT;
end
Tb=T;
fprintf('Bubble point temperature, T(R) = %8.2f\n',T)
disp(' ')
T=f*Td+(1-f)*Tb;
eT=1;
for i=1:20
   Ki=eval(fK);fT=sum(zi./(f*(Ki-1)+1))-1;
   Tsav=T;T=T+dT;
   Ki=eval(fK);fdT=sum(zi./(f*(Ki-1)+1))-1;
   eT=fT*dT/(fdT-fT);
   T=Tsav-eT;
   if abs(eT)<.1, break, end
end
Ki=eval(fK)
x=zi./(f*(Ki-1)+1);y=x.*Ki;
fprintf('Flash temperature, T(R) = %8.2f, V/F = %8.4f\n',T,f)
disp('Species: Ethylene    Ethane    Propane    n-Butane')
fprintf('Feed z =');disp(zi)
fprintf('x =        ');disp(x)
fprintf('y =        ');disp(y)
```

```
>> e5d2d1
Dew point temperature, T(R) =   574.80

Bubble point temperature, T(R) =   490.69

Flash temperature, T(R) =  523.98, V/F =  0.4000
Species: Ethylene    Ethane    Propane    n-Butane
Feed z =   0.2000   0.2000   0.4000   0.2000
x =        0.1013   0.1329   0.4649   0.3010
y =        0.3481   0.3007   0.3027   0.0485
Ki =       3.4382   2.2630   0.6510   0.1613
```

Example 5.2-2 ---
The following mixture is fed to a flash drum at 200 psia.

Ethylene C_2H_4: 20%	Ethane C_2H_6: 20%	Propane C_3H_8: 40%	n-Buane C_4H_{10}: 20%

Determine the fraction of the feed vaporized and the composition of the vapor and liquid streams leaving the flash drum if the drum is at 400°R, 600°R, and 525°R.

Data:
Equilibrium K values for light hydrocarbon systems
===

$\ln K = -A/T^2 + B - C \ln(P) + D/P + E/P^2$, where P is in psia, T is in °R

Compound	A	B	C	D	E

===

Ethylene	600076.9	7.90595	.84677	0	42.94594
Ethane	687248.2	7.90694	.866	0	49.02654
Propane	970688.6	7.15059	.76984	6.90224	0
n-Butane	1280557	7.94986	.96455	0	0

===

Solution --
```
% Example 5.2-2, Isothermal Flash with T specified
% Dew point temperature calculation
%
P=200; % psia
T=input('Drum temperature T(R) = ');
A=[600076.9 687248.2 970688.6 1280577];
B=[7.90595 7.90694 7.15059 7.94986];
C=[0.84677 0.866 0.76984 0.96455];
D=[0 0 6.90224 0];
E=[42.94594 49.02654 0 0];
zi=[.2 .2 .4 .2];
fK='exp(-A/(T*T)+B-C*log(P)+D/P+E/(P*P))';
Ki=eval(fK);Km=Ki-1;
f0=Km*zi';f1=sum(Km.*zi./Ki);
if f0<0
```

```
    disp('Feed is subcooled liquid')
elseif f1>0
    disp('Feed is superheated vapor')
else
    for i=1:20
        Km=Ki-1;
        F=sum((Km.*zi)./(f*Km+1));
        dF=-sum((Km.^2).*zi./(f*Km+1).^2);
        eR=F/dF;f=f-eR;
        if abs(eR)<.0001, break, end
    end
    x=zi./(f*Km+1);y=x.*Ki;
    fprintf('Flash temperature, T(R) = %8.2f, V/F = %8.4f\n',T,f)
    disp('Species: Ethylene    Ethane    Propane    n-Butane')
    fprintf('Feed z =');disp(zi)
    fprintf('x =       ');disp(x)
    fprintf('y =       ');disp(y)
    fprintf('Ki =      ');disp(Ki)
end

>> e5d2d2
Drum temperature T(R) = 400
Feed is subcooled liquid

>> e5d2d2
Drum temperature T(R) = 600
Feed is superheated vapor

>> e5d2d2
Drum temperature T(R) = 525
Flash temperature, T(R) =  525.00, V/F =   0.4116
Species: Ethylene    Ethane    Propane    n-Butane
Feed z =  0.2000   0.2000   0.4000   0.2000
x =       0.0992   0.1308   0.4651   0.3049
y =       0.3441   0.2989   0.3070   0.0501
Ki =      3.4674   2.2851   0.6600   0.1642
```

TK Nguyen's program (KEQUI) can perform vapor-liquid equilibrium for light hydrocarbons using *K*-values.

Equilibrium using K values, Aug 20, 03

1:Bubble T   5:Iso-Flash   9:Psat
2:Dew point T   6:V/F-Flash   N:New system
3:Bubble P   7:K ratio
4:Dew point P   8:Tsat

Calc

Quit

T, R = 560   P,psia = 163.64   Choose an option

n-Butane

Species	y	x	K ratio	
Ethylene	.2	.03737	5.352E+00	
Ethane	.2	.05436	3.679E+00	
Propane	.4	.33644	1.189E+00	
n-Butane	.2	.57183	3.498E-01	

Equilibrium using K values, Aug 20, 03

1:Bubble T   5:Iso-Flash   9:Psat
2:Dew point T   6:V/F-Flash   N:New system
3:Bubble P   7:K ratio
4:Dew point P   8:Tsat

Calc

Quit

T, R = 560   P,psia = 449.3   Choose an option

n-Butane

Species	x	y	K ratio	
Ethylene	.2	.45448	2.272E+00	
Ethane	.2	.30636	1.532E+00	
Propane	.4	.21276	5.319E-01	
n-Butane	.2	.02641	1.320E-01	

Equilibrium using K values, Aug 20, 03

1:Bubble T   5:Iso-Flash   9:Psat
2:Dew point T   **6:V/F-Flash**   N:New system
3:Bubble P   7:K ratio
4:Dew point P   8:Tsat

Calc

Quit

P,psia = 200   Choose an option   V/F =.40000

n-Butane

Species	Feed	x	y	K ratio
Ethylene	.2	.10125	.34812	3.438E+00
Ethane	.2	.13287	.30069	2.263E+00
Propane	.4	.46490	.30265	6.510E-01
n-Butane	.2	.30098	.04854	1.613E-01

Chapter 5

5.3 Vapor-Liquid Equilibrium with Non-ideal Liquid

In this section we will consider the vapor liquid equilibrium calculation of some real binary system where the pressure is low enough for the vapor phase to be an ideal gas. At equilibrium, the fugacity of species i in the vapor phase is equal to that in the liquid phase

$$\hat{f}_i^v = \hat{f}_i^l \tag{5.3-1}$$

The fugacity of species i in the vapor phase can be expressed in terms of the mole fraction, y_i, fugacity coefficient, $\hat{\varphi}_i^v$, and total pressure, P, as

$$\hat{f}_i^v = y_i \hat{\varphi}_i^v P \tag{5.3-2}$$

The fugacity of species i in the liquid phase can be expressed in terms of the mole fraction, x_i, activity coefficient, γ_i, and fugacity of pure component, f_i, as

$$\hat{f}_i^l = x_i \gamma_i f_i \tag{5.3-3}$$

Therefore

$$y_i \hat{\varphi}_i^v P = x_i \gamma_i f_i \tag{5.3-4}$$

If the vapor phase obeys ideal gas law, $\hat{\varphi}_i^v = 1$, and at low pressure, $f_i = P_i^{\text{sat}}$, Eq. (5.3-4) becomes

$$y_i P = x_i \gamma_i P_i^{\text{sat}} \tag{5.3-5}$$

The activity coefficient, γ_i, can be obtained from experimental data and fitted to different activity coefficient models. The better-known models are the Margules, Van Laar, Wilson, NTRL, and UNIQAC equations. The activity coefficient model is normally obtained from the excess Gibbs energy, g^E, defined by

$$g^E = \sum x_i \overline{G}_i^E \tag{5.3-6}$$

In this equation, the partial molar excess Gibbs energy is given by

$$\overline{G}_i^E = \overline{G}_i - \overline{G}_i^{ideal} = \mu_i - \mu_i^{ideal} = RT \ln \frac{\hat{f}_i^l}{\hat{f}_i^{ideal}} = RT \ln \gamma_i$$

Therefore, the excess Gibbs energy is given in terms of activity coefficient as

$$g^E = RT \sum x_i \ln \gamma_i \tag{5.3-7}$$

The activity coefficient model must satisfy the following two conditions:

1) It must provide an ideal solution as the mole fraction of one species approach one. That is

$$g^E = 0 \text{ for } x_1 = 1 \text{ or } x_2 = 1$$

2) It must satisfy the Gibbs-Duhem equation

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_1} \right)_{T,P} = 0$$

The simplest non-ideal equation for the excess Gibbs energy that satisfies these two conditions is

$$g^E = Ax_1x_2 \tag{5.3-8}$$

From the definition of the partial excess Gibbs energy we have

$$\overline{G}_1^E = \left(\frac{\partial G^E}{\partial n_1} \right)_{T,P,n_2} = \left(\frac{\partial (ng^E)}{\partial n_1} \right)_{T,P,n_2} = A \left(\frac{\partial \left(\frac{n_1 n_2}{n_1 + n_2} \right)}{\partial n_1} \right)_{T,P,n_2}$$

$$\overline{G}_1^E = A \left[\frac{n_2}{n_1 + n_2} - \frac{n_1 n_2}{(n_1 + n_2)^2} \right] = A \frac{n_2^2}{(n_1 + n_2)^2}$$

Therefore

$$\overline{G}_1^E = RT \ln \gamma_1 = A \frac{n_2^2}{(n_1 + n_2)^2}$$

The equation for activity coefficient in terms of mole fraction is then

$$RT\ln \gamma_1 = Ax_2^2 \tag{5.3-9a}$$

Similarly

$$RT\ln \gamma_2 = Ax_1^2 \tag{5.3-9b}$$

The parameter A can be obtained by fitting Eq. (5.3-9) with experimental data. This parameter may change with temperature and pressure, but it is independent of the composition of the system. More sophisticated model for the excess Gibbs energy will yield activity coefficient equation with more than one parameter that might better fit the experimental data.

The four common equations for activity coefficient are listed in Table 5.3-1. The Wilson model is preferred due to its improved ability to correct for temperature changes[4]. However the Wilson model should not be used for vapor-liquid equilibrium system that contains two liquid phases (LLE).

Table 5.3-1 Common Binary Activity Coefficient Models

Model		Recommended for
Margules	$\ln \gamma_1 = x_2^2[a + 2(b - a)x_1]$ $\ln \gamma_2 = x_1^2[b + 2(a - b)x_2]$	Aromatics, alcohol, ketones, and ethers
Van Laar	$\ln \gamma_1 = \dfrac{A}{[1 + (Ax_1 / Bx_2)]^2}$ $\ln \gamma_2 = \dfrac{B}{[1 + (Bx_2 / Ax_1)]^2}$	
Wilson	$\ln \gamma_1 = -\ln[x_1 + x_2 \Lambda_{12}]$ $+ x_2 \left[\dfrac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \dfrac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right]$ $\ln \gamma_2 = -\ln[x_2 + x_1 \Lambda_{21}]$ $+ x_1 \left[\dfrac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} - \dfrac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} \right]$	Aromatics, alcohol, ketones, ethers, C_4-C_{18} hydrocarbons
NRTL	$\ln \gamma_1 = x_2^2 \left[\dfrac{\tau_{21} \Lambda_{21}^2}{(x_1 + x_2 \Lambda_{21})^2} + \dfrac{\tau_{12} \Lambda_{12}}{(x_2 + x_1 \Lambda_{12})^2} \right]$ $\ln \gamma_2 = x_1^2 \left[\dfrac{\tau_{21} \Lambda_{21}}{(x_1 + x_2 \Lambda_{21})^2} + \dfrac{\tau_{12} \Lambda_{12}^2}{(x_2 + x_1 \Lambda_{12})^2} \right]$	Aqueous organics, LLE

Example 5.3-1 ---
Find the bubble point pressure and vapor composition for a liquid mixture of 41.2 mol% ethanol (1) and n-hexane (2) at 331°K.[5]
Data: Activity from Van Laar equations:

$$\ln \gamma_1 = \frac{A}{[1 + (Ax_1 / Bx_2)]^2} \qquad\qquad \ln \gamma_2 = \frac{B}{[1 + (Bx_2 / Ax_1)]^2}$$

$A = 2.409$, and $B = 1.970$

Vapor pressure: (P_i^{sat} in kPa and T in °K)

$$\ln P_1^{sat} = 16.1952 - \frac{3423.53}{T - 55.7152} \qquad \ln P_2^{sat} = 14.0568 - \frac{2825.42}{T - 42.7089}$$

[4]http://students.aiche.org/pdfs/thermodynamics.pdf, 11/27/04
[5] Kyle, B.G., Chemical and Process Thermodynamics, Prentice Hall, 1999, pg. 279

Solution --

At 331°K

$$P_1{}^{sat} = \exp[16.1952 - 3423.53/(331 - 55.7152)] = 42.9 \text{ kPa}$$

$$P_2{}^{sat} = \exp[14.0568 - 2825.42/(331 - 42.7089)] = 70.54 \text{ kPa}$$

For the liquid solution with $x_1 = 0.412$ and $x_2 = 0.588$, we have

$$\ln \gamma_1 = \frac{2.409}{\left[1 + (2.409x_1 / 1.970x_2)\right]^2} = 0.699 \Rightarrow \gamma_1 = 2.011$$

$$\ln \gamma_2 = \frac{1.790}{\left[1 + (1.790x_2 / 2.409x_1)\right]^2} = 0.4195 \Rightarrow \gamma_2 = 1.521$$

The partial pressure of ethanol is evaluated from

$$P_1 = x_1\gamma_1 P_1{}^{sat} = (0.412)(2.011)(42.9) = 35.55 \text{ kPa}$$

Similarly, the partial pressure of n-hexane is given by

$$P_2 = x_2\gamma_2 P_2{}^{sat} = (0.588)(1.521)(70.54) = 63.09 \text{ kPa}$$

The bubble point pressure is then

$$P = P_1 + P_2 = 35.55 + 63.09 = \textbf{98.64 kPa}$$

Mole fraction of ethanol in the vapor phase is calculated from

$$y_1 = P_1/P = 35.55/98.64 = 0.360$$

The actual data for this system is $P_{exp} = 101.3$ kPa, and $y_{1,exp} = 0.350$

Example 5.3-2 ---
Estimate the bubble point temperature and vapor composition for a acetone (1) and water (2) liquid mixture with $x_1 = 0.01$ at a total pressure of 101.3 kPa[6]. Use the Wilson model with the parameters

$$\Lambda_{12} = 0.1173, \quad \Lambda_{21} = 0.4227$$

Vapor pressure: (P_i^{sat} in kPa and T in °K)

$$\ln P_1^{sat} = 14.71712 - \frac{2975.95}{T - 34.5228} \qquad \ln P_2^{sat} = 16.5362 - \frac{3985.44}{T - 38.9974}$$

Solution --

Since the vapor mole fractions are unknown, we start with the equation

$$y_1 + y_2 = 1 \tag{E-1}$$

Substituting $y_i = x_i \gamma_i P_i^{sat}/P$ into equation (E-1) yields

$$x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat} = P \tag{E-2}$$

For $x_1 = 0.01$, $x_2 = 0.99$, $\Lambda_{12} = 0.1173$, and $\Lambda_{21} = 0.4227$ we have

$$\ln \gamma_1 = -\ln[x_1 + x_2 \Lambda_{12}] + x_2 \left[\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right] = 2.5703 \Rightarrow \gamma_1 = 13.069$$

$$\ln \gamma_2 = -\ln[x_2 + x_1 \Lambda_{21}] + x_1 \left[\frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} - \frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} \right] = 7.4112 \times 10^{-4} \Rightarrow \gamma_2 = 1.0007$$

With the numerical values for mole fractions and pressure, equation (E-2) becomes

$$(0.01)(13.069)\exp(14.71712 - 2975.95/(T - 34.5228))$$
$$+ (0.99)(1.0007)\exp(16.5362 - 3985.44/(T - 38.9974)) = 101.3 \qquad \text{(E-3)}$$

$$.13069\exp(14.71712 - 2975.95/(T - 34.5228))$$
$$+ 0.9907\exp(16.5362 - 3985.44/(T - 38.9974)) = 101.3 \qquad \text{(E-4)}$$

Since the boiling point of pure water at 101.3 kPa is 373°K and acetone is more volatile than water we will use 370°K as the first guess to the root of the nonlinear algebraic equation (E-4). The solution can be determined using Matlab function fsolve with inline function as follows:

```
>> fun=inline('.13069*exp(14.71712 - 2975.95/(T - 34.5228))+ 0.9907*exp(16.5362 - 3985.44/(T - 38.9974)) - 101.3')
```

---
[6] Kyle, B.G., Chemical and Process Thermodynamics, Prentice Hall, 1999, pg. 279

```
>> T=fsolve(fun,370,optimset('Display','off'))
T =
  361.7142
```

The bubble point temperature of the acetone-water mixture is **361.7°K**. At this temperature, the vapor pressure of acetone is

$$P_1^{sat} = \exp(14.1603 - 2948.78/(391.7925 - 44.5633)) = 289.45 \text{ kPa}$$

The mole fraction of benzene in the vapor phase is then

$$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{(0.45)(289.45)}{200} = \textbf{0.6513}$$

The mole fraction of toluene in the vapor phase is

$$y_2 = 1 - y_1 = \textbf{0.3487}$$

Example 5.3-3 --
Estimate the dew point temperature and liquid composition for a acetone (1) and water (2) vapor mixture with $y_1 = 0.40$ at a total pressure of 101.3 kPa[7]. Use the Wilson model with the parameters
$$\Lambda_{12} = 0.1173, \Lambda_{21} = 0.4227$$

Vapor pressure: (P_i^{sat} in kPa and T in °K)

$$\ln P_1^{sat} = 14.71712 - \frac{2975.95}{T - 34.5228} \qquad \ln P_2^{sat} = 16.5362 - \frac{3985.44}{T - 38.9974}$$

Solution --

Since the liquid mole fractions are unknown, we start with the equation

$$x_1 + x_2 = 1 \tag{E-1}$$

Substituting $x_i = y_i P / \gamma_i P_i^{sat}$ into equation (E-1) yields

$$y_1 P / \gamma_1 P_1^{sat} + y_2 P / \gamma_2 P_2^{sat} = 1 \tag{E-2}$$

Since the activity coefficients depend on the liquid mole fractions, we assume a value for x_1:

$$\text{Let } x_1 = 0.1, \text{ then } x_2 = 1 - x_1 = 0.9$$

---

[7] Kyle, B.G., Chemical and Process Thermodynamics, Prentice Hall, 1999, pg. 279

Start Iteration

With $\Lambda_{12} = 0.1173$, and $\Lambda_{21} = 0.4227$ we have

$$\ln \gamma_1 = -\ln[x_1 + x_2\Lambda_{12}] + x_2\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right] \Rightarrow \gamma_1 = 5.42913$$

$$\ln \gamma_2 = -\ln[x_2 + x_1\Lambda_{21}] + x_1\left[\frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}} - \frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}}\right] \Rightarrow \gamma_2 = 1.0484$$

With the numerical values for mole fractions, pressure, and activity coefficients, equation (E-2) becomes

$$(0.1)(101.3)/5.42913/\exp(14.71712 - 2975.95/(T - 34.5228))$$
$$+ (0.9)(101.3)/1.0484/\exp(16.5362 - 3985.44/(T - 38.9974)) = 1 \qquad \text{(E-3)}$$

We solve equation (E-3) for temperature and obtain $T = 359.196^{\circ}$K with an initial guess of 370°K. We now need to calculate the liquid mole fractions

$$x_1 = y_1P/\gamma_1P_1^{\text{sat}} = 0.0289813, \text{ and}$$

$$x_2 = y_2P/\gamma_2P_2^{\text{sat}} = 0.971019$$

We now need to update values for the activity coefficients:

$$\ln \gamma_1 = -\ln[x_1 + x_2\Lambda_{12}] + x_2\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right] \Rightarrow \gamma_1 = 10.2315$$

$$\ln \gamma_2 = -\ln[x_2 + x_1\Lambda_{21}] + x_1\left[\frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}} - \frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}}\right] \Rightarrow \gamma_2 = 1.00555$$

The liquid mole fractions are then reevaluated:

$$x_1 = y_1P/\gamma_1P_1^{\text{sat}} = 0.0153783, \text{ and}$$

$$x_2 = y_2P/\gamma_2P_2^{\text{sat}} = 1.01239$$

The summation of the liquid mole fractions is given by

$$x_1 + x_2 = 0.0153783 + 1.01239 = 1.02777$$

Since the summation is not equal to 1, we need to recalculate the liquid mole fractions using the normalized mole fractions as the guessed values

$$x_1 = 0.0153783/1.02777 = 0.0149628$$

$$x_2 = 1.01239/1.02777 = 0.985037$$

We then go back to the **Start Iteration** and repeat the procedure using 359.196^{o}K as the initial temperature for the solution of the non-linear equation (E-3). The final results after two iterations are

$$x_1 = 0.0122297, x_2 = 0.987814, \text{ and } T = 359.942^{o}K$$

Table 3.5-2 lists the Matlab program used for the calculation.

Table 5.3-2 Matlab program for dew point calculation

```
% Example 5.3-3
%
y1=.4;y2=1-y1;
P=101.3;
% Assume a value for x1
x1=.1;x2=1-x1;
lamda12 = 0.1173;lamda21 = 0.4227;
%
dT=1;
% Assume T
T=370;
% Solving for T using Newton's method
for k=1:20
A1=x1 + x2*lamda12; A2=x2 + x1*lamda21;
gama1=exp(-log(A1)+x2*(lamda12/A1-lamda21/A2));
gama2=exp(-log(A2)+x1*(lamda21/A2-lamda12/A1));
fprintf('x1 = %g, x2 = %g\n',x1,x2)
fprintf('gama1 = %g, gama2 = %g\n',gama1,gama2)
for i=1:20
fT=y1/gama1/exp(14.71712   -2975.95/(T-34.5228))  +  y2/gama2/exp(16.5362  -
3985.44/(T - 38.9974))-1/P;
T=T+dT;
fT2=y1/gama1/exp(14.71712   -2975.95/(T-34.5228))  +  y2/gama2/exp(16.5362  -
3985.44/(T - 38.9974))-1/P;
eT=fT*dT/(fT2-fT);
% New value for T
T=T-dT-eT;
fprintf('T(K) = %g\n',T)
if abs(eT)<.001, break, end
end
x1=y1*P/gama1/exp(14.71712 -2975.95/(T-34.5228));x2=y2*P/gama2/exp(16.5362 -
3985.44/(T - 38.9974));
% Update the values of gama1 and gama2 at new values of x1 and x2
A1=x1 + x2*lamda12; A2=x2 + x1*lamda21;
gama1=exp(-log(A1)+x2*(lamda12/A1-lamda21/A2));
gama2=exp(-log(A2)+x1*(lamda21/A2-lamda12/A1));
fprintf('x1 = %g, x2 = %g\n',x1,x2)
```

```
fprintf('gama1 = %g, gama2 = %g\n',gama1,gama2)
x1=y1*P/gama1/exp(14.71712 -2975.95/(T-34.5228));x2=y2*P/gama2/exp(16.5362 -
3985.44/(T - 38.9974));
% Check if x1+x2=1;
sumx=x1+x2;
fprintf('x1 = %g, x2 = %g, sumx = %g\n',x1,x2, sumx)
% New values for x1 and x2
x1=x1/sumx;x2=x2/sumx;
if abs(sumx-1)<.0001, break, end
end

>> e5d3d3
x1 = 0.1, x2 = 0.9
gama1 = 5.42913, gama2 = 1.0484
T(K) = 355.948
T(K) = 359.037
T(K) = 359.199
T(K) = 359.196
T(K) = 359.196
x1 = 0.0289813, x2 = 0.971019
gama1 = 10.2315, gama2 = 1.00555
x1 = 0.0153783, x2 = 1.01239, sumx = 1.02777
x1 = 0.0149628, x2 = 0.985037
gama1 = 12.2028, gama2 = 1.00161
T(K) = 359.946
T(K) = 359.942
T(K) = 359.942
x1 = 0.0126257, x2 = 0.987374
gama1 = 12.5979, gama2 = 1.00116
x1 = 0.0122297, x2 = 0.987814, sumx = 1.00004
```

Example 5.3-4 ---
Construct a *Txy* diagram for a mixture of ethanol (1) with hexane (2) at a total pressure of
101.3 kPa. Use the Wilson model with the parameters

$$\Lambda_{12} = 0.0952, \Lambda_{21} = 0.2713$$

Vapor pressure: (P_i^{sat} in kPa and *T* in °K)

$$\ln P_1^{\text{sat}} = 16.1952 - \frac{3423.53}{T - 55.7172} \qquad \ln P_2^{\text{sat}} = 14.0568 - \frac{2825.42}{T - 42.7089}$$

Solution ---

To construct a *Txy* diagram, we start with a value of x_1. The problem becomes a bubble point
temperature calculation. Since the composition in the vapor phase is not known, we have

$$y_1 + y_2 = 1 \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(E-1)}$$

Substituting $y_i = x_i \gamma_i P_i^{sat}/P$ into equation (E-1) yields

$$x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat} = P \qquad \text{(E-2)}$$

For a given value of x_1, the activity coefficients can be obtained from

$$\ln \gamma_1 = -\ln[x_1 + x_2\Lambda_{12}] + x_2 \left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}} \right] = 2.5703 \Rightarrow \gamma_1 = 13.069$$

$$\ln \gamma_2 = -\ln[x_2 + x_1\Lambda_{21}] + x_1 \left[\frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}} - \frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} \right] = 7.4112\times10^{-4} \Rightarrow \gamma_2 = 1.0007$$

With the known values for mole fractions, activity coefficient, and pressure, equation (E-2) becomes

$$x_1 \gamma_1 \exp(16.1952 - 3423.53/(T\text{-}55.7152))$$
$$+ (1 - x_1)\gamma_2 \exp(14.0568\text{-}2825.42/(T - 42.7089)) = 101.3 \qquad \text{(E-3)}$$

Equation (E-3) can be solved by Newton method for the temperature at a given value of x_1. The boiling point of pure ethanol and hexane can be obtained from the vapor pressure equation. We start the calculation with $x_1 = 0.002$ and use the boiling point of hexane as the initial guess for the bubble point temperature of the mixture. After each bubble point calculation, we increase x_1 by a small amount and repeat the calculation using the previous temperature as the initial guess. The following Matlab program can be used to construct a *Txy* diagram at 101.3 kPa.

```
-----------------------------------------------------------------------------------------------------
% Example 5.3-4: Construct a Txy diagramfor ethanol (1) and hexane (2) mixture
% at a total pressure (kPa) of
P = 101.3;
% Use the Wilson equation with parameters
G12 = 0.0952; G21 = 0.2713;
% Vapor pressure data: P(kPa), T(K)
p1sat = 'exp(16.1952-3423.53/(T-55.7152))';
p2sat = 'exp(14.0568-2825.42/(T-42.7089))';
% Estimate boiling points
Tb1 = 3423.53/(16.1952-log(P))+55.7152;
Tb2 = 2825.42/(14.0568-log(P))+42.7089;
x1=[0 .002 .004 .006 .008 .01 .015];
x2=linspace(.02,.92,46);
x3=[.93 .94 .95 .96 .97 .98 .985 .990 .995 1];
xp=[x1 x2 x3];np=length(xp);
yp=xp;Tp=xp;
Tp(1)=Tb2;Tp(np)=Tb1;
dT = .01;
% Will not work with this guess: T = y1*Tb1+y2*Tb2
T=Tb2;
for i=2:np
   x1=xp(i);x2=1-x1;
% Evaluate activity coefficients
 tem1 = x1 + x2*G12; tem2 = x2 + x1*G21;
 gam1 = exp(-log(tem1)+x2*(G12/tem1-G21/tem2));
 gam2 = exp(-log(tem2)+x1*(G21/tem2-G12/tem1));
 for k=1:20
    fT=x1*gam1*eval(p1sat)+x2*gam2*eval(p2sat)-P;
    T=T+dT;
     fT2=x1*gam1*eval(p1sat)+x2*gam2*eval(p2sat)-P;
 dfT=(fT2-fT)/dT; eT=fT/dfT;
 T=T-dT-eT;
  if abs(eT)<.001, break ,end
end
Tp(i)=T;
yp(i)=x1*gam1*eval(p1sat)/P;
fprintf('T(K) = %8.2f , x=%8.4f;y = %8.4f, iteration = %g\n',T,x1,yp(i),k)
end
plot(xp,Tp,yp,Tp,':')
axis([0 1 330 355])
xlabel('x,y');ylabel('T(K)');
grid on
legend('x','y')
```
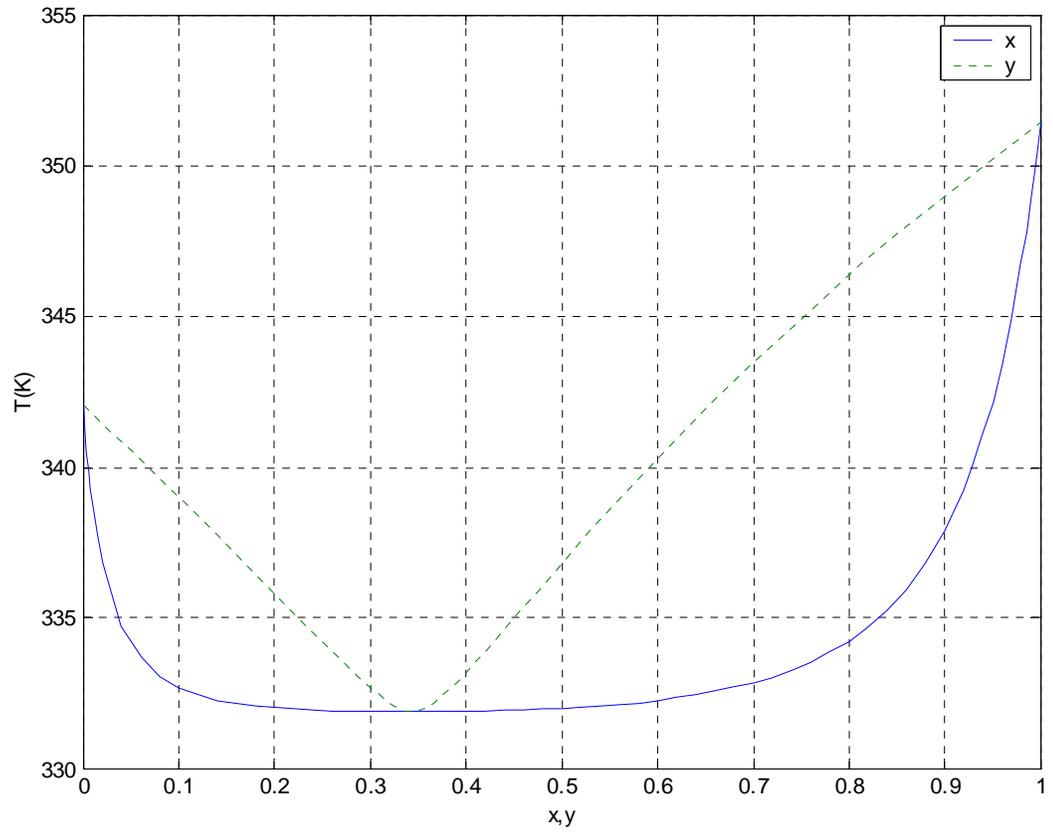
Figure E-1: *Txy* diagram for ethanol-hexane mixture at 101.3 kPa.

Chapter 5
5.4 Fitting Activity Coefficient Models with VLE Data

One vapor-liquid equilibrium data point is sufficient to determine the two parameters of he activity coefficient equations. This data point provides T, P, x_1, and y_1 so that the activity coefficients can be determined from

$$\gamma_i = y_i P / x_i P_i^{\text{sat}} \tag{5.4-1}$$

The equations for the Margules model are

$$\ln \gamma_1 = x_2^2 [a + 2(b - a)x_1], \qquad \ln \gamma_2 = x_1^2 [b + 2(a - b)x_2] \tag{5.4-2a,b}$$

Solving for the two parameters a and b from Eqs. (5.4-2a) and (5.4-2b) yields

$$a = \left(2 - \frac{1}{x_2} \right) \frac{\ln \gamma_1}{x_2} + 2 \frac{\ln \gamma_2}{x_1}, \qquad b = \left(2 - \frac{1}{x_1} \right) \frac{\ln \gamma_2}{x_1} + 2 \frac{\ln \gamma_1}{x_2} \tag{5.4-3a,b}$$

The equations for the Van Laar model are

$$\ln \gamma_1 = \frac{A}{\left[1 + (A x_1 / B x_2) \right]^2}, \qquad \ln \gamma_2 = \frac{B}{\left[1 + (B x_2 / A x_1) \right]^2} \tag{5.4-4a,b}$$

Solving for the two parameters A and B from Eqs. (5.4-4a) and (5.4-4b) yields

$$A = \left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1} \right)^2 \ln \gamma_1, \qquad B = \left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2} \right)^2 \ln \gamma_2 \tag{5.4-5a,b}$$

If more than one data point is available, curve fitting should be used to determine the parameters for the activity coefficient equations. As an example, Figure 5.4-1 plots the model equation that predicts temperature as a function of time using two parameters ε and h. This is similar to the activity coefficient model where the activity coefficient depends on liquid mole fraction and two parameters. The relationship between the temperature T_i obtained from the model equation and the experimental value $T_{i,\text{exp}}$ can be expressed generally as

$$T_{i,\text{exp}} = T_i (t; \varepsilon, h) + e_i \tag{B.1-2}$$

In this equation e_i is a random error that can be negative or positive. T_i is a function of the independent variable t_i and the parameters h and ε. The random error is also called the residual, which is the difference between the calculated and measured values.
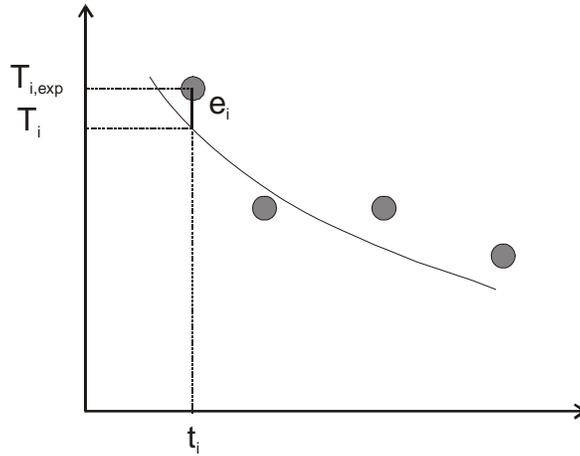
Figure 5.4-1. Relationship between the model equation and the data

Nonlinear regression is based on determining the values of the parameters that minimize the sum of the squares of the residuals called an objective function F_{obj}.

$$F_{obj} = \sum_{i=1}^{N} e_i^2 = \sum_{i=1}^{N} \left(T_{i,exp} - T_i\right)^2 = \sum_{i=1}^{N} \left(T_i - T_{i,exp}\right)^2 \qquad \text{(B.1-3)}$$

In this equation N is the number of data points or measured temperatures in this case. The two parameters are adjusted until the objection function reaches a minimum. This nonlinear regression procedure is presented in more details in Appendix B.

In some cases, the activity coefficient equations can be rearranged so that a linear curve fitting can be used to obtain the parameters.
The equations for the Margules model are

$$\ln \gamma_1 = x_2^2[a + 2(b-a)x_1], \qquad \ln \gamma_2 = x_1^2[b + 2(a-b)x_2] \qquad \text{(5.4-2a,b)}$$

These equations can be rearranged to

$$\frac{\ln \gamma_1}{x_2} = ax_2 + 2(b-a)x_1x_2, \qquad \frac{\ln \gamma_2}{x_1} = bx_1 + 2(a-b)x_1x_2 \qquad \text{(5.4-6a,b)}$$

Adding Eq.(5.4-6a) to (5.4-6b) yields

$$\frac{\ln \gamma_1}{x_2} + \frac{\ln \gamma_2}{x_1} = ax_2 + bx_1$$

We now define a new function $Q = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$, so that

$$\frac{Q}{x_1 x_2} = \frac{\ln \gamma_1}{x_2} + \frac{\ln \gamma_2}{x_1} = ax_2 + bx_1 = a(1 - x_1) + bx_1$$

$$\frac{Q}{x_1 x_2} = a + (b - a)x_1 \qquad\qquad (5.4\text{-}7)$$

The plot of $\dfrac{Q}{x_1 x_2}$ versus x_1 will yield a straight line with slope $= (b - a)$ and intercept $= a$. If

data is available for only one component, we can plot $\dfrac{\ln \gamma_1}{x_2^2}$ vs. x_1 or $\dfrac{\ln \gamma_2}{x_1^2}$ vs. x_2 to obtain

numerical values for the parameters a and b. If data is available for both components, Eq. (5.4-7) should be used to average out the experimental error.

 The Van Laar equations can also be arranged so that the data can be fitted by a linear equation. The equations for the Van Laar model are

$$\ln \gamma_1 = \frac{A}{[1 + (Ax_1 / Bx_2)]^2}, \qquad\qquad \ln \gamma_2 = \frac{B}{[1 + (Bx_2 / Ax_1)]^2} \qquad (5.4\text{-}4a,b)$$

Taking the inverse of each term we have

$$\frac{1}{\ln \gamma_1} = \frac{[1 + (Ax_1 / Bx_2)]^2}{A}, \qquad\qquad \frac{1}{\ln \gamma_2} = \frac{[1 + (Bx_2 / Ax_1)]^2}{B} \qquad (5.4\text{-}8a,b)$$

Taking the square root of each term yields

$$\frac{1}{\sqrt{\ln \gamma_1}} = \frac{1}{\sqrt{A}} + \frac{\sqrt{A}}{B}\frac{x_1}{x_2}, \qquad\qquad \frac{1}{\sqrt{\ln \gamma_2}} = \frac{1}{\sqrt{B}} + \frac{\sqrt{B}}{A}\frac{x_2}{x_1} \qquad (5.4\text{-}9a,b)$$

Again, if there is only data for one component, we can plot either Eq. (5.4-9a) or (5.4-9b) to obtain the numerical values for A and B. If there are two sets of data, we will use the following linear form

$$\frac{x_1 x_2}{Q} = \frac{1}{A} + \frac{A - B}{AB}x_1 \qquad\qquad (5.4\text{-}10)$$

Example 5.4-1 ---
Use the given VLE data for the ethanol (1)-benzene (2) system at 40°C to determine Margules and Van Laar parameters[6]. The vapor pressures for ethanol and benzene at 40°C are 134.02 mmHg and 182.78 mmHg, respectively.

x_1	.020	.095	.204	.378	.490	.592	.702	.802	.880	.943	.987
y_1	.145	.280	.332	.362	.384	.405	.440	.507	.605	.747	.912
P,mmHg	208.4	239.8	249.1	252.3	248.8	245.7	237.3	219.4	196.3	169.5	145.6

Solution ---

---

[6] Kyle, B.G., Chemical and Process Thermodynamics, Prentice Hall, 1999, pg. 281

First, we need to determine the activity coefficients from the experimental data from the following equation

$$y_i P = x_i \gamma_i P_i^{\text{sat}}$$

Applying the equation for the first data point ($x_1 = .020$, $y_1 = .145$, and $P = 208.4$) yields

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^{\text{sat}}} = \frac{(0.145)(208.4)}{(0.02)(134.02)} = 11.274$$

$$\gamma_2 = \frac{(1 - y_1)P}{(1 - x_1)P_2^{\text{sat}}} = \frac{(0.855)(208.4)}{(0.98)(182.78)} = 0.99474$$

From equation (5.4-7)

$$\frac{Q}{x_1 x_2} = a + (b - a)x_1 \tag{5.4-7}$$

The plot of $\dfrac{Q}{x_1 x_2}$ versus x_1 will yield a straight line with slope = $(b - a)$ and intercept = a.

Table 5.4-1a lists the Matlab program used to determine the Margules parameters using linear curve fitting. Figure E-1 shows the fitted line and the experimental data. Figure E-2 shows the calculated and measured mole fraction of ethanol. The two obtained Margules parameters are

$$a = 2.173, \text{ and } b = 1.539$$

Table 5.4-1a ---

```
%  Example 5.4-1, Determination of Margules parameters a and b
x=[.020 .095 .204 .378 .490 .592 .702 .802 .880 .943 .987];
y=[.145 .280 .332 .362 .384 .405 .440 .507 .605 .747 .912];
P=[208.4 239.8 249.1 252.3 248.8 245.7 237.3 219.4 196.3 169.5 145.6];
Pvap1=134.02;Pvap2=182.78;
% Evaluate gamma,g from y*P = x*g*Pvap
x2=1-x;
g1=y.*P./(x*Pvap1);g2=(1-y).*P./(x2*Pvap2);
% Parameters for Margules equation
ym=(x.*log(g1)+x2.*log(g2))./(x.*x2);
c=polyfit(x,ym,1);
%  c(1) = slope, c(2) = intercept
a=c(2);b=c(1)+a;
fprintf('Margules parameters: a = %g  b = %g \n',a,b)
xp=0:.02:1;xp2=1-xp;
g1c=exp(xp2.*xp2.*(a+2*(b-a)*xp));g2c=exp(xp.*xp.*(b+2*(a-b)*xp2));
P1c=xp.*g1c*Pvap1;P2c=xp2.*g2c*Pvap2;y1c=P1c./(P1c+P2c);
xc=[0 1];
yc=polyval(c,xc);
figure(1)
plot(xc,yc,x,ym,'o')
grid on
legend('Fitted','Data')
xlabel('x1');ylabel('Q/(x1*x2)')
figure(2)
plot(xp,y1c,x,y,'o')
grid on
xlabel('x1');ylabel('y1')
legend('Fitted','Data')
>> e5d4d1
Margules parameters: a = 2.17278  b = 1.53949
```
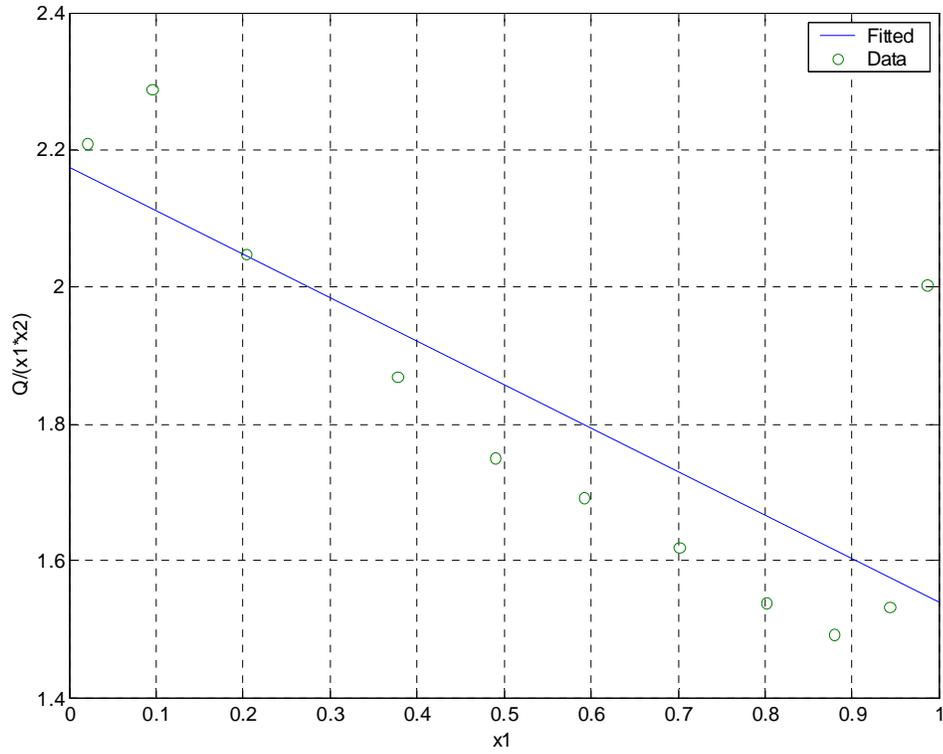
Figure E-1 Determination of Margues parameters

Figure E-2 Calculated and measured mole fraction of ethanol.

Chapter 5

For Van Laar model, the plot of $\dfrac{x_1 x_2}{Q}$ versus x_1 will yield a straight line with slope $= \dfrac{A - B}{AB}$

and intercept $= \dfrac{1}{A}$. Table 5.4-1b lists the Matlab program used to determine the Van Laar parameters using linear curve fitting. Figure E-3 shows the fitted line and the experimental data. Figure E-4 shows the calculated and measured mole fraction of ethanol. The two obtained Van Laar parameters are

$$A = 2.186, \text{ and } B = 1.555$$

Table 5.4-1b --

```
%  Example 5.4-1, Determination of Van Laar parameters A and B
x=[.020 .095 .204 .378 .490 .592 .702 .802 .880 .943 .987];
y=[.145 .280 .332 .362 .384 .405 .440 .507 .605 .747 .912];
P=[208.4 239.8 249.1 252.3 248.8 245.7 237.3 219.4 196.3 169.5 145.6];
Pvap1=134.02;Pvap2=182.78;
% Evaluate gamma,g from y*P = x*g*Pvap
x2=1-x;
g1=y.*P./(x*Pvap1);g2=(1-y).*P./(x2*Pvap2);
ym=(x.*log(g1)+x2.*log(g2))./(x.*x2);
xp=0.02:.02:.98;xp2=1-xp;
% Parameters for van Laar equation
yv=1.0./ym;
c=polyfit(x,yv,1);
%  c(1) = slope, c(2) = intercept
A=1/c(2);B=A/(A*c(1)+1);
fprintf('Van Laar parameters: A = %g  B = %g \n',A,B)
g1v=exp(A./(1+A*xp./(B*xp2)).^2);g2v=exp(B./(1+B*xp2./(A*xp)).^2);
P1=xp.*g1v*Pvap1;P2=xp2.*g2v*Pvap2;y1v=P1./(P1+P2);
xc=[0 1];
yc=polyval(c,xc);
figure(1)
plot(xc,yc,x,yv,'o')
grid on
legend('Fitted','Data')
xlabel('x1');ylabel('(x1*x2)/Q')
figure(2)
plot(xp,y1v,x,y,'o')
grid on
xlabel('x1');ylabel('y1')
legend('Fitted','Data')

>> e5d4d1b
Van Laar parameters: A = 2.18558  B = 1.55458
```
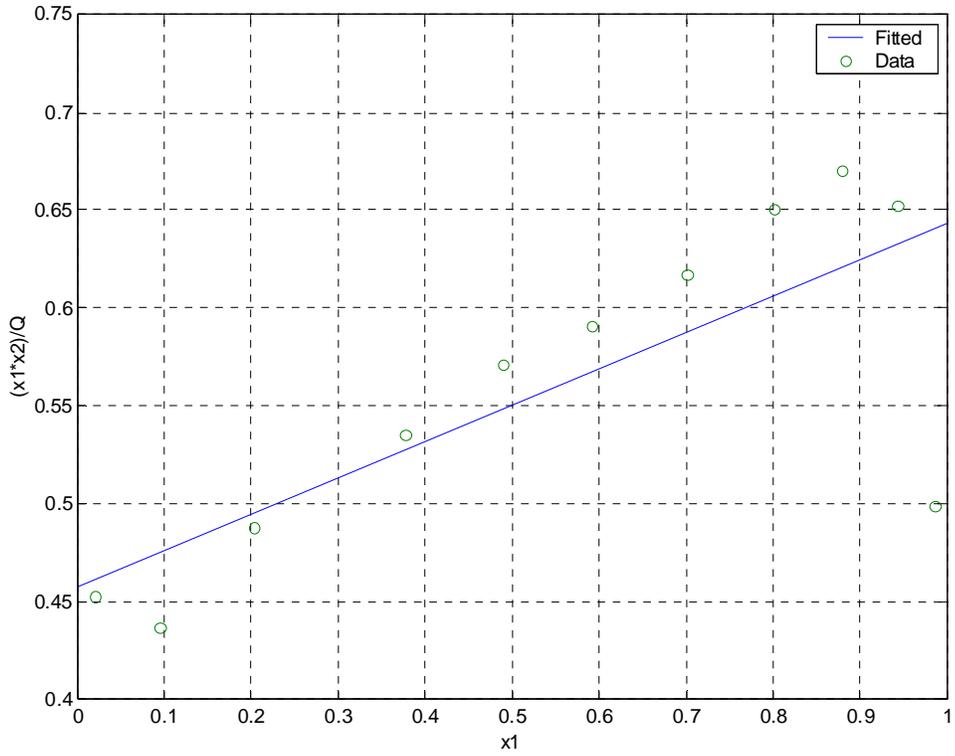
Figure E-3 Determination of Van Laar parameters
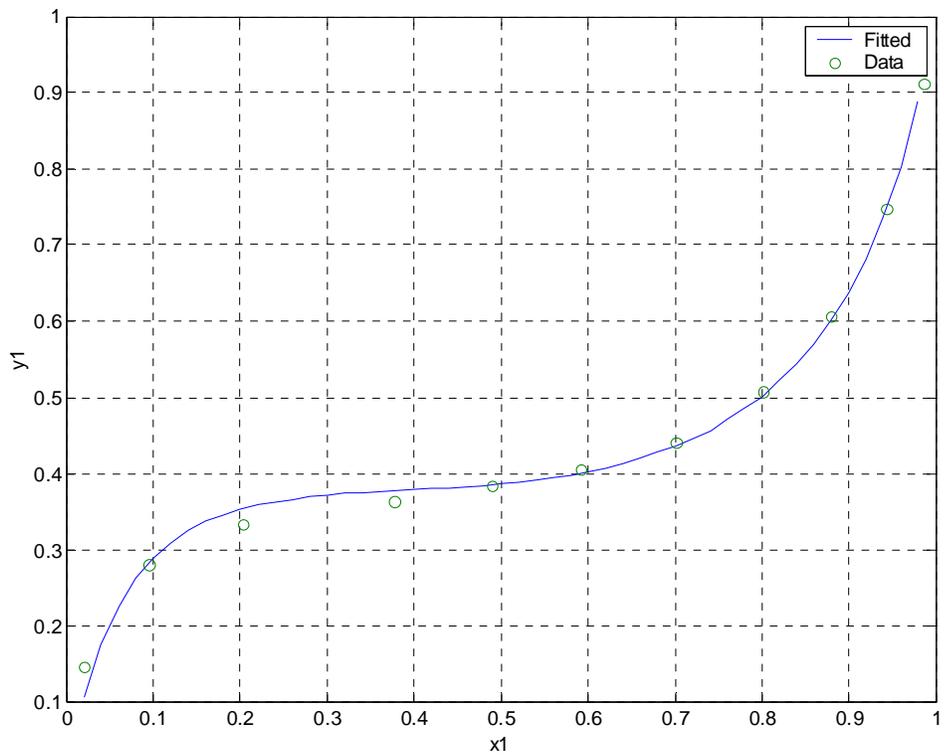
Figure E-4 Calculated and measured mole fraction of ethanol.

Example 5.4-2 ---
Use the given VLE data for the methanol (1)-carbon tetrachloride (2) system at 20°C to determine Wilson parameters[7]. The vapor pressures for methanol and carbon tetrachloride at 20°C are 96.87 mmHg and 92.08 mmHg, respectively.

x_1	.020	.040	.100	.200	.300	.600	.700	.800	.900	.960
y_1	.344	.391	.430	.449	.462	.494	.512	.546	.662	.792
P,mmHg	136.6	146.4	154.8	158.0	159.5	159.9	157.5	152.0	135.5	117.2

Solution ---
The activity coefficients can be calculated from the experimental data using the following equation

$$y_i P = x_i \gamma_i P_i^{sat}$$

Applying the equation for the first data point (x_1 = .020, y_1 = .344, and P = 136.6) yields

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^{sat}} = \frac{(0.344)(136.6)}{(0.02)(96.87)} = 24.3$$

$$\gamma_2 = \frac{(1-y_1)P}{(1-x_1)P_2^{sat}} = \frac{(0.656)(136.6)}{(0.98)(92.08)} = 0.993$$

The experimental Q^{exp} function is evaluated as

$$Q^{exp} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \tag{E-1}$$

The calculated Q^{cal} function is obtained by substituting Eqs. (E-2) and (E-3) for ln γ_1 and ln γ_2 into equation (E-1)

$$\ln \gamma_1 = -\ln[x_1 + x_2\Lambda_{12}] + x_2\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right] \tag{E-2}$$

$$\ln \gamma_2 = -\ln[x_2 + x_1\Lambda_{21}] + x_1\left[\frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}} - \frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}}\right] \tag{E-3}$$

$$Q^{cal} = - x_1\ln[x_1 + x_2\Lambda_{12}] - x_2\ln[x_2 + x_1\Lambda_{21}] \tag{E-4}$$

The parameters Λ_{12} and Λ_{21} can be obtained by minimizing the following objective function

$$F_{obj} = \sum_{i=1}^{N}\left(Q^{exp} - Q^{cal}\right)_i^2$$

---

[7] Kyle, B.G., Chemical and Process Thermodynamics, Prentice Hall, 1999, pg. 287

Table 4.5-2 lists the Matlab program used to determine the Wilson parameters Fminsearch. Figure E-5 shows the calculated and measured mole fraction of methanol. The two obtained Wilson parameters are

$$\Lambda_{12} = 0.0666, \text{ and } \Lambda_{21} = 3.118$$

Table 5.4-1b ---

```
%  Example 5.4-2
%  Determine parameters in the Wilson equation by minimizing the objective
%    function sum[(Qexp-Qcal)i]^2, using fmins (Matlab function)
%  Initial guesses
G12 = .2; G21 =.4;
gcal=fminsearch('ofq',[G12 G21]);
fprintf('G12 =  %g , G21 = %g \n',gcal(1),gcal(2))
G12=gcal(1);G21=gcal(2);
x=[.020 .040 .100 .200 .300 .600 .700 .800 .900 .960];
y=[.344 .391 .430 .449 .462 .494 .512 .546 .662 .792];
Pvap1=96.87;Pvap2=92.08;
xp=0.02:.02:.98;xp2=1-xp;
tem=G12./(xp+xp2*G12)-G21./(xp2+xp*G21);
g1=exp(xp2.*tem)./(xp+xp2*G12);g2=exp(-xp.*tem)./(xp2+xp*G21);
P1=xp.*g1*Pvap1;P2=xp2.*g2*Pvap2;y1w=P1./(P1+P2);
plot(xp,y1w,x,y,'o')
grid on
xlabel('x1');ylabel('y1')
legend('Fitted','Data')


--------------------------------------------------
function yy=ofq(G)
%  Example 5.4-2, function to evaluate the objective function Fobj
%    ofq=sum[(Qexp-Qcal)i]^2
x=[.020 .040 .100 .200 .300 .600 .700 .800 .900 .960];
y=[.344 .391 .430 .449 .462 .494 .512 .546 .662 .792];
P=[136.6 146.4 154.8 158.0 159.5 159.9 157.5 152.0 135.5 117.2];
Pvap1=96.87;Pvap2=92.08;
% Evaluate gamma,g from y*P = x*g*Pvap
x2=1-x;G12=G(1);G21=G(2);
g1=y.*P./(x*Pvap1);g2=(1-y).*P./(x2*Pvap2);
%
Qexp=(x.*log(g1)+x2.*log(g2));
Qcal=-x.*log(x+G12*x2)-x2.*log(x2+G21*x);
yy=sum((Qexp-Qcal).^2);

>> e5d4d2
G12 =  0.0665678 , G21 = 0.311822
```
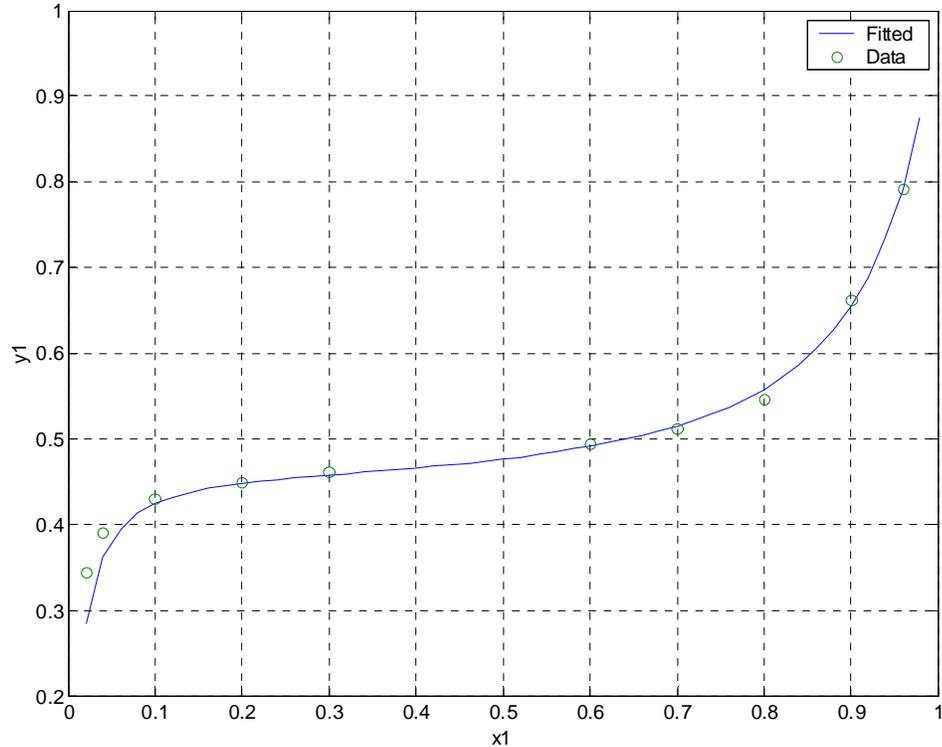
Figure E-5 Calculated and measured mole fraction of methanol.

5.5 Azeotropes

When deviations from Raoult's law are large enough, the *Tx* and *Ty* curves can go through a maximum or a minimum. The extreme point (either minimum or maximum) is called azeotrope where the liquid mole fraction is equal to the vapor mole fraction for each species:

$$x_i = y_i \qquad\qquad (5.5\text{-}1)$$

A system that exhibits a maximum in pressure (positive deviations from Raoult's law) will exhibits a minimum in temperature called minimum boiling azeotrope as shown the top part of Figure 5.5-1 for a mixture of chloroform and hexane. The *Pxy* diagram is plotted at 318 K and the *Txy* diagram is plotted at 1 atm. This is the case when the like interaction is stronger than the unlike interaction between the molecules. The mixture will require less energy to go to the vapor phase and hence will boil at a lower temperature that that of the pure components.

If the unlike interaction is stronger than the like interaction we have negative deviations from Raoult's law and the system will exhibit a minimum in pressure or a maximum in temperature called maximum boiling azeotrope. A mixture of acetone and chloroform shows this behavior in the bottom part of Figure 5.5-1. The *Pxy* diagram is plotted at 328 K and the *Txy* diagram is plotted at 1 atm. The data for vapor pressure and Wilson model are from the Thermosolver program by Koretsky. This program can also plot *Pxy* and *Txy* diagrams for different mixtures. Table 5.5-1 lists the Matlab program used to produce Figure 5.5-1.
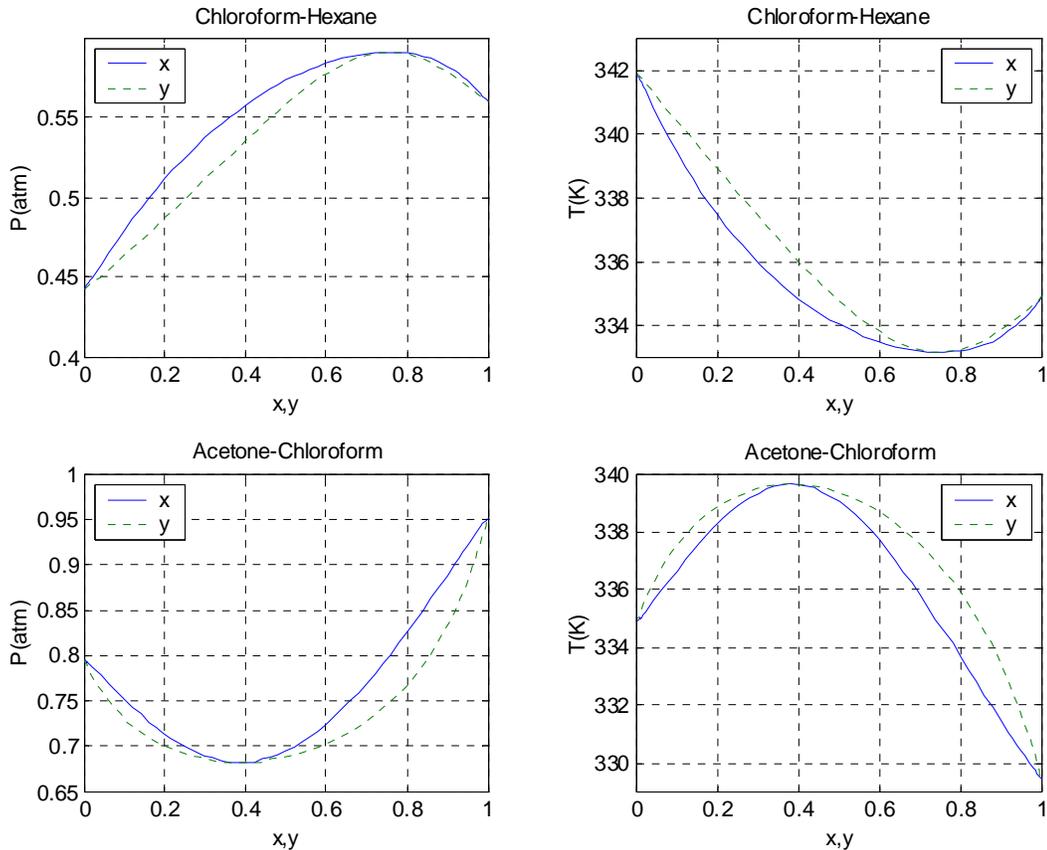
Figure 5.5-1 Top: minimum boiling azeotrope for chloroform and n-Hexane system.
Bottom: maximum boiling azeotrope for acetone and chloroform system

Table 5.5-1 ---
```
% Figure 5.5-1: Construct a Txy diagramfor chloroform (1) and hexane (2) mixture
% at a total pressure (atm) of
P = 1;
% Use the Wilson equation with parameters
G12 = 1.2042; G21 = 0.39799;
% Vapor pressure data: P(atm), T(K)
p1sat = 'exp(9.33984-2696.79/(T-46.14))';
p2sat = 'exp(9.20324-2697.55/(T-48.78))';
% Estimate boiling points
Tb1 = 2696.79/(9.33984-log(P))+46.14;
Tb2 = 2697.55/(9.20324-log(P))+48.78;
x1=[0 .002 .004 .006 .008 .01 .015];
x2=linspace(.02,.92,46);
x3=[.93 .94 .95 .96 .97 .98 .985 .990 .995 1];
xp=[x1 x2 x3];np=length(xp);
yp=xp;Tp=xp;
Tp(1)=Tb2;Tp(np)=Tb1;
dT = .01;
T=Tb2;
```

```matlab
for i=2:np
   x1=xp(i);x2=1-x1;
% Evaluate activity coefficients
 tem1 = x1 + x2*G12; tem2 = x2 + x1*G21;
 gam1 = exp(-log(tem1)+x2*(G12/tem1-G21/tem2));
 gam2 = exp(-log(tem2)+x1*(G21/tem2-G12/tem1));
 for k=1:20
    fT=x1*gam1*eval(p1sat)+x2*gam2*eval(p2sat)-P;
    T=T+dT;
     fT2=x1*gam1*eval(p1sat)+x2*gam2*eval(p2sat)-P;
 dfT=(fT2-fT)/dT; eT=fT/dfT;
 T=T-dT-eT;
  if abs(eT)<.001, break ,end
end
Tp(i)=T;
yp(i)=x1*gam1*eval(p1sat)/P;
fprintf('T(K) = %8.2f , x=%8.4f;y = %8.4f, iteration = %g\n',T,x1,yp(i),k)
end
subplot(2,2,2); plot(xp,Tp,yp,Tp,':')
axis([0 1 333 343])
xlabel('x,y');ylabel('T(K)');title('Chloroform-Hexane')
grid on
legend('x','y')
%
% Construct a Pxy diagramfor chloroform (1) and hexane (2) mixture
% at a temperature (K) of
T=318;
p1vap=eval(p1sat);p2vap=eval(p2sat);
xp2=1-xp;
tem1 = xp + xp2*G12; tem2 = xp2 + xp*G21;
 gam1 = exp(-log(tem1)+xp2.*(G12./tem1-G21./tem2));
 gam2 = exp(-log(tem2)+xp.*(G21./tem2-G12./tem1));
 p1=xp.*gam1*p1vap;p2=xp2.*gam2*p2vap;
 Pp=p1+p2;yp=p1./Pp;
 subplot(2,2,1); plot(xp,Pp,yp,Pp,':')
axis([0 1 0.4 0.6])
xlabel('x,y');ylabel('P(atm)');title('Chloroform-Hexane')
grid on
legend('x','y',2)
%
% Figure 5.5-1: Construct a Txy diagramfor acetone (1) and chloroform (2) mixture
% at a total pressure (atm) of
P = 1;
% Use the Wilson equation with parameters
G12 = 1.324; G21 = 1.7314;
% Vapor pressure data: P(atm), T(K)
p1sat = 'exp(10.0179-2940.46/(T-35.93))';
p2sat = 'exp(9.33984-2696.79/(T-46.14))';
% Estimate boiling points
```

```
Tb1 = 2940.46/(10.0179-log(P))+35.93;
Tb2 = 2696.79/(9.33984-log(P))+46.14;
x1=[0 .002 .004 .006 .008 .01 .015];
x2=linspace(.02,.92,46);
x3=[.93 .94 .95 .96 .97 .98 .985 .990 .995 1];
xp=[x1 x2 x3];np=length(xp);
yp=xp;Tp=xp;
Tp(1)=Tb2;Tp(np)=Tb1;
dT = .01;
T=Tb2;
for i=2:np
   x1=xp(i);x2=1-x1;
% Evaluate activity coefficients
 tem1 = x1 + x2*G12; tem2 = x2 + x1*G21;
 gam1 = exp(-log(tem1)+x2*(G12/tem1-G21/tem2));
 gam2 = exp(-log(tem2)+x1*(G21/tem2-G12/tem1));
 for k=1:20
    fT=x1*gam1*eval(p1sat)+x2*gam2*eval(p2sat)-P;
    T=T+dT;
     fT2=x1*gam1*eval(p1sat)+x2*gam2*eval(p2sat)-P;
 dfT=(fT2-fT)/dT; eT=fT/dfT;
 T=T-dT-eT;
  if abs(eT)<.001, break ,end
end
Tp(i)=T;
yp(i)=x1*gam1*eval(p1sat)/P;
fprintf('T(K) = %8.2f , x=%8.4f;y = %8.4f, iteration = %g\n',T,x1,yp(i),k)
end
subplot(2,2,4); plot(xp,Tp,yp,Tp,':')
axis([0 1 329 340])
xlabel('x,y');ylabel('T(K)');title('Acetone-Chloroform')
grid on
legend('x','y')
%
% Construct a Pxy diagramfor acetone (1) and chloroform (2) mixture
% at a temperature (K) of
T=328;
p1vap=eval(p1sat);p2vap=eval(p2sat);
xp2=1-xp;
tem1 = xp + xp2*G12; tem2 = xp2 + xp*G21;
 gam1 = exp(-log(tem1)+xp2.*(G12./tem1-G21./tem2));
 gam2 = exp(-log(tem2)+xp.*(G21./tem2-G12./tem1));
 p1=xp.*gam1*p1vap;p2=xp2.*gam2*p2vap;
 Pp=p1+p2;yp=p1./Pp;
 subplot(2,2,3); plot(xp,Pp,yp,Pp,':')
axis([0 1 0.65 1.0])
xlabel('x,y');ylabel('P(atm)');title('Acetone-Chloroform')
grid on
legend('x','y',2)
```

Chapter 5

The total pressure, P^{ideal}, for an ideal mixture is given by

$$P^{ideal} = x_1 P_1^{sat} + (1 - x_1)P_2^{sat}$$

(5.5-1)

For a non-ideal system, the total pressure is given by

$$P = x_1 \gamma_1 P_1^{sat} + (1 - x_1)\gamma_2 P_2^{sat}$$

(5.5-2)

If γ_1 and $\gamma_2 > 1$ we have $P > P^{ideal}$ or a positive deviation from Raoult's law. Similarly, if γ_1 and $\gamma_2 < 1$ we have $P < P^{ideal}$ or a negative deviation from Raoult's law. Figure 5.5-2 shows both positive and negative deviation of the Px curves.
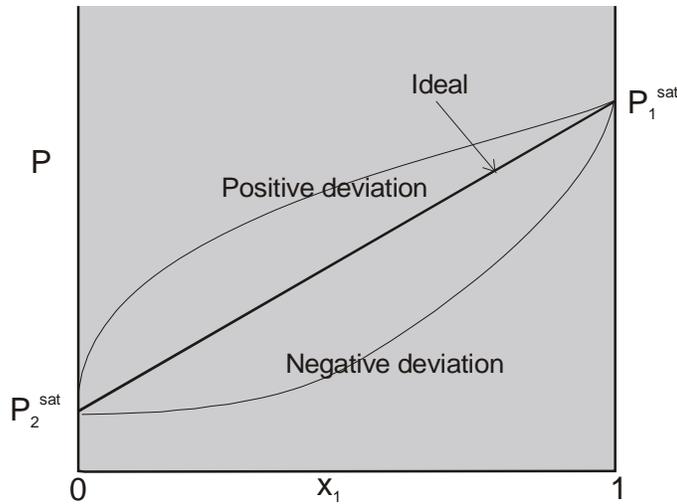
Figure 5.5-2 Positive and negative deviation from Raoult's law.

The azeotrope can be used to determine the two parameters for an activity coefficient model. For vapor-liquid equilibrium at low pressure we have

$$y_i P = x_i \gamma_i P_i^{sat}$$

(5.5-3)

Since the vapor and liquid compositions are equal at the azeotrope, the condition for equilibrium becomes

$$P = \gamma_i P_i^{sat}$$

(5.5-4)

Since both the saturation pressure and the azeotrope pressure are measurable, the activity coefficient can simply be obtained from Eq. (5.5-2) at the azeotropic composition.

Example 5.5-1 --
At $T = 64.3°K$ and $P = 760$ mmHg, the system methanol (1)-methyl ketone (2) forms an azeotrope containing 84.2 mol% of methanol[8]. The vapor pressures for methanol and carbon tetrachloride at $20°C$ are 96.87 mmHg and 92.08 mmHg, respectively. Determine the parameters in Wilson equation.

Vapor pressure: (P_i^{sat} in mmHg and T in °C)

$$\log_{10} P_1^{sat} = 7.87863 - \frac{1474.11}{T + 230} \qquad \log_{10} P_2^{sat} = 6.97421 - \frac{1209.6}{T + 216}$$

Solution --
The saturation pressures at $64.3°K$ can be determined from the given Antoine 's equations to give

$$P_1^{sat} = 736.94 \text{ mmHg, and } P_2^{sat} = 455.86 \text{ mmHg.}$$

We then use Eq. (5.5-4) to determine the activity coefficients

$$P = \gamma_i P_i^{sat} \Rightarrow \gamma_i = \frac{P}{P_i^{sat}} \tag{5.5-4}$$

Hence

$$\gamma_1 = \frac{760}{736.94} = 1.031, \qquad \gamma_2 = \frac{760}{455.86} = 1.667$$

The Wilson equations are given by

$$\ln \gamma_1 = - \ln[x_1 + x_2\Lambda_{12}] + x_2 \left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}} \right] \tag{E-1}$$

$$\ln \gamma_2 = - \ln[x_2 + x_1\Lambda_{21}] + x_1 \left[\frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}} - \frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} \right] \tag{E-2}$$

Eqs (E-1) and (E-2) can be combined as x_1(E-1) + x_2(E-2) to give

$$x_1\ln \gamma_1 + x_2\ln \gamma_2 = - x_1\ln[x_1 + x_2\Lambda_{12}] - x_2\ln[x_2 + x_1\Lambda_{21}] \tag{E-3}$$

Combining the log's terms yields

$$\left[\gamma_1(x_1 + x_2\Lambda_{12}) \right]^{x_1} \left[\gamma_2(x_2 + x_1\Lambda_{21}) \right]^{x_2} = 1 \tag{E-4}$$

---

[8] Kyle, B.G., <u>Chemical and Process Thermodynamics</u>, Prentice Hall, 1999, pg. 328

Solving for Λ_{21} in terms of Λ_{12} and substituting into (E-1) gives an equation with just one unknown Λ_{12}

$$\left\{\frac{\gamma_2 x_2}{1-\left[\dfrac{\Lambda_{12}x_1}{x_1+\Lambda_{12}x_2}\right]+\left(\dfrac{x_1}{x_2}\right)\ln[\gamma_1(x_1+\Lambda_{12}x_2)]}\right\}^{x_2/x_1}[\gamma_1(x_1+\Lambda_{12}x_2)]=1 \qquad (E-4)$$

Equation (E-4) can be solved with the known values of activity coefficients and liquid mole fractions:

$$\gamma_1=1.031,\ \gamma_2=1.667,\ x_1=0.842,\ \text{and }x_2=0.158$$

Once Λ_{12} is evaluated, we can determine Λ_{21} from Eq. (E-1)

$$\ln\gamma_1=-\ln[x_1+x_2\Lambda_{12}]+x_2\left[\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}}-\frac{\Lambda_{21}}{x_2+x_1\Lambda_{21}}\right] \qquad (E-1)$$

Rearranging Eq. (E-1) so that only the unknown Λ_{21} is on the left side of the equation yields

$$\frac{\Lambda_{21}}{x_2+x_1\Lambda_{21}}=\frac{\Lambda_{12}}{x_1+x_2\Lambda_{12}}-\frac{[\ln\gamma_1+\ln(x_1+x_2\Lambda_{12})]}{x_2} \qquad (E-5)$$

The RHS of Eq. (E-5) is a known quantity C, therefore

$$\frac{\Lambda_{21}}{x_2+x_1\Lambda_{21}}=C\Rightarrow\Lambda_{21}=Cx_2+Cx_1\Lambda_{21}$$

The value of Λ_{21} is then evaluated

$$\Lambda_{21}=\frac{Cx_2}{1-Cx_1} \qquad (E-6)$$

Table 5.5-1 lists the Matlab program that solves equation (E-4) for Λ_{12} by Newton method and evaluates Λ_{21} from equation (E-6). The following values are obtained

$$\Lambda_{12}=1.0818,\ C=0.79349,\ \text{and }\Lambda_{21}=0.3778$$

Table 5.5-1 --
```
%  Example 5.5-1, Determination of Wilson parameters from azeotropic composition
g1=1.031;g2=1.667;x=.842;x2=1-x;
g2x2=g2*x2;x2x=x2/x;
f='(g2x2/(1-G12*x/(x+G12*x2)+log(g1*(x+G12*x2))/x2x))^x2x*g1*(x+G12*x2)-1';
G12=1;dG=.01;
for i=1:20
  fG=eval(f);G12=G12+dG;fG2=eval(f);
  dfG=(fG2-fG)/dG;eG=fG/dfG;
  G12=G12-dG-eG;
  if abs(eG)<.001, break, end
end
fprintf('G12 = %8.4f\n',G12)
c=G12/(x+x2*G12)-(log(g1)+log(x+x2*G12))/x2;
G21=c*x2/(1-c*x);
fprintf('G21 = %8.4f\n',G21)

>> e5d5d1
G12 =   1.0818
G21 =   0.3778
```

5.6 Estimation of Activity Coefficients

We sometime need to estimate activity coefficients at the desired conditions from data available at other conditions.

Example 5.6-1 ---

We need equilibrium data for the design of an absorber to remove acetone from an air stream using water as a solvent[9]. The equilibrium data for the acetone (1)-water (2) system are given at 25°C as follows:

x_1	0.0194	0.0289	0.0449	0.0556	0.0939
y_1	0.5234	0.6212	0.7168	0.7591	0.8351
P(mmHg)	50.1	61.8	81.3	91.9	126.1

Use the given data to determine the vapor equilibrium mole fractions of acetone in the system where air is also present so that the total pressure is maintained at 760 mmHg. At 25°C the vapor pressures are: $P_1^{sat} = 230.05$ mmHg and $P_2^{sat} = 23.76$ mmHg.

Solution ---

Figure E-1 Air is present in the system B where data are needed.

---

[9] Kyle, B.G., <u>Chemical and Process Thermodynamics</u>, Prentice Hall, 1999, pg. 352

In this problem we need to estimate activity coefficients at the desired condition (Figure E-1B) from data available at other conditions (Figure E-1A). We first determine the activity coefficients from the data available from system A using the equilibrium relation

$$y_i P = x_i \gamma_i P_i^{\text{sat}} \qquad\qquad\qquad\qquad \text{(E-1)}$$

For the first data point $(x_1 = 0.0194, y_1 = 0.5234, \text{ and } P = 50.1 \text{ mmHg})$ we have

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^{\text{sat}}} = \frac{(0.5234)(50.1)}{(0.0194)(230.05)} = 5.88$$

Similar calculations lead to the following table

x_1	0.0194	0.0289	0.0449	0.0556	0.0939
γ_1	5.88	5.77	5.64	5.45	4.88
P(mmHg)	50.1	61.8	81.3	91.9	126.1

At equilibrium in system B where air is present we also use the equilibrium relation for acetone

$$y_1 P = x_1 \gamma_1 P_1^{\text{sat}} \qquad\qquad\qquad\qquad \text{(E-2)}$$

In equation (E-2), P is the total pressure of system B, 760 mmHg, and γ_1 is the activity coefficient obtained from the data of system A. We have assumed that air is essentially insoluble in acetone-water solution and therefore the activity coefficients of system B are the same as those of system A. The vapor mole fraction of acetone in system B is then calculated from

$$y_1 = \frac{x_1 \gamma_1 P_1^{\text{sat}}}{P} = \frac{x_1 \gamma_1 (230.05)}{760}$$

For the first data point $(x_1 = 0.0194 \text{ and } \gamma_1 = 5.88)$ we have

$$y_1 = \frac{(0.0194)(5.88)(230.05)}{760} = 0.0345$$

The following table lists the mole fractions of acetone in the vapor phase in system B at the given mole fractions of acetone in the liquid phase:

x_1	0.0194	0.0289	0.0449	0.0556	0.0939
y_1	0.0345	0.0505	0.0767	0.0917	0.1387
P(mmHg)	760	760	760	760	760

Example 5.6-2 --
We want to estimate the solubility (mole fraction) of ethane (1) in n-heptanol (2) at 25°C and 20 atm[10]. At 25°C the solubility of ethane in n-heptanol at 1 atm is $x_1 = 0.0159$. The activity coefficients in this system can be represented by

$$\ln \gamma_1 = B(1 - x_1)^2$$

The K_1 values ($K_1 = f_1^L/f_1^G$) for ethane are given and n-heptanol may be considered nonvolatile. At 25°C and 1 atm: $K_1 = 27.0$ and at 25°C and 20 atm: $K_1 = 1.62$
Solution ---

At 25°C and 20 atm we have

$$\hat{f}_1^G = \hat{f}_1^L \Rightarrow y_1 f_1^G = x_1 \gamma_1 f_1^L \Rightarrow y_1 = x_1 \gamma_1 (f_1^L/f_1^G) \Rightarrow y_1 = x_1 \gamma_1 K_1$$

Since n-heptanol may be considered nonvolatile, $y_1 = 1$, the above equation becomes

$$1 = 1.62 x_1 \gamma_1 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(E-1)}$$

We can use equation (E-1) to find the solubility if γ_1 is known. We now evaluate γ_1 at 25°C and 1 atm

$$y_1 = x_1 \gamma_1 K_1 \Rightarrow 1 = (0.0159)\gamma_1(27) \Rightarrow \gamma_1 = \frac{1}{(0.0159)(27)} = 2.3294$$

We then determine the parameter B from the activity coefficient equation $\ln \gamma_1 = B(1 - x_1)^2$

$$B = \frac{\ln(2.3294)}{(1 - 0.0159)^2} = 0.8731$$

If we assume that B is the same for the system at 20 atm then we can solve equation (E-1). Taking the log of equation (E-1) yields

$$0 = \ln(1.62) + \ln(x_1) + \ln(\gamma_1) = \ln(1.62) + \ln(x_1) + 0.8731(1 - x_1)^2 \quad \text{(E-2)}$$

The solution of the nonlinear algebraic equation (E-2) can be determined using Matlab function fsolve with inline function as follows:

```
>> ff=inline('log(1.62)+log(x)+0.8731*(1-x)^2')
>> x=fsolve(ff,0.5,optimset('Display','off'))
x =
   0.4933
```

Hence the solubility of ethane in n-heptanol at 25°C and 20 atm is $x_1 = 0.4933$

5.7 Phase Behavior in Partially Miscible Systems

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[10] Kyle, B.G., Chemical and Process Thermodynamics, Prentice Hall, 1999, pg. 354

When like interactions are significantly stronger than unlike interactions, liquids can split into two different partially miscible phases to lower the total Gibbs phases energy of the system. The separation method of liquid-liquid extraction, found in the chemical, petroleum, and related process industries, uses the partial liquid miscibility to separate a component from a liquid stream. The application of the extraction method involves the use of solvent to preferentially dissolve one of two or more components from another liquid phase. This process requires a system of three or more components. We will first focus our attention to understand the behavior of binary systems.
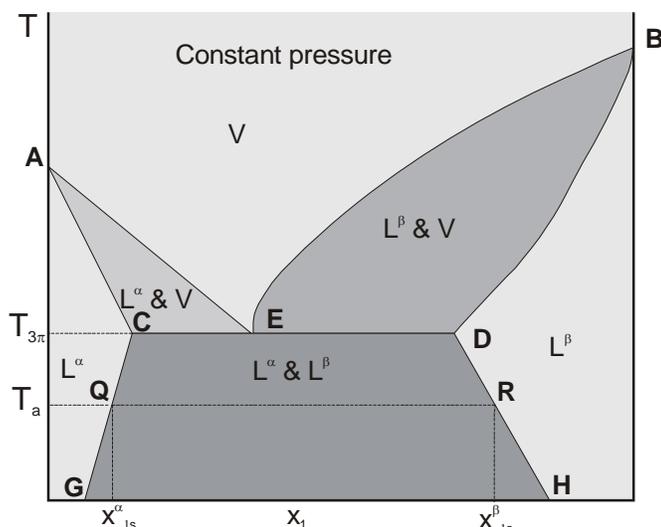
Figure 5.7-1 Constant-pressure diagram for a partially miscible binary system[11].

The phase behavior of a partially miscible binary system at constant pressure is shown in Figure 5.7-1. Point E denotes the state where two liquid phases and a vapor phase are in equilibrium. According to the phase rule for $m = 2$ components, we have

$$f = m - \pi + 2 = 2 - 3 + 2 = 1$$

There is only one degree of freedom for this system at E. Figure 5.7-1 is depicted at a specified pressure, therefore the temperature, $T_{3\pi}$, and compositions are fixed by the equilibrium constraints. The liquid phase α contains mostly species 2 with a mole fraction of species 1 equal to $x^{\alpha}_{1s,C}$ where the subscript s denotes the saturated or maximum solubility of species 1 in the solution. The second liquid phase β contains mole fraction of species 1 equal to $x^{\beta}_{1s,D}$. At temperature less than $T_{3\pi}$ a three-phase system would have a vapor pressure less than the pressure specified by Figure 5.7-1, and therefore the vapor phase cannot exit at this specified pressure. Below the temperature $T_{3\pi}$, Figure 5.7-1 is divided into three liquid regions label L^{α}, L^{β}, and L^{α} & L^{β}. In the region L^{α} or L^{β} only a single liquid phase can exists and in the region L^{α} & L^{β} two liquid phases exist. The region L^{α} represents liquid phase α that is rich in species 2 and the region L^{β} represents liquid phase β that is rich in species 1. At the temperature T_a the liquid phase L^{α} can have a concentration of species 1 in the range $0 < x^{\alpha}_1 \leq x^{\alpha}_{1s}$, and the liquid phase L^{β} can have a concentration of species 1 in the range $x^{\beta}_{1s} \leq x^{\beta}_1 < 1$. If the overall mole fraction of species 1 is in the range $x^{\alpha}_{1s} < x_1 < x^{\beta}_{1s}$, there will be two

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[11] Kyle, B.G., Chemical and Process Thermodynamics, Prentice Hall, 1999, pg. 342

separate liquid phases with mole fraction of species 1 in each phase to be x^{α}_{1s} and x^{β}_{1s} respectively.

Example 5.7-1 ---
If one mole of species 1 is mixed with one mole of species 2 at a temperature T_a such that $x^{\alpha}_{1s} = 0.18$ and $x^{\beta}_{1s} = 0.81$, determine the amount of liquid in each phase.

Solution --

The overall mole fraction of species 1 in the mixture is 0.5, which is in the range $x^{\alpha}_{1s} < x_1 < x^{\beta}_{1s}$. Therefore we will have two liquid phases.

Let n^{α} and n^{β} be the moles of liquid in each phase α and β respectively, we have

$$n^{\alpha} + n^{\beta} = 2$$

Applying the mole balance for species 1 yields

$$x^{\alpha}_{1s}n^{\alpha} + x^{\beta}_{1s}n^{\beta} = 1 \Rightarrow 0.18n^{\alpha} + 0.81n^{\beta} = 1$$

$$0.18(2 - n^{\beta}) + 0.81n^{\beta} = 1 \Rightarrow n^{\beta} = \frac{1 - (0.18)(2)}{0.81 - 0.18} = 1.0159$$

$$n^{\alpha} = 0.9841$$

Hence we have 0.9841 moles of liquid α with 0.18 mole fraction of species 1 and 1.0159 moles of liquid β with 0.81 mole fraction of species 1.

Example 5.7-2 ---
If one mole of species 1 is mixed with 9 moles of species 2 at a temperature T_a such that $x^{\alpha}_{1s} = 0.18$ and $x^{\beta}_{1s} = 0.81$, determine the amount of liquid in each phase.

Solution --

The overall mole fraction of species 1 in the mixture is 0.1 which is less than $x^{\alpha}_{1s} = 0.18$. Therefore all ten moles are in liquid phase α with $x_1 = 0.10$.

Chapter 5
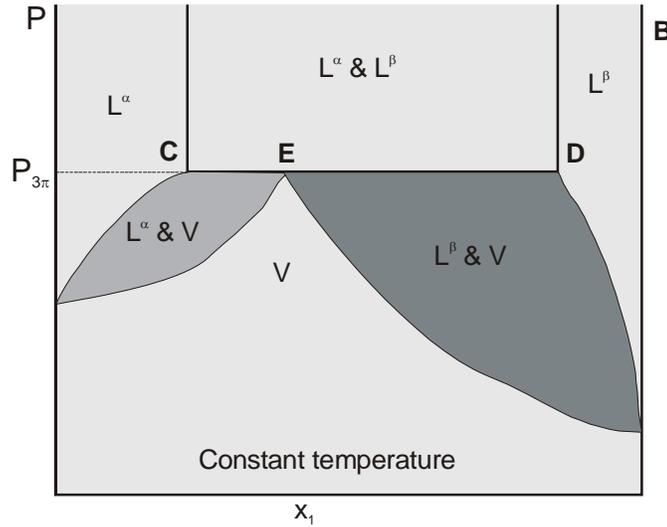
Figure 5.7-2 Constant-temperature diagram for a partially miscible binary system[12].

The phase behavior of a partially miscible binary system at constant temperature is shown in Figure 5.7-2. Point E denotes the state where two liquid phases and a vapor phase are in equilibrium. Since the temperature specified by Figure 5.7-2 satisfies the requirement for one degree of freedom, the pressure, $P_{3\pi}$, and compositions are fixed by the equilibrium constraints. At pressure higher than $P_{3\pi}$ the vapor phase cannot exist. Above the pressure $P_{3\pi}$, Figure 5.7-2 is divided into three liquid regions label L^{α}, L^{β}, and L^{α} & L^{β}. In the region L^{α} or L^{β} only a single liquid phase can exists and in the region L^{α} & L^{β} two liquid phases exist. The region L^{α} represents liquid phase α that is rich in species 2 and the region L^{β} represents liquid phase β that is rich in species 1. The boundaries for the liquid phases are almost vertical because of negligible change in mutual solubility with pressure. For a binary mixture of species 1 and 2 in LLE (liquid-liquid equilibrium) we have

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} \tag{5.7-1}$$

The fugacity of species i in each liquid phase can be expressed in term of the mole fraction, x_i, activity coefficient, γ_i, and fugacity of pure component, f_i, as

$$x_i^{\alpha} \gamma_i^{\alpha} f_i = x_i^{\beta} \gamma_i^{\beta} f_i \tag{5.7-2}$$

We will assume that the following equations describe the behavior of the activity coefficients

$$\ln \gamma_1 = A(1 - x_1)^2, \text{ and} \qquad\qquad \ln \gamma_2 = A \, x_1^{\,2} \tag{5.7-3a,b}$$

Substituting Eqs. (5.7-3a,b) into Eq. (5.72) yields

$$x^{\alpha}_1 \exp[A(1 - x^{\alpha}_1)^2] = x^{\beta}_1 \exp[A(1 - x^{\beta}_1)^2] \tag{5.7-4}$$

[12] Kyle, B.G., <u>Chemical and Process Thermodynamics</u>, Prentice Hall, 1999, pg. 342

$$(1 - x^{\alpha}_1)\exp[A(x^{\alpha}_1)^2] = (1 - x^{\beta}_1)\exp[A(x^{\beta}_1)^2] \tag{5.7-5}$$

Equations (5.7-4) and (5.7-5) can be solved for the two unknowns x^{α}_1 and x^{β}_1 (or x^{α}_{1s} and x^{β}_{1s} as denoted in Figure 5.7-1). The reason for partial liquid miscibility can be understood if we consider the Gibbs free energy change on forming a solution from n_1 mol of pure liquid 1 and n_2 mol of pure liquid 2. We have

$$\Delta G = G - n_1 g_1 - n_2 g_2 \tag{5.7-6}$$

In this equation, G is the Gibbs free energy of the solution and is given by

$$G = n_1 \mu_1 + n_2 \mu_2 \tag{5.7-7}$$

Combining Eqs. (5.7-6) and (5.7-7) gives

$$\Delta G = n_1(\mu_1 - g_1) + n_2(\mu_2 - g_2) \tag{5.7-8}$$

Dividing Eq. (5.7-8) by the total number of moles $(n_1 + n_2)$ yields only intensive properties

$$\frac{\Delta G}{n_1 + n_2} = x_1(\mu_1 - g_1) + x_2(\mu_2 - g_2) \tag{5.7-9}$$

From the definition of the fugacity, we have

$$\mu_i - \mu_i^o = RT \ln \frac{\hat{f}_i^l}{f_i^o} = RT \ln x_i \gamma_i \tag{5.7-10}$$

If the standard state is pure liquid $\mu_i^o = g_i$ and $f_i^o = f_i$, Eq. (5.7-9) becomes

$$\Delta g = x_1 RT \ln x_1 \gamma_1 + x_2 RT \ln x_2 \gamma_2$$

Rearranging the equation gives

$$\frac{\Delta g}{RT} = x_1 \ln x_1 + x_1 \ln \gamma_1 + x_2 \ln x_2 + x_2 \ln \gamma_2 \tag{5.7-11}$$

If Eqs. (5.7-3a,b: $\ln \gamma_1 = A(1 - x_1)^2$, and $\ln \gamma_2 = A x_1^2$) are used for the activity coefficient, we have

$$\frac{\Delta g}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + x_1 A(1 - x_1)^2 + x_2 A x_1^2 \tag{5.7-12}$$

Equation (5.7-12) is plotted in Figure 5.7-3 for three values of A: $A = 1$, 2, and 3 for the bottom, middle, and top curve respectively. The solid portion of the top curve between C and D represents a hypothetical single liquid phase. Since the points on this curve have a higher free energy than points on the dash line CD, the liquid will exist in two liquid phases with compositions corresponding to the points C and D to lower the free energy of the system.
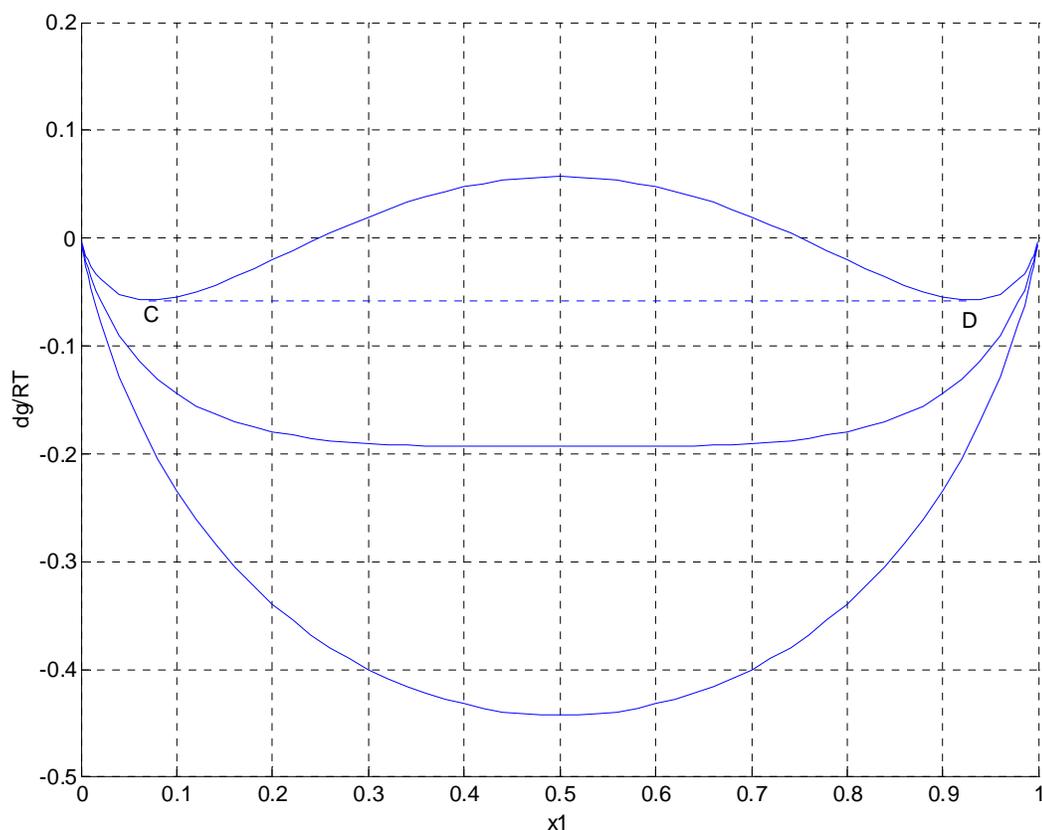
Figure 5.7-3 Constant-pressure diagram for a binary system with
$\ln \gamma_1 = A(1 - x_1)^2$ and $\ln \gamma_2 = A\,x_1^2$.

Table 5.7-1 lists the Matlab program used to plot Figure 5.7-3.

Table 5.7-1 ---
```
% Figure 5.7-3
clf
Av=1:3;
nv=length(Av);
x1=0.02:0.02:0.98;x=[.001 .003 .005 .007 .01 .015 x1 .985 .99 .993 .995 .997 .999];
x2=1-x;
hold on;
for i=1:nv
   A=Av(i);
 dg=x.*log(x)+x2.*log(x2)+A*x.*x2.^2+A*x2.*x.^2;
 plot(x,dg)
end
x=[0.0707    0.9292];x2=1-x;
dg=x.*log(x)+x2.*log(x2)+A*x.*x2.^2+A*x2.*x.^2;
plot(x,dg,':');xlabel('x1');ylabel('dg/RT');
grid on
```

The compositions corresponding to the points C and D can be determined by solving Eqs. (5.7-4) and (5.7-5) with $A = 3$:

$$x^\alpha_1\exp[3(1 - x^\alpha_1)^2] = x^\beta_1\exp[3(1 - x^\beta_1)^2] \tag{5.7-13}$$

$$(1 - x^\alpha_1)\exp[3(x^\alpha_1)^2] = (1 - x^\beta_1)\exp[3(x^\beta_1)^2] \tag{5.7-14}$$

We can find the solution to Eqs. (5.7-13) and (5.7-14) by minimizing the following objective functions

$$y = f1^2 + f2^2 \tag{5.7-15}$$

In this equation, we have

$$f1 = x^\alpha_1\exp[3(1 - x^\alpha_1)^2] - x^\beta_1\exp[3(1 - x^\beta_1)^2] = 0 \tag{5.7-16}$$

$$f2 = (1 - x^\alpha_1)\exp[3(x^\alpha_1)^2] - (1 - x^\beta_1)\exp[3(x^\beta_1)^2] = 0 \tag{5.7-17}$$

The objective function, y, will be minimized (equal to zero) when $f1 = 0$ and $f2 = 0$. Table 5.7-2 lists the function LLE representing the objective function y. The Matlab command fminsearch is then used to minimize the objective function.

Table 5.7-2 ---
```
 function y=lle(x)
f1=x(1)*exp(3*(1-x(1))^2)-x(2)*exp(3*(1-x(2))^2);
f2=(1-x(1))*exp(3*x(1)^2)-(1-x(2))*exp(3*x(2)^2);
y=f1*f1+f2*f2;

>> fminsearch('lle',[.1 .9])
ans =
   0.0707   0.9292
```

The compositions corresponding to the points C and D are

$$x^\alpha_1 = 0.0707 \text{ and } x^\beta_1 = 0.9292$$

Any mixture with an overall composition in the range $0.0707 < x_1 < 0.9292$ will exist as a LLE system with liquid phase α that is rich in species 2 and liquid phase β that is rich in species 1.

Example 5.7-3 ---

Calculate the equilibrium composition of the two liquid phases in a binary mixture of methyl diethylamine (1) and water (2) at 1 bar and 20°C[13]. The following Margules model can be used for this binary system:

$$\ln \gamma_1 = \frac{(A + 3B)}{RT}(1 - x_1)^2 - \frac{4B}{RT}(1 - x_1)^3$$

$$\ln \gamma_2 = \frac{(A - 3B)}{RT}x_1^2 + \frac{4B}{RT}x_1^3$$

In these equations, $A = 6349$ J/mol and $B = -384$ J/mol

Solution --

We have for LLE system

$$x_i^\alpha \gamma_i^\alpha f_i = x_i^\beta \gamma_i^\beta f_i \tag{E-1}$$

Therefore

$$x^\alpha_1 \exp[\frac{(A + 3B)}{RT}(1 - x^\alpha_1)^2 - \frac{4B}{RT}(1 - x^\alpha_1)^3] = x^\beta_1 \exp[\frac{(A + 3B)}{RT}(1 - x^\beta_1)^2 - \frac{4B}{RT}(1 - x^\beta_1)^3]$$

$$(1 - x^\alpha_1)\exp[\frac{(A - 3B)}{RT}(x^\alpha_1)^2 + \frac{4B}{RT}(x^\alpha_1)^3] = (1 - x^\beta_1)\exp[\frac{(A - 3B)}{RT}(x^\beta_1)^2 + \frac{4B}{RT}(x^\beta_1)^{23}]$$

We can find the solution to the above equations by minimizing the following objective functions

$$y = f1^2 + f2^2 \tag{E-2}$$

In this equation, we have

$$f1 = x^\alpha_1 \exp[\frac{(A + 3B)}{RT}(1 - x^\alpha_1)^2 - \frac{4B}{RT}(1 - x^\alpha_1)^3] - x^\beta_1 \exp[\frac{(A + 3B)}{RT}(1 - x^\beta_1)^2 - \frac{4B}{RT}(1 - x^\beta_1)^3]$$

$$f2 = (1 - x^\alpha_1)\exp[\frac{(A - 3B)}{RT}(x^\alpha_1)^2 + \frac{4B}{RT}(x^\alpha_1)^3] - (1 - x^\beta_1)\exp[\frac{(A - 3B)}{RT}(x^\beta_1)^2 + \frac{4B}{RT}(x^\beta_1)^{23}]$$

The objective function, y, will be minimized (equal to zero) when $f1 = 0$ and $f2 = 0$. Table E-1 lists the function **E5d7d3** representing the objective function y. The **Matlab** command **fminsearch** is then used to minimize the objective function.

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[13] Koretsky M.D., Engineering and Chemical Thermodynamics, Wiley, 2004, pg. 400

Table E-1 --

```
function y=e5d7d3(x)
RT=8.314*293.15;
A=6349;B=-384;
c1=(A+3*B)/RT;c2=(A-3*B)/RT;c3=4*B/RT;
f1=x(1)*exp(c1*(1-x(1))^2-c3*(1-x(1))^3)-x(2)*exp(c1*(1-x(2))^2-c3*(1-x(2))^3);
f2=(1-x(1))*exp(c2*x(1)^2+c3*x(1)^3)-(1-x(2))*exp(c2*x(2)^2+c3*x(2)^3);
y=f1*f1+f2*f2;

>> fminsearch('e5d7d3',[.1 .9])
ans =
   0.1014   0.8553
```

The equilibrium compositions are

$$x^{\alpha}_1 = 0.1014 \text{ and } x^{\beta}_1 = 0.8553$$

The solutions can also be obtained from the intersections of the curves of $x_1\gamma_1$ and $(1 - x_1)\gamma_2$ versus x_1 as shown in Figure E-1.
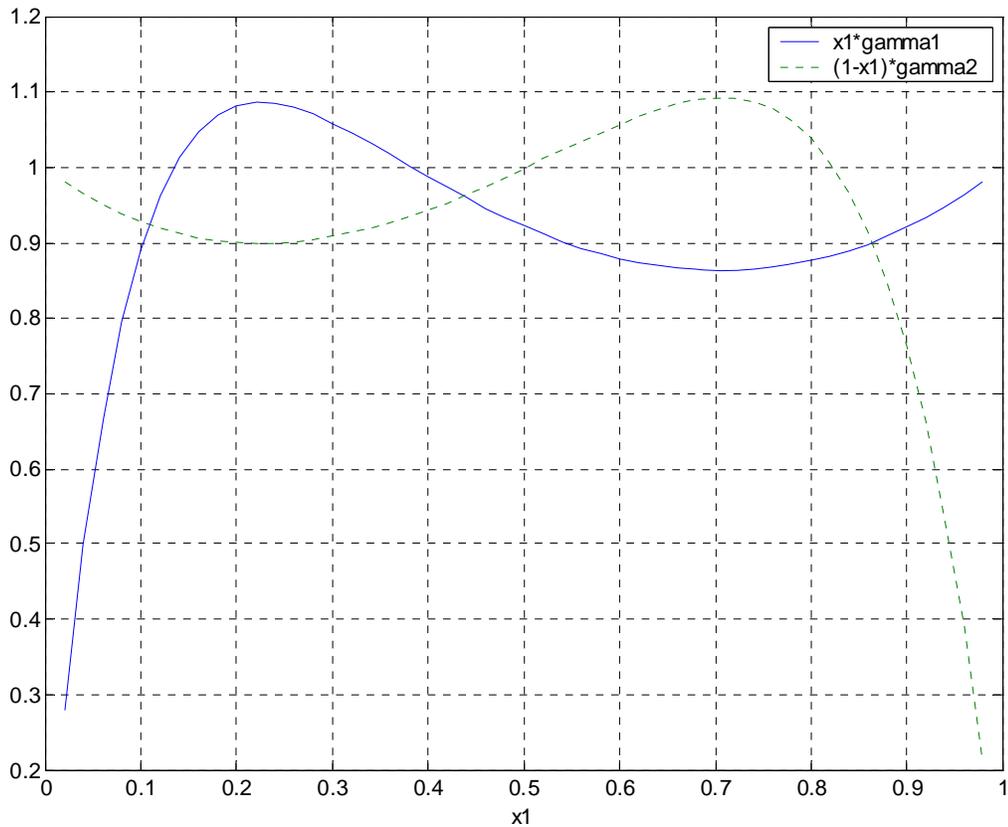
Figure E-1 Plot of $x_1\gamma_1$ and $(1 - x_1)\gamma_2$ versus x_1.

Chapter 5

Applied Phase Equilibrium

5.8 Vapor-Liquid-Liquid Equilibrium: VLLE
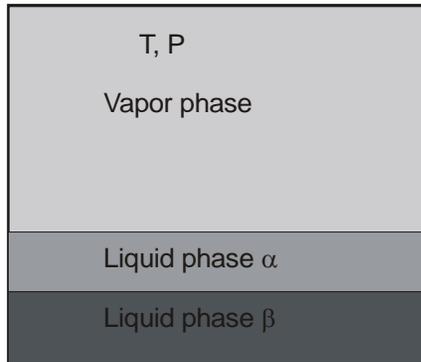
Figure 5.8-1a VLLE problem.
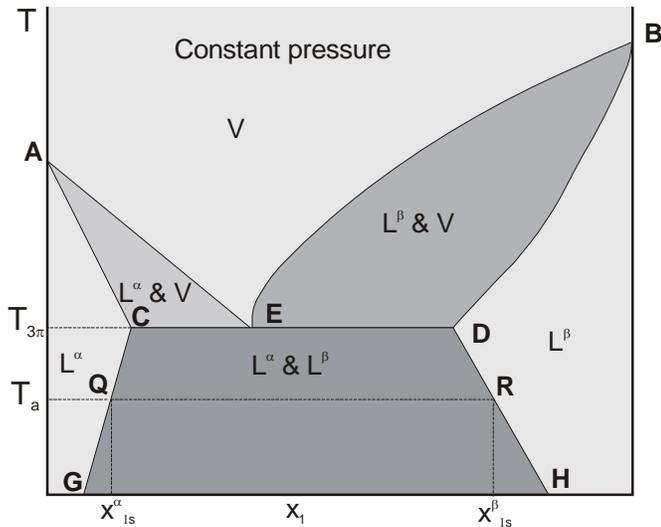
Figure 5.8-1b A partial miscible system.

We will consider a system as shown in Figure 5.8-1a when three phases are in equilibrium: a vapor phase and two liquid phases, α and β. The phase behavior of a partially miscible binary system at constant pressure is shown in Figure 5.8-1b. Point E denotes the state where two liquid phases and a vapor phase are in equilibrium. According to the phase rule for $m = 2$ components, we have

$$f = m - \pi + 2 = 2 - 3 + 2 = 1$$

There is only one degree of freedom for this system at E. Figure 5.8-1b is depicted at a specified pressure, therefore the temperature, $T_{3\pi}$, and compositions are fixed by the equilibrium constraints. Below the temperature $T_{3\pi}$, Figure 5.8-1b is divided into three liquid regions label L^{α}, L^{β}, and L^{α} & L^{β}. In the region L^{α} or L^{β} only a single liquid phase can exists and in the region L^{α} & L^{β} two liquid phases exist. The region L^{α} represents liquid phase α that is rich in species 2 and the region L^{β} represents liquid phase β that is rich in species 1. At the temperature T_a the liquid phase L^{α} can have a concentration of species 1 in the range $0 < x^{\alpha}_1 \leq x^{\alpha}_{1s}$, and the liquid phase L^{β} can have a concentration of species 1 in the range $x^{\beta}_{1s} \leq x^{\beta}_1 < 1$. If the overall mole fraction of species 1 is in the range $x^{\alpha}_{1s} < x_1 < x^{\beta}_{1s}$, there will be two separate liquid phases with mole fraction of species 1 in each phase to be x^{α}_{1s} and x^{β}_{1s} respectively.

At the temperature $T_{3\pi}$ only liquid phase α is present at low x_1 and only liquid phase β is present at high x_1. However, at mole fraction x_1 in between these two single-phase regions, both α and β liquid phases can coexist along with the vapor. The ordinates of point C, D, and

E provide the mole fractions of species 1 in liquid phase α, in liquid phase β, and in vapor phase, respectively.

For a binary mixture of species 1 and 2 in VLLE (Vapor-liquid-liquid equilibrium) we have

$$\hat{f}_i^{\,v} = \hat{f}_i^{\,\alpha} = \hat{f}_i^{\,\beta} \tag{5.8-1}$$

The fugacity of species *i* in each liquid phase can be expressed in term of the mole fraction, x_i, activity coefficient, γ_i, and fugacity of pure component, f_i, as

$$\hat{f}_i^{\,v} = x_i^{\alpha}\gamma_i^{\alpha} f_i = x_i^{\beta}\gamma_i^{\beta} f_i \tag{5.8-2}$$

For system at low pressure $\hat{f}_i^{\,v} = y_i P$ and $f_i = P_i^{\text{sat}}$. Therefore

$$y_1 P = x_1^{\alpha}\gamma_1^{\alpha} P_1^{\text{sat}} = x_1^{\beta}\gamma_1^{\beta} P_1^{\text{sat}} \tag{5.8-3}$$

$$(1 - y_1)P = (1 - x_1^{\alpha})\gamma_2^{\alpha} P_2^{\text{sat}} = (1 - x_1^{\beta})\gamma_2^{\beta} P_2^{\text{sat}} \tag{5.8-4}$$

We will assume that the following equations describe the behavior of the activity coefficients

$$\ln \gamma_1 = A(1 - x_1)^2, \text{ and} \qquad\qquad \ln \gamma_2 = A\,x_1^2 \tag{5.8-5a,b}$$

Substituting the expression for activity coefficients into Eqs. (5.8-3) and (5.8-4) yields

$$y_1 P = x^{\alpha}{}_1 \exp[A(1 - x^{\alpha}{}_1)^2]P_1^{\text{sat}} = x^{\beta}{}_1 \exp[A(1 - x^{\beta}{}_1)^2]P_1^{\text{sat}} \tag{5.8-6}$$

$$(1 - y_1)P = (1 - x^{\alpha}{}_1)\exp[A(x^{\alpha}{}_1)^2]P_2^{\text{sat}} = (1 - x^{\beta}{}_1)\exp[A(x^{\beta}{}_1)^2]P_2^{\text{sat}} \tag{5.8-7}$$

At a given temperature, the four unknowns y_1, $x^{\alpha}{}_1$, $x^{\beta}{}_1$, and *P* can be determined from the solutions of the above four nonlinear equations.

Example 5.8-1[14] ---
A binary mixture exhibits vapor-liquid-liquid equilibrium at 300°K. The following Margules model can be used for this binary system:

$$\ln \gamma_1 = \frac{b}{RT}(1 - x_1)^2 \text{ and } \ln \gamma_2 = \frac{b}{RT}\,x_1^2, \text{ where } b = 6235 \text{ J/mol.}$$

The saturation pressures are given by $P_1^{\text{sat}} = 100$ kPa and $P_2^{\text{sat}} = 50$ kPa. Determine the composition of the three phases and the total pressure.

Solution ---
For the two liquid phases in equilibrium we have

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[14] Koretsky M.D., Engineering and Chemical Thermodynamics, Wiley, 2004, pg. 406

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} \tag{E-1}$$

The fugacity of species i in each liquid phase can be expressed in term of the mole fraction, x_i, activity coefficient, γ_i, and fugacity of pure component, f_i, as

$$x_i^{\alpha} \gamma_i^{\alpha} f_i = x_i^{\beta} \gamma_i^{\beta} f_i \tag{E-2}$$

We are given following equations for the behavior of the activity coefficients

$$\ln \gamma_1 = A(1 - x_1)^2, \text{ and} \qquad\qquad \ln \gamma_2 = A\, x_1^2 \tag{E-3}$$

Substituting Eqs. (E-3) into Eq. (E-2) yields

$$x^{\alpha}{}_1 \exp[A(1 - x^{\alpha}{}_1)^2] = x^{\beta}{}_1 \exp[A(1 - x^{\beta}{}_1)^2] \tag{E-4}$$

$$(1 - x^{\alpha}{}_1)\exp[A(x^{\alpha}{}_1)^2] = (1 - x^{\beta}{}_1)\exp[A(x^{\beta}{}_1)^2] \tag{E-5}$$

We can find the solution to Eqs. (E-4) and (E-5) by minimizing the following objective functions

$$y = f1^2 + f2^2 \tag{E-6}$$

In this equation, we have

$$f1 = x^{\alpha}{}_1 \exp[A(1 - x^{\alpha}{}_1)^2] - x^{\beta}{}_1 \exp[A(1 - x^{\beta}{}_1)^2] = 0 \tag{E-7}$$

$$f2 = (1 - x^{\alpha}{}_1)\exp[A(x^{\alpha}{}_1)^2] - (1 - x^{\beta}{}_1)\exp[A(x^{\beta}{}_1)^2] = 0 \tag{E-8}$$

The objective function, y, will be minimized (equal to zero) when $f1 = 0$ and $f2 = 0$. Table E-1 lists the function e5d8d1 representing the objective function y. The Matlab command fminsearch is then used to minimize the objective function.

Table E-1 --
```
function y=e5d8d1(x)
RT=8.314*300;
A=6235/RT;
f1=x(1)*exp(A*(1-x(1))^2)-x(2)*exp(A*(1-x(2))^2);
f2=(1-x(1))*exp(A*x(1)^2)-(1-x(2))*exp(A*x(2)^2);
y=f1*f1+f2*f2;

>> fminsearch('e5d8d1',[.1 .9])
ans =
   0.1448   0.8552
```

The equilibrium compositions are

$$x^{\alpha}{}_1 = \mathbf{0.1448} \text{ and } x^{\beta}{}_1 = \mathbf{0.8552}$$

We have $A = \dfrac{6235}{RT} = \dfrac{6235}{(8.314)(300)} = 2.4998$. The partial pressures are calculated as

$$P_1 = x^{\alpha}{}_1\exp[A(1 - x^{\alpha}{}_1)^2]P_1{}^{sat} = (0.1448)\exp[(2.4998)(0.8552)^2](100) = 90.11 \text{ kPa}$$

$$P_2 = (1 - x^{\alpha}{}_1)\exp[A(x^{\alpha}{}_1)^2]P_2{}^{sat} = (0.8552)\exp[(2.4998)(0.1448)^2](50) = 45.06 \text{ kPa}$$

$$P = P_1 + P_2 = 90.11 + 45.06 = \textbf{135.17 kPa}$$

The mole fraction of species 1 in the vapor phase is then

$$y_1 = P_1/P = 90.11/135.17 = \textbf{0.6667}$$

Example 5.8-2[15] --
At 70°C the system 1-2 exhibits partial liquid miscibility with $x^{\alpha}{}_1 = 0.3$ and $x^{\beta}{}_1 = 0.7$. The vapor pressures are given by $P_1{}^{sat} = 600$ mmHg and $P_2{}^{sat} = 500$ mmHg. Calculate:
1) The vapor mole fraction of species 1 and the total pressure when two liquid phases and a vapor phase are in equilibrium.
2) The vapor mole fraction of species 1 and the total pressure when a vapor phase is in equilibrium with a liquid phase containing a mole fraction of species 1 of 0.1.
The following Margules model can be used for this binary system:

$$\ln \gamma_1 = A(1 - x_1)^2 \text{ and } \ln \gamma_2 = Ax_1{}^2$$

Solution ---
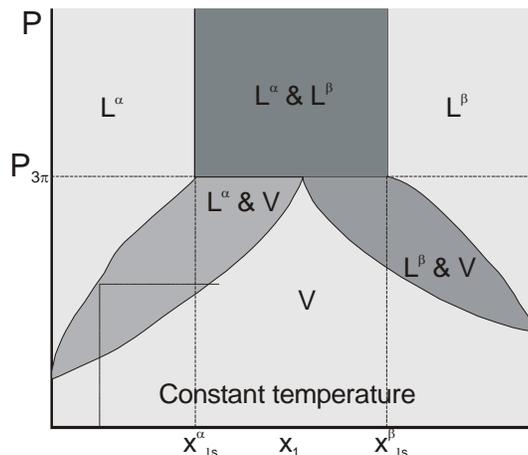
Figure E-1 Constant-temperature diagram for a partially miscible binary system

1) <u>The vapor mole fraction of species 1 and the total pressure when two liquid phases and a vapor phase are in equilibrium.</u>

For the two liquid phases in equilibrium we have

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[15] Kyle, B.G., <u>Chemical and Process Thermodynamics</u>, Prentice Hall, 1999, pg. 369

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} \tag{E-1}$$

The fugacity of species i in each liquid phase can be expressed in term of the mole fraction, x_i, activity coefficient, γ_i, and fugacity of pure component, f_i, as

$$x_i^{\alpha}\gamma_i^{\alpha} f_i = x_i^{\beta}\gamma_i^{\beta} f_i \tag{E-2}$$

Applying Eq. (E-2) to species 1 yields

$$x_1^{\alpha}\gamma_1^{\alpha} = x_1^{\beta}\gamma_1^{\beta} \Rightarrow \ln x_1^{\alpha} + \ln \gamma_1^{\alpha} = \ln x_1^{\beta} + \ln \gamma_1^{\beta} \tag{E-3}$$

Since $x_1^{\alpha} = 0.3$ and $x_1^{\beta} = 0.7$ we have

$$\ln 0.3 + A(1 - 0.3)^2 = \ln 0.7 + A(1 - 0.7)^2$$

$$A(0.7^2 - 0.3^2) = \ln(7/3) \Rightarrow A = 2.1182$$

The values of the activity coefficients are then

$$\gamma_1^{\alpha} = \exp[A(1 - x_1)^2] = \exp[(2.1182)(0.7)^2] = 2.8234$$

$$\gamma_2^{\alpha} = \exp[Ax_1^2] = \exp[(2.1182)(0.3)^2] = 1.2100$$

The partial pressure of each species is calculated as

$$P_1 = x_1^{\alpha}\gamma_1^{\alpha}P_1^{\text{sat}} = (0.3)(2.8234)(600) = 508.21 \text{ mmHg}$$

$$P_2 = x_2^{\alpha}\gamma_2^{\alpha}P_2^{\text{sat}} = (0.7)(1.2100)(500) = 423.51 \text{ mmHg}$$

The total pressure is

$$P = P_1 + P_2 = \textbf{931.72 mmHg}$$

The vapor mole faction is then

$$y_1 = P_1/P = \textbf{0.545}$$

2) The vapor mole fraction of species 1 and the total pressure when a vapor phase is in equilibrium with a liquid phase containing a mole fraction of species 1 of 0.1.

Since $x_1 = 0.1 \leq x_1^{\alpha} = 0.3$, we have liquid phase α. The values of the activity coefficients are then

$$\gamma_1^{\alpha} = \exp[A(1 - x_1)^2] = \exp[(2.1182)(0.9)^2] = 5.5610$$

$$\gamma_2^{\alpha} = \exp[Ax_1^2] = \exp[(2.1182)(0.1)^2] = 1.0214$$

The partial pressure of each species is calculated as

$$P_1 = x_1^\alpha \gamma_1^\alpha P_1^{sat} = (0.1)(5.5610)(600) = 333.66 \text{ mmHg}$$

$$P_2 = x_2^\alpha \gamma_2^\alpha P_2^{sat} = (0.9)(1.0214)(500) = 459.63 \text{ mmHg}$$

The total pressure is

$$P = P_1 + P_2 = \textbf{793.29 mmHg}$$

The vapor mole faction is then

$$y_1 = P_1/P = \textbf{0.4206}$$

Example 5.8-3[16] ---
At 25°C a binary system containing components 1 and 2 is in a state of vapor-liquid-liquid equilibrium. The compositions of the saturated liquid phases are: $x^\alpha_{1s} = 0.02$ and $x^\beta_{1s} = 0.98$. The vapor pressures are given by $P_1^{sat} = 0.1$ atm and $P_2^{sat} = 1.0$ atm. Calculate:
1) The vapor mole fraction of species 1 and the total pressure when two liquid phases and a vapor phase are in equilibrium.
2) The vapor mole fraction of species 1 and the total pressure when a vapor phase is in equilibrium with a liquid phase containing a mole fraction x_1 of 0.01.
3) At 25°C a vapor containing 20% species 1 and 80% species 2 initially at 0.1 atm is compressed isothermally. Find the dew point pressure and liquid composition.

Solution ---
1) <u>The vapor mole fraction of species 1 and the total pressure when two liquid phases and a vapor phase are in equilibrium.</u>

Since the system is at low pressure, we have

$$y_1 P = x_1^\alpha \gamma_1^\alpha P_1^{sat} = x_1^\beta \gamma_1^\beta P_1^{sat} \tag{E-1}$$

$$(1 - y_1)P = (1 - x_1^\alpha)\gamma_2^\alpha P_2^{sat} = (1 - x_1^\beta)\gamma_2^\beta P_2^{sat} \tag{E-2}$$

Since we do not have the data for activity coefficient and $x_1^\beta = x^\beta_{1s} = 0.98 \approx 1$, we assume $\gamma_1^\beta = 1$ (Raoult's law). Therefore

$$P_1 = y_1 P = x_1^\beta \gamma_1^\beta P_1^{sat} = (0.98)(1)(0.1) = 0.098 \text{ atm}$$

Similarly

$$P_2 = (1 - y_1)P = (1 - x_1^\alpha)\gamma_2^\alpha P_2^{sat} = (0.98)(1)(1) = 0.98 \text{ atm}$$

The total pressure is

$$P = P_1 + P_2 = \textbf{1.078 atm}$$

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[16] Kyle, B.G., <u>Chemical and Process Thermodynamics</u>, Prentice Hall, 1999, pg. 370

The vapor mole faction is then

$$y_1 = P_1/P = \textbf{0.0909}$$

2) The vapor mole fraction of species 1 and the total pressure when a vapor phase is in equilibrium with a liquid phase containing a mole fraction x_1 of 0.01.
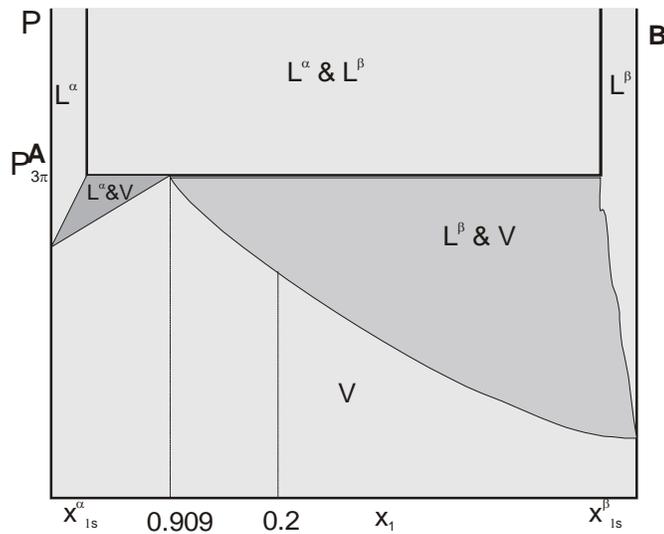
Figure E-1 Constant-temperature diagram for a partially miscible binary system.

From part (1) we have $P_1 = 0.098$ atm. Since $x_1^{\alpha} = 0.02$ we assume Henry's law will apply for species 1 in liquid phase α

$$P_1 = 0.098 \text{ atm} = x_1^{\alpha} H_1^{\alpha} \Rightarrow H_1^{\alpha} = \frac{0.098}{0.02} = 4.9 \text{ atm}$$

For $x_1 = 0.01 \Rightarrow P_1 = x_1 H_1^{\alpha} = (0.01)(4.9) = 0.049$ atm

Since $x_2^{\alpha} = 0.99$ we assume Raoult's law will apply for species 2 in liquid phase α

$$P_2 = x_2^{\alpha} P_2^{\text{sat}} = (0.99)(1) = 0.99 \text{ atm}$$

The total pressure is

$$P = P_1 + P_2 = 0.049 + 0.99 = \textbf{1.039 atm}$$

The vapor mole faction is then

$$y_1 = P_1/P = 0.049/1.039 = \textbf{0.0472}$$

3) At 25°C a vapor containing 20% species 1 and 80% species 2 initially at 0.1 atm is compressed isothermally. Find the dew point pressure and liquid composition.

From the phase diagram (Figure E-1), we have liquid phase β at the dew point for the vapor mixture with 20% species 1.

The mole fraction of species 1 in liquid phase β will be close to 1 and the mole fraction of species 2 in liquid phase β will be close to zero. Therefore we can apply Raoult's law to species 1 and Henry's law to species 2.

$$P_1 = y_1 P = x_1^\beta P_1^{sat} \tag{E-3}$$

$$P_2 = y_2 P = x_2^\beta H_2^\beta \tag{E-4}$$

The Henry's law constant can be determined from the data given in part (1)

$$P_2 = 0.98 \text{ atm} = x^\beta{}_{2s}H_2^\beta = 0.02 H_2^\beta \Rightarrow H_2^\beta = \frac{0.98}{0.02} = 49 \text{ atm}$$

Since the mole fraction in the liquid phase must add up to 1, we have

$$x_1^\beta + x_2^\beta = 1$$

Substituting the mole fractions from Eqs. (E-3) and (E-4) into the above expression yields

$$\frac{y_1 P}{P_1^{sat}} + \frac{y_2 P}{H_2^{sat}} = 1 \Rightarrow P = \frac{1}{\dfrac{y_1}{P_1^{sat}} + \dfrac{y_2}{H_2^{sat}}}$$

The dew point pressure is then

$$P = \frac{1}{\dfrac{y_1}{P_1^{sat}} + \dfrac{y_2}{P_2^{sat}}} = \frac{1}{\dfrac{0.2}{0.1} + \dfrac{0.8}{49}} = \mathbf{0.496 \text{ atm}}$$

The mole fraction of species 1 in liquid phase β is given by

$$x_1^\beta = \frac{y_1 P}{P_1^{sat}} = \frac{(0.2)(0.496)}{0.1} = \mathbf{0.9919}$$

Chapter 5

A hydrocarbon has a vapor pressure of 2 atm at 20°C. The solubility of water in this liquid hydrocarbon is $x_{ws} = 0.00021$. Estimate the necessary equilibrium data to design a distillation column to remove water from the hydrocarbon.

Solution --
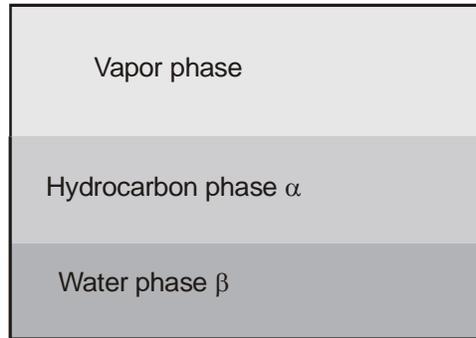
Figure E-1 Vapor-liquid-liquid equilibrium system.

Let α denotes the hydrocarbon phase and β denotes the water phase. We have the following equilibrium relations

$$P_h = x_h^{\alpha}\gamma_h^{\alpha}P_h^{sat} = x_h^{\beta}\gamma_h^{\beta}P_h^{sat} \tag{E-1}$$

$$P_w = (1 - x_h^{\alpha})\gamma_w^{\alpha}P_w^{sat} = (1 - x_h^{\beta})\gamma_w^{\beta}P_w^{sat} \tag{E-2}$$

The solubility of liquid hydrocarbon in liquid water is also negligible so we have

$$\gamma_h^{\alpha} \approx 1, \ \gamma_w^{\beta} \approx 1, \text{ and } x_w^{\beta} \approx 1.$$

Therefore

$$P_h = x_h^{\alpha}\gamma_h^{\alpha}P_h^{sat} = (1)(1)P_h^{sat} = P_h^{sat}$$

$$P_w = x_w^{\beta}\gamma_w^{\beta}P_w^{sat} = (1)(1)P_w^{sat} = P_w^{sat}$$

The mole fraction of water in the vapor phase is

$$y_w = \frac{P_w}{P_h + P_w} = \frac{17.5}{2 \times 760 + 17.5} = 0.0114$$

---

[17] Kyle, B.G., Chemical and Process Thermodynamics, Prentice Hall, 1999, pg. 370

For the estimation of equilibrium data for the hydrocarbon liquid containing less than the saturation water content, we assume that Henry's law applies to the water in this α phase:

$$P_w = x_w{}^\alpha \gamma_w{}^\alpha P_w{}^{sat} = x_w{}^\alpha H_w{}^\alpha$$

The Henry's law constant, $H_w{}^\alpha$, can be evaluated from the saturation condition

$$H_w{}^\alpha = \frac{P_w}{x_w{}^\alpha} = \frac{17.5}{0.00021} = 8.33 \times 10^4 \text{ mmHg}$$

The partial pressure of water vapor is then

$$P_w = 8.33 \times 10^4 x_w{}^\alpha$$

The partial pressure of hydrocarbon is essentially the vapor pressure

$$P_h = x_h{}^\alpha \gamma_h{}^\alpha P_h{}^{sat} = (1)(1)P_h{}^{sat} = P_h{}^{sat} = (2)(760) = 1520 \text{ mmHg}$$

The vapor mole fraction of water is

$$y_w = \frac{P_w}{P_h + P_w} = \frac{8.33 \times 10^4 x_w{}^\alpha}{8.33 \times 10^4 x_w{}^\alpha + 1520}$$

The relative volatility of water to hydrocarbon, α_{wh}, is a measure of the ease of separation by distillation. The relative volatility is defined as

$$\alpha_{wh} = \frac{y_w / x_w}{y_h / x_h} \approx y_w/x_w$$

Therefore

$$\alpha_{wh} = y_w/x_w = \frac{8.33 \times 10^4}{8.33 \times 10^4 x_w{}^\alpha + 1520}$$

For $x_w{}^\alpha < 10^{-4}$, $\alpha_{wh} = \dfrac{8.33 \times 10^4}{8.33 \times 10^4 x_w{}^\alpha + 1520} \approx \dfrac{8.33 \times 10^4}{1520} = \mathbf{55}$

The higher the value of α_{wh} compares to unity, the better the separation. The value of 55 for relativity volatility for this system indicates that separation by distillation would be very easy to accomplish.

5.9 The Thermodynamics of Osmosis

We will consider the equilibrium state of liquid mixtures in two regions separated by a membrane that is permeable to some of the species present and impermeable to others. This situation is illustrated in Figure 5.9-1 where a semi-permeable membrane separates regions **A** that contains a nondiffusing solute and region **B** that contains only water.
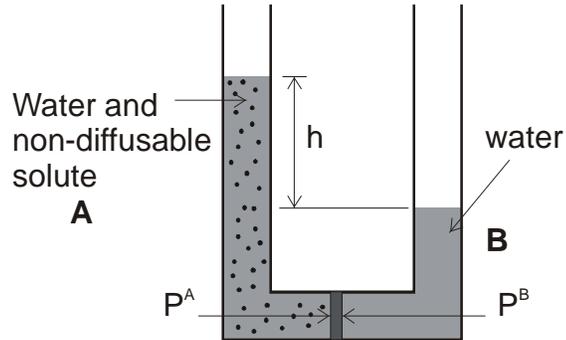
Figure 5.9-1 Osmotic pressure $\pi = P^A - P^B \approx \rho^A gh$

Water will diffuse from region **B** into region **A** until the chemical potential or fugacity of water on each side of the membrane is the same. This phenomenon is called osmosis and the pressure difference between regions **A** and **B** at equilibrium is the osmotic pressure of region **A**. The chemical potential of species i, μ_i, is defined by the following relations

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{P,S,n_j} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_j}$$

In these expressions, the subscript j denotes the moles of every species except i is a constant. The definition can be obtained from the following diagram

G   P   H   **G**reat **P**hysicists **H**ave **S**tudy
                     Under **V**ery **A**ble **T**eachers
T ——→ S

A   V   U
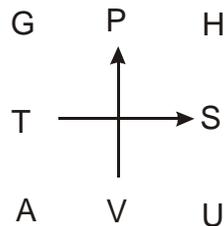
We now want an expression that gives us the solution osmotic pressure as a function of the solute concentration. At equilibrium

$$\bar{f}_W^A (T, P^A, x_s) = f_W^B (T, P^B) \tag{5.9-1}$$

where $f_W^B (T, P^B)$ is the fugacity of water as a pure component and $\bar{f}_W^A (T, P^A, x_s)$ is the fugacity of water as it exists in solution with solute at mole fraction x_s. A similar equation is not written for the solute since it cannot diffuse through the membrane. Equation (5.9-1) can be expressed in terms of the pure water fugacity using the activity coefficient γ_W^A

$$\gamma_W^A \, x_W^A \, f_W^A (T, P^A) = f_W^B (T, P^B) \tag{5.9-2}$$

The fugacity is a thermodynamic function defined by

$$f(T, P) = P\exp\left[\frac{g(T,P) - g^{IG}(T,P)}{RT} \right] = P\exp\left[\frac{1}{RT} \int_0^P \left(v - \frac{RT}{P} \right) dP \right]$$

In this expression $g(T, P)$ is the molar Gibbs free energy and $g^{IG}(T, P)$ is the molar Gibbs free energy as the fluid approached ideal gas state. The water fugacities at states (T, P^A) and (T, P^B) are then

$$\ln \frac{f(T,P^A)}{P^A} = \frac{1}{RT} \int_0^{P^A} \left(v - \frac{RT}{P} \right) dP$$

$$\ln \frac{f(T,P^B)}{P^B} = \frac{1}{RT} \int_0^{P^B} \left(v - \frac{RT}{P} \right) dP$$

Since $P^A > P^B$

$$\ln \frac{f(T,P^A)}{P^A} = \frac{1}{RT} \int_0^{P^B} \left(v - \frac{RT}{P} \right) dP + \frac{1}{RT} \int_{P^B}^{P^A} \left(v - \frac{RT}{P} \right) dP$$

$$\ln \frac{f(T,P^A)}{P^A} = \ln \frac{f(T,P^B)}{P^B} + \frac{1}{RT} \int_{P^B}^{P^A} v\,dP - \int_{P^B}^{P^A} \frac{dP}{P}$$

v is the molar volume of water, an incompressible liquid

$$\ln \frac{f(T,P^A)}{P^A} = \ln \frac{f(T,P^B)}{P^B} + \frac{v(P^A - P^B)}{RT} - \ln \frac{P^A}{P^B}$$

$$\ln \frac{f(T,P^A)}{P^A} = \ln \frac{f(T,P^B)}{P^A} + \frac{v(P^A - P^B)}{RT}$$

$$\frac{f(T,P^A)}{P^A} = \frac{f(T,P^B)}{P^A} \exp\left[\frac{v(P^A - P^B)}{RT}\right]$$

From the equality of fugacity, equation (5.9-2) $\gamma_W^A x_W^A f_W^A (T, P^A) = f_W^B (T, P^B)$, we have

$$\gamma_W^A x_W^A f_W^A (T, P^B) \exp\left[\frac{v_W^L(P^A - P^B)}{RT}\right] = f_W^B (T, P^B)$$

Since $f_W^A (T, P^B) = f_W^B (T, P^B) =$ pure water fugacity

$$\gamma_W^A x_W^A = \exp\left[\frac{-v_W^L(P^A - P^B)}{RT}\right]$$

The osmotic pressure is then

$$\pi = P^A - P^B = -\frac{RT}{v_W^L} \ln\left(\gamma_W^A x_W^A\right) \tag{5.9-3}$$

For an ideal aqueous solution at 298°K with $x_W = 0.98$, $\gamma_W = 1$, the osmotic pressure is

$$\pi = P^A - P^B = -\frac{RT}{v_W^L} \ln(x_W)$$

$$\pi = -\frac{\left(8.314 \times 10^{-5} \frac{bar \cdot m^3}{mol \cdot^o K}\right)(298^o K)}{18 \times 10^{-6} m^3 / mol} \ln(0.98) = 27.8 \text{ bar}$$

For ideal solution and small solute concentration, $x_W^A \approx 1$, and $\ln(x_W^A) \approx - (1 - x_W^A)$

Hence
$$\pi = -\frac{RT}{v_W^L} \ln(x_W^A) \approx \frac{RT}{v_W^L} (1 - x_W^A) = \frac{RT}{v_W^L} x_S^A \tag{5.9-4}$$

$$x_S^A = \frac{Moles \quad solute}{Moles \quad solute + Moles \quad solvent} \approx \frac{Moles \quad solute}{Moles \quad solvent}$$

$$\frac{x_S^A}{v_W^L} = \frac{Moles \quad solute}{(Moles \quad solvent)\left(\dfrac{Volume \quad solvent}{Moles \quad solvent}\right)} = \frac{Moles \quad solute}{Volume \quad solvent} = C_S$$

The ideal dilute solution osmotic pressure, described by equation (5.9-4), is known as *van't Hoff's law*. This equation can also be written in terms of the mass concentration ρ_S

$$\pi = \frac{RT}{v_W^L} x_S^A = RT\,C_S = RT\frac{\rho_S}{Mw_S} \tag{5.9-5}$$

where $\rho_S = \dfrac{Mass \quad solute}{Volume \quad solvent}$ and Mw_S = molecular weight of solute. Equation (5.9-5) can be used to determine solvent activity coefficient in a solvent-solute system provided a semi-permeable membrane can be found.

$$\pi = P^A - P^B = -\frac{RT}{v_W^L} \ln\left(\gamma_W^A x_W^A\right)$$

Osmotic pressure measurements are more commonly used to determine the molecular weights of proteins and other macromolecules using an osmometer shown in Figure 5.9-2. At equilibrium the osmotic pressure π is equal to ρgh, where ρ is the solution density and h is the difference in liquid heights. Equation (5.9-5) is then solved for the molecular weight of the solute.

$$Mw_S = RT\frac{\rho_S}{\pi}$$
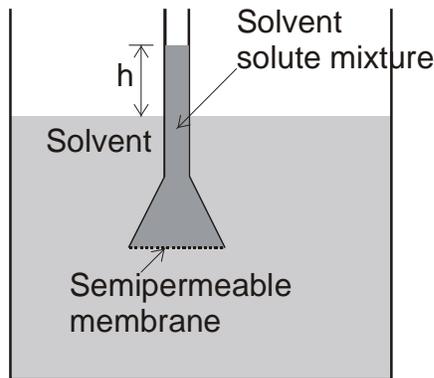
Figure 5.9-2 A graphical depiction of a simple osmometer.

Example 5.9-1.[18] ---
The polymer polyvinyl chloride (*PVC*) is soluble in solvent cyclohexanone. At 25°C it is found that if a 2 g of a specific batch of *PVC* per liter of solvent is placed in an osmometer, the height h to which the pure cyclohexanone rises is 0.85 cm. Use this information to estimate the molecular weight of the *PVC* polymer. Density of cyclohexanone is 0.98 g/cm³.

Solution --

$$\pi = \rho gh = 980\frac{kg}{m^3} \times 9.81\frac{m}{s^2} \times 8.5\times10^{-3}\,m = 81.72\,Pa$$

$$Mw_S = RT\frac{\rho_S}{\pi}$$

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[18] Sandler, Chemical and Engineering Thermodynamics, Wiley, 1999, p.605

$$Mw_S = 8.314 \frac{Pa \cdot m^3}{mol \cdot K} \times 298.15 \ K \times 2,000 \ \frac{g}{m^3} / 81.72 \ Pa = 60,670 \ \text{g/mol}$$

If the dilute solution contains N ideal solutes then

$$\pi = RT \sum_{i=1}^{N} C_{S,i}$$

The term *osmole* is defined as one mole of a nondiffusing and nondissociating substance. One mole of a dissociating substance such as NaCl is equivalent to two osmoles. The number of osmoles per liter of solution is called *osmolarity*. For physiological solutions, it is convenient to work in terms of milliosmoles (mOsm) or milliosmolar (mOsM). The number of particles formed by a given solute determines osmotic pressure. Each nondiffusing particle in the solution contributes the same amount to the osmotic pressure regardless of the size of the particle.

The osmotic pressure difference between the interstitial and plasma fluids is due to the plasma proteins since the proteins do not readily pass through the capillary wall. The osmotic pressure created by the proteins is given the special name of *colloid osmotic pressure* or *oncotic pressure*. For human plasma, the colloid osmotic pressure is about 28 mmHg; 19 mmHg caused by the plasma proteins and 9 mmHg caused by the cations within the plasma that are retained through electrostatic interaction with the negative surface charges of the proteins.
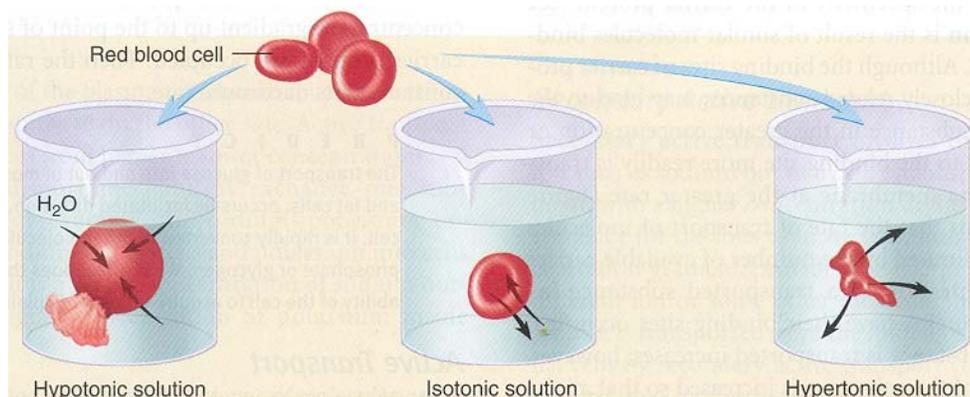
Figure 5.9-3 Osmosis of water through red blood cell[19].

If a cell such as red blood cell is placed in a *hypotonic* solution that has a lower concentration of solutes or osmolarity, then the establishment of osmotic equilibrium requires the osmosis of water into the cell resulting in swelling of the cell. If the cell is placed in a *hypertonic* solution with a higher concentration of solutes or osmolarity, then osmotic equilibrium requires osmosis of water out of the cell resulting in shrinkage of the cell. An *isotonic* solution has the same osmolarity of the cell and will not cause any osmosis of water as shown in Figure 5.9-3. A 0.9 weight percent solution of sodium chloride or a 5 weight percent solution of glucose is just about isotonic with respect to a cell.

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[19] Seeley R.R, Stephens T.D., Tate P., <u>Anatomy & Physiology</u>, McGraw Hill, 2003

Example 5.9-2[20]. ---

Experiments show that at 0°C a 0.2 molarity sucrose solution has an osmotic pressure (relative to pure water) of 4.76 atm whereas a 0.2 molarity NaCl solution has an osmotic pressure of 8.75 atm. Estimate the fraction of the NaCl molecules that are dissociated at this temperature and concentration.

Solution ---
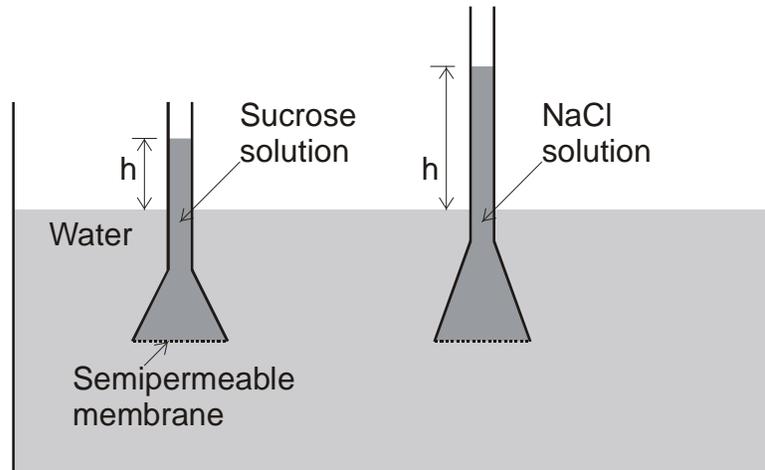
Assume that all the sucrose dissolves and let α be the dissociated fraction of NaCl. When a salt dissociates each ion contributes to the osmotic pressure

$$NaCl \Leftrightarrow Na^{+} + Cl^{-}$$
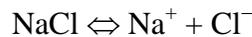
If α is the fraction of NaCl that is dissociated then $1 - \alpha$ is the fraction that is not dissociated. Since each dissociated NaCl molecule contributes 2 ions and each undissociated molecules contributes 1 molecules, the osmolarity of the NaCl solution is

$$\sum_{i=1}^{N} C_{NaCl,i} = [2\alpha + (1 - \alpha)]C_{NaCl}$$

The osmolarity of the sucrose solution is

$$\sum_{i=1}^{N} C_{Sucrose,i} = C_{Sucrose}$$

Therefore,

$$\frac{\pi_{NaCl}}{\pi_{Sucrose}} = \frac{RT(\alpha + 1)C_{NaCl}}{RTC_{Sucrose}} = \alpha + 1 = \frac{8.75}{4.76} = 1.838$$

Hence $\alpha = \mathbf{0.838}$

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[20] Weiss T.F., <u>Cellular Biophysics Transport</u>, MIT Press, 1996, pg. 258

Chapter 5

5.10 Distribution of a solute between two liquid phases

5.10a Solubility of a Solid in a Liquid Phase The solubility of a solid in a liquid solvent and the distribution of a solute between two liquid phases will be considered in this section. When a solute is transported from one phase to another, the solute must cross the interface between phases as shown in Figue 5.10-1. We assume that the solute at the interface is in phase equilibrium. If the mole fraction y_i is known at a given temperature, x_i can be determined from the equilibrium relation and vice-versa.

Mass transfer from the liquid to the gas phase

Mass transfer from the gas to the liquid phase
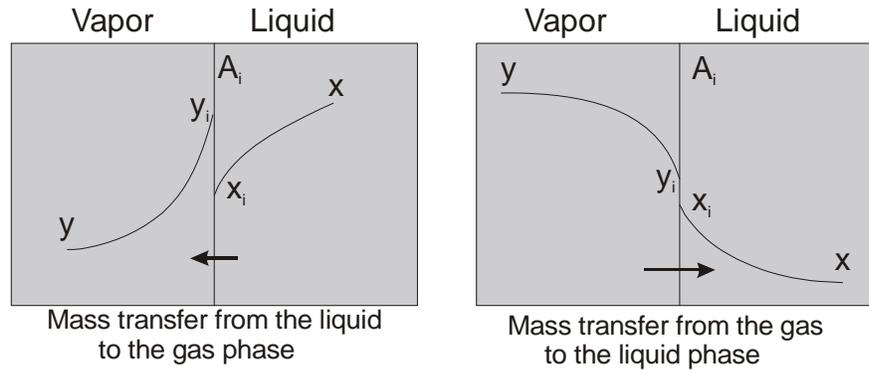
Figure 5.10-1 Solute transport across the interface.

5.10a Solubility of a solid in a liquid solvent Consider a binary system with solute (2) in equilibrium with solvent (1) as shown in Figure 5.10-2. We assume that the solvent is not soluble in the solid so that the solid solute will exist as a pure phase. At equilibrium, the fugacity of the solute in the solid phase, f_2^s, is equal to the fugacity of the solute in solution, f_2^{sol}. The fugacity f_2^{sol} is related to the fugacity of pure liquid solute, f_2^L, at the equilibrium temperature and pressure of the solution by

$$f_2^{sol} = \gamma_2 x_2 f_2^L = f_2^s \qquad (5.10\text{-}1)$$
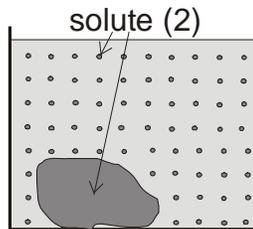
Figure 5.10-2 Solute (2) in solvent (1).

In equation (5.10-1) x_2 is the solubility or the equilibrium mole fraction of solute in solution and γ_2 is the activity coefficient of the solute. Solving for the solubility gives

$$x_2 = \frac{1}{\gamma_2} \frac{f_2^s}{f_2^L} \qquad (5.10\text{-}2)$$

The ratio f_2^s / f_2^L may be estimated by[21]

$$\frac{f_2^s}{f_2^L} = \exp\left[\frac{\Delta H^m}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right)\right] \tag{5.10-3}$$

In this expression, ΔH^m is the enthalpy of fusion at the normal melting temperature T_m. For an ideal solution the activity γ_2 is equal to 1. For non-ideal solutions, an appropriate activity coefficient model must be used to calculate the solubility. For non-polar solutes and solvents, the activity coefficient might be obtained from the *Scatchard-Hildebrand equation*:

$$\gamma_2 = \exp\left[\frac{V_2^L(\delta_1 - \delta_2)^2 \Phi_1^2}{RT}\right] \tag{5.10-4}$$

In this equation V_2^L is the molar volume of the solute as a subcooled liquid at the temperature of the solution. However, V_2^L is usually assumed to be the same as the molar volume of the solute as a liquid at the melting point. The δs are the solubility parameters for the solute and the solvent, and Φ_1 is the volume fraction of the solvent defined by the following equation.

$$\Phi_1 = \frac{x_1 V_1^L}{x_1 V_1^L + x_2 V_2^L} \tag{5.10-5}$$

The solubility parameter is given by

$$\delta_i = \left(\frac{\Delta H_i^{vap} - RT}{V_i^L}\right)^{1/2} \tag{5.10-6}$$

The heat of evaporation can be obtained from the heat of sublimation and the heat of fusion.

$$\Delta H_i^{vap} = \Delta H_i^{sub} - \Delta H_i^m \tag{5.10-7}$$

If the vapor pressure of the solid is known as a function of temperature, the heat of sublimation can be estimated.

$$\ln P^{sat} = A - \frac{B}{T} \tag{5.10-8}$$

If the solid is in equilibrium with the vapor we have

$$dG^V = -S^V dT + V^V dP^{sat} = -S^S dT + V^S dP^{sat} = dG^S \tag{5.10-9}$$

Rearranging this equation gives

[21] Fournier, R. L., "Basic Transport Phenomena in Biomedical Engineering", Taylor & Francis, 2007, p. 57

$$\frac{dP^{sat}}{dT} = \frac{S^V - S^S}{V^V - V^S} = \frac{\Delta S^{SV}}{\Delta V^{SV}} \tag{5.10-10}$$

Since $\Delta S^{SV} = \Delta H^{SV}/T$, and we can neglect the volar volume of the solid in comparision to the volume of the vapor, equation (5.10-10) becomes

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{SV} P^{sat}}{RT^2} \tag{5.10-11}$$

We assume ideal gas law in equation (5.10-11), which may be written as follows:

$$\frac{d \ln P^{sat}}{d\left(\dfrac{1}{T}\right)} = -\frac{\Delta H^{SV}}{R} \tag{5.10-12}$$

Taking derivative of equation (5.10-8), $\ln P^{sat} = A - \dfrac{B}{T}$, we obtain

$$\frac{d \ln P^{sat}}{d\left(\dfrac{1}{T}\right)} = -B = -\frac{\Delta H^{SV}}{R} \Rightarrow \Delta H^{SV} = \Delta H_i^{sub} = RB \tag{5.10-13}$$

Example 5.10-1.[22] --
A drug has a molecular weight of 230 and a melting temperature of 155°C. Estimate the solubility of this drug in benzene and in n-hexane at 25°C assuming

          a) Ideal solution
          b) Nonideal solution using the *Scatchard-Hildebrand equation*

Data:

Heat of fusion of the drug	4300 cal/mol
Density of the drug	1.04 g/cm^3 at 25°C
Vapor pressure of the solid drug	$\ln P^{sat}(\text{mm Hg}) = 27.3 - \dfrac{8926}{T(\text{K})}$
Molar volume of benzene	89.4 cm^3/mol
Solubility parameter for benzene	9.2 (cal/cm^3)$^{1/2}$
Molar volume of n-hexane	131.6 cm^3/mol
Solubility parameter for n-hexane	7.3 (cal/cm^3)$^{1/2}$

Solution --

a) The ideal solubility of the drug is given by

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[22] Fournier, R. L., "Basic Transport Phenomena in Biomedical Engineering", Taylor & Francis, 2007, p. 58

$$x_2 = \frac{1}{\gamma_2} \frac{f_2^s}{f_2^L} = \exp\left[\frac{\Delta H^m}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right)\right] \text{ where } \gamma_2 = 1$$

$$x_2 = \exp\left[\frac{4300 \text{ cal/mol}}{1.987 \text{ cal/(mol}\cdot\text{K)}}\left(\frac{1}{273.15+155} - \frac{1}{298.15}\right)\text{K}^{-1}\right] = 0.110$$

The solubility is the same whether the solvent is benzene or n-hexane.

b) Nonideal solution using the *Scatchard-Hildebrand equation*

$$\ln P^{sat}(\text{mm Hg}) = 27.3 - \frac{8926}{T(\text{K})}$$

$$\frac{d\ln P^{sat}}{d\left(\dfrac{1}{T}\right)} = -8926 = -\frac{\Delta H^{SV}}{R} \Rightarrow \Delta H^{SV} = \Delta H_i^{sub} = 8926R$$

$$\Delta H_2^{sub} = (8926 \text{ K})(1.987 \text{ cal/mol·K}) = 17736.9 \text{ cal/mol}$$

The heat of evaporation of the drug is then estimated:

$$\Delta H_i^{vap} = \Delta H_i^{sub} - \Delta H_i^m = 17{,}736.9 - 4{,}300 = 13{,}436.9$$

The solubility parameter of the drug is given by

$$\delta_1 = \left(\frac{\Delta H_i^{vap} - RT}{V_i^L}\right)^{1/2}$$

$$\delta_1 = \left(\frac{13{,}436.9 \text{ cal/mol} - (1.987 \text{ cal/mol}\cdot\text{K})(298 \text{ K})}{\left(\dfrac{1}{1.04}\text{cm}^3/g\right)(230 \text{ g/mol})}\right)^{1/2} = 7.62 \text{ (cal/cm}^3)^{1/2}$$

The drug solubility is calculated from

$$x_2 = \frac{1}{\gamma_2} \frac{f_2^s}{f_2^L} = \frac{1}{\gamma_2} \exp\left[\frac{\Delta H^m}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right)\right]$$

Substituting $\gamma_2 = \exp\left[\dfrac{V_2^L(\delta_1 - \delta_2)^2\Phi_1^2}{RT}\right]$ and $\Phi_1 = \dfrac{x_1 V_1^L}{x_1 V_1^L + x_2 V_2^L}$ into the above equation we have

$$x_2 = \frac{\exp\left[\dfrac{\Delta H^m}{R}\left(\dfrac{1}{T_m} - \dfrac{1}{T}\right)\right]}{\exp\left\{\dfrac{V_2^L(\delta_1 - \delta_2)^2}{RT}\left[\dfrac{(1-x_2)V_1^L}{(1-x_2)V_1^L + x_2 V_2^L}\right]\right\}}$$

The above equation is implicit in the solubility x_2 and can be written as

$$f(x_2) = x_2 - \frac{\exp\left[\dfrac{\Delta H^m}{R}\left(\dfrac{1}{T_m} - \dfrac{1}{T}\right)\right]}{\exp\left\{\dfrac{V_2^L(\delta_1 - \delta_2)^2}{RT}\left[\dfrac{(1-x_2)V_1^L}{(1-x_2)V_1^L + x_2 V_2^L}\right]\right\}} = 0$$

The nonlinear equation $f(x_2) = 0$ can be solved using Matlab function fzero with the ideal solution as the initial guess. The solubility of drug in benzene is evaluated using the fzero('solubility',0.11) with the function *solubility* representing $f(x_2) = 0$.

```
>> x2=fzero('solubility',0.11)

x2 =

 5.3999e-002

function y=solubility(x)
dHm=4300; % cal/mol
R=1.987; % cal/(mol*K)
TK=273.15; % K
Tm=155+TK;
dHsub=R*8926; % cal/mol
dHvap=dHsub-dHm;
VL2=230/1.04; % molar volume of drug (cm3/mol)
T=25+TK;
del2=((dHvap-R*T)/VL2)^0.5; % solubility parameter for the drug (cal/cm3)^0.5
VL1=89.4; % molar volume of solvent, benzene (cm3/mol)
del1=9.2; % solubility parameter for benzene (cal/cm3)^0.5
tem1=VL2*(del1-del2)^2/(R*T);
tem2=(1-x)*VL1/((1-x)*VL1+x*VL2);
gamma2=exp(tem1*tem2^2);
y=x-exp(dHm*(1/Tm-1/T)/R)/gamma2;
```

The solubility of drug in n-hexane is evaluated using the fzero('solhexane',0.11) with the function *solhexane* representing $f(x_2) = 0$.

```
>> x2=fzero('solhexane',0.11)
```

x2 = 1.0748e-001

```
function y=solhexane(x)
dHm=4300; % cal/mol
R=1.987; % cal/(mol*K)
TK=273.15; % K
Tm=155+TK;
dHsub=R*8926; % cal/mol
dHvap=dHsub-dHm;
VL2=230/1.04; % molar volume of drug (cm3/mol)
T=25+TK;
del2=((dHvap-R*T)/VL2)^0.5; % solubility parameter for the drug (cal/cm3)^0.5
VL1=131.6; % molar volume of solvent, n-hexane (cm3/mol)
del1=7.3; % solubility parameter for n-hexane (cal/cm3)^0.5
tem1=VL2*(del1-del2)^2/(R*T);
tem2=(1-x)*VL1/((1-x)*VL1+x*VL2);
gamma2=exp(tem1*tem2^2);
y=x-exp(dHm*(1/Tm-1/T)/R)/gamma2;
```

The drug and n-hexane form an ideal solution since the solubility calculated using non-ideal model ($x_2 = 0.1075$) is very close to the ideal model ($x_{2,\text{ideal}} = 0.11$).

5.10b Distribution of a solute between liquid phases One or more of the components in a liquid mixture might be separated by contacting the mixture with another liquid in the process of liquid extraction. The separation is due to the unequal distribution of a solute between two partially miscible liquid phases. Through the process of liquid extraction, a product such as penicillin produced in fermentation mixtures can be extracted into a suitable solvent and purified from the fermentation broth. Choice of solvent extraction would depend on toxicity, cost, degree of miscibility with the fermentation broth, and selectivity for the solute.

We normally have three components, A, B, and C and two phases in equilibrium in a liquid-liquid system. From the phase rule, the degree of freedom F is given by

$$F = C + 2 - P = 3 + 2 - 2 = 3 \qquad (5.10\text{-}14)$$

The variables are temperature, pressure, and four concentrations. Four concentration occur since the mole fraction of the components in a phase must be equal to one:

$$x_A + x_B + x_C = 1$$

If pressure and temperature are fixed, which is the usual case, then, at equilbrium, setting one concentration in either phase defines the system. Consider an equilibrium system from the mixing of N_1 moles of solutes, N_2 moles of solvent 2, and N_3 moles of solvent 3. At equilibrium, the fugacity of component i in phase I is equal to its fugacity in phase II.

$$\gamma_i^I \, x_i^I \, f_i^I \, (T, P) = \gamma_i^{II} \, x_i^{II} \, f_i^{II} \, (T, P) \qquad (5.10\text{-}15)$$

In this equation $f_i^I(T, P) = f_i^{II}(T, P) = f_i(T, P)$ = fugacity of pure component i at the same temperature and pressure of the system. Equation (5.10-15) becomes

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II} \qquad (5.10\text{-}16)$$

The distribution coefficient or the equilibrium constant K_i is defined as the ratio of the mole fraction of component i in the two phases.

$$K_i = \frac{x_i^I}{x_i^{II}} = \frac{\gamma_i^{II}}{\gamma_i^I} \qquad (5.10\text{-}17)$$

In liquid-liquid equilibrium system, the two partially miscible liquid phases usually form a non-ideal solution. The activity coefficients should be determined from multi-component activity models that can describe liquid-liquid equilibrium system.

Equilateral triangular coordinates can be used to represent the equilibrium data for a three-component system as shown in Figure 5.10-3. Each of the three corners represents a pure component, A, B, or C. The point M represents a mixture with $x_A = 0.4$, $x_B = 0.2$, and $x_C = 0.4$. The perpendicular distance from the point M to the base AB represents the mole fraction x_C of C in the mixture at M, the distance to the base CB represents the mole fraction x_A of A, and the distance to the base AC represents the mole fraction x_B of B.
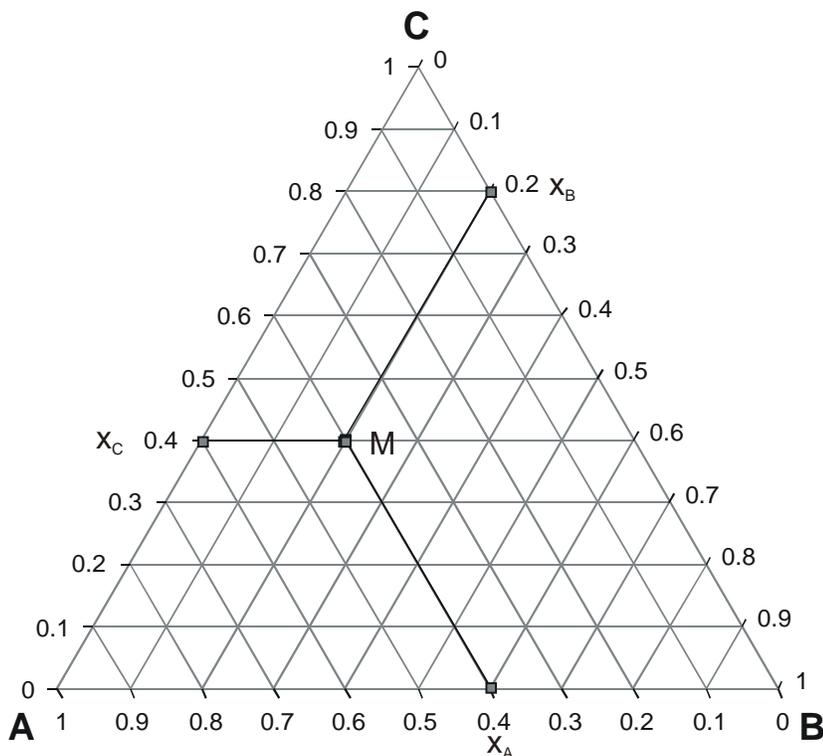
Figure 5.10-3 Equilateral triangular coordinates.

A common phase diagram where components A and B are partially miscible is shown in Figure 5.10-4. In this system, liquid C dissolves completely in A or B. Liquid A is only slightly soluble in B and B slightly soluble in A. The phase diagram is separated into two regions by a curved or phase envelope. The region outside the curved envelope is the one phase region and the region inside the curved envelope is the two-phase region. Any original mixture with composition in the two-phase region will separate out into two phases with the equilibrium compositions connected by the tie line. For example, a mixture with 5 moles of A, 3 moles of B, and 2 moles of C will not exist at equilibrium as a solution at point M. Instead this mixture will separate into liquid phase I and liquid phase II with compositions given by point a and b respectively. Liquid phase I has the compositions $x_{A,I} = 0.79$, $x_{B,I} = 0.03$, and $x_{C,I} = 0.18$. Liquid phase II has the compositions $x_{A,II} = 0.08$, $x_{B,II} = 0.68$, and $x_{C,II} = 0.24$. The moles of liquid in each phase can be determined from the materials balance.

$$x_{A,I}L^I + x_{A,II}L^{II} = 5 \text{ moles}$$
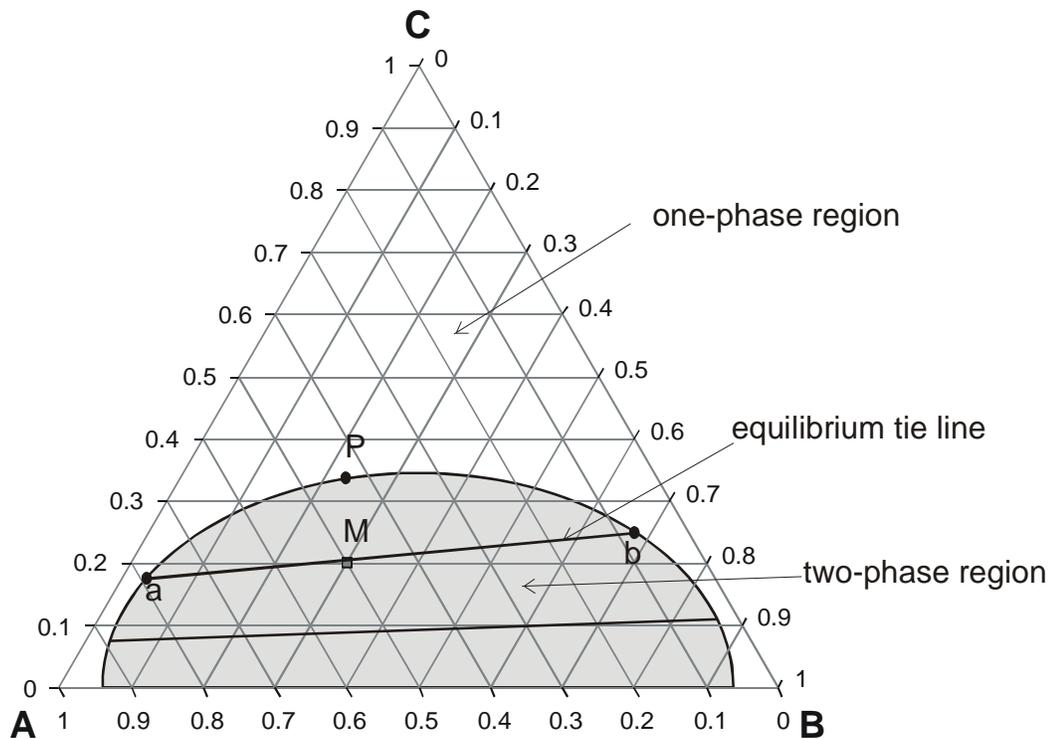
Figure 5.10-4 Liquid-liquid phase diagram where components
A and B are partially miscible.

Since $L^I + L^{II} = 10$ moles, we have

$$0.79L^I + (0.08)(10 - L^I) = 5 \Rightarrow L^I = \frac{5 - 0.8}{0.79 - 0.08} = 5.916 \text{ moles}$$

$$L^{II} = 4.084 \text{ moles}$$

The liquid-liquid equilibrium system will be simplified if the two solvents are immiscible. Usually solvents are selected to minimize their mutual solubility so immiscible system is a reasonable assumption. In many biological applications the solute concentration is so low that the activity coefficients approach their infinite dilution values and the distribution coefficient is a constant. Consider an equilibrium system from the mixing of N_1 moles of solutes, N_2 moles of solvent 2, and N_3 moles of solvent 3. If the solute concentration is low then $N_1 \ll N_2$ and $N_1 \ll N_3$. For a system with two immiscible liquid phases at equilibrium, a mole balance of the solutes is given by

$$N_1 = x_{1,I}L^I + x_{1,II}L^{II} \tag{5.10-18}$$

In this equation L^I is the moles of solvent 2 and some solute in liquid phase I and L^{II} is the moles of solvent 3 and some solute in liquid phase II. Since the solute is present at such small quantity the value of L^I and L^{II} are assumed to be constant and equal to N_2 and N_3 respectively. Equation (5.10-18) becomes

$$N_1 = x_{1,I}N_2 + x_{1,II}N_3 \tag{5.10-18}$$

If the distribution coefficient is known, $x_{1,I} = K_1 x_{1,II}$, then the mole fraction of the solute in phase II can be solved:

$$N_1 = K_1 x_{1,II} N_2 + x_{1,II} N_3 \Rightarrow x_{1,II} = \frac{N_1}{K_1 N_2 + N_3} \tag{5.10-19}$$

Example 5.10-2.[23] --
We have 0.01 moles (N_1) of drug dissolved in 100 moles of water (N_3). We then add to this phase 100 moles (N_2) of octanol. The octanol-water partition coefficient for the drug is 89.

$$K_i = \frac{x_i^I}{x_i^{II}} = 89$$

For this system, octanol (phase I) and water (phase II) are immiscible. Estimate the mole fractions of the drug in the two phases once equilibrium has been attained and the % extraction of the drug from the aqueous phase.

Solution --

Making a mole balance for the drug gives

$$N_1 = x_{1,I}N_2 + x_{1,II}N_3$$

Substituting $x_{1,I} = K_1 x_{1,II}$ into the above equation we obtain

$$N_1 = K_1 x_{1,II}N_2 + x_{1,II}N_3$$

The mole fraction of the drug in the water phase is

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[23] Fournier, R. L., "Basic Transport Phenomena in Biomedical Engineering", Taylor & Francis, 2007, p. 71

$$x_{1,\text{II}} = \frac{N_1}{K_1 N_2 + N_3} = \frac{0.01}{89 \times 100 + 100} = 1.11 \times 10^{-6}$$

The mole fraction of the drug in the octanol phase is

$$x_{1,\text{I}} = K_1\, x_{1,\text{II}} = (89)(\,1.11 \times 10^{-6}) = 9.889 \times 10^{-5}$$

The % extraction of the drug from the aqueous phase is given by

$$\% \text{ extraction} = \frac{x_{1,I} N_2}{N_1} \times 100 = \frac{9.889 \times 10^{-5} \times 100}{0.01} \times 100 = \mathbf{98.89\%}$$

Example 5.10-3.[24] --
Purification of an Antibiotic

Benzylpenicillin is an older antibiotic effective against pneumococcal and meningoccal infections, anthrax, and Lyme disease. As part of a purification process, 200 mg of benzylpenicilin is mixed with 25 ml of n-octanol and 25 mL of water. After equilibrium is established, there is a water-rich phase that contains essentially no n-octanol and an octanol-rich phase that contains 74 mol % n-octanol and 26 mol % water. Determine the concentrations of benzylpenicillin in each of these phases.

Data: The molecular weight of benzylpenicillin is 334.5, that of n-octanol is 130.23, the liquid density of n-octanol is 0.826 g/cm^3, and

$$K_{\text{OW,B}} = \frac{C_B^O}{C_B^W} = \frac{\text{mg B/(ml n-octanol)}}{\text{mg B/(ml water)}} = 65.5$$

Solution ---

Since n-octanol is insoluble in water, the number of moles of n-octanol in the octanol-rich phase is

$$\frac{25 \text{ mL} \times 0.826 \text{ g/mL}}{130.23 \text{ g/mol}} = 0.1586 \text{ mol}$$

The amount of water in the octanol-rich phase is

$$0.1586 \text{ mol octanol} \times \frac{0.26 \text{ mol water}}{0.74 \text{ mol octanol}} = 0.0557 \text{ mol water}$$

Assuming no change in volume upon mixing, the volume of the octanol-rich phase is

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[24] Sandler, S. I., "Chemical, Biochemical, and Engineering Thermodyanmics", Wiley, 2006, p. 643

$$V^O = \frac{0.1586 \text{ mol} \times 130.23 \text{ g/mol}}{0.826 \text{ g/mL}} + \frac{0.0557 \text{ mol} \times 18 \text{ g/mol}}{1 \text{ g/mL}} = 26.0028 \text{ mL}$$

The volume of the water-rich phase is

$$V^W = 50 \text{ mL} - 26.0028 \text{ mL} = 23.997 \text{ mL}$$

The total number of moles of benzylpenicillin is

$$\frac{0.2 \text{ g}}{334.4 \text{ g/mol}} = 5.981 \times 10^{-4} \text{ mol}$$

Making a mole balance on of benzylpenicillin gives

$$5.981 \times 10^{-4} \text{ mol} = C_B^W V^W + C_B^O V^O = C_B^W V^W + K_{\text{OW,B}} C_B^W V^O$$

$$5.981 \times 10^{-4} \text{ mol} = C_B^W (23.997 + 65.5 \times 26.003) = C_B^W \times 1727.52 \text{ mL}$$

$$C_B^W = 3.462 \times 10^{-7} \text{ mol/mL} = 1.158 \times 10^{-4} \text{ g/mL} = \textbf{0.1158 mg/mL}$$

$$C_B^O = K_{\text{OW,B}} C_B^W = 65.5 \times 3.462 \times 10^{-7} = 2.268 \times 10^{-5} \text{ mol/mL}$$

$$C_B^O = 7.585 \times 10^{-3} \text{ g/mL} = \textbf{7.585 mg/mL}$$

5.10c Single-Stage Equilibrium Extraction
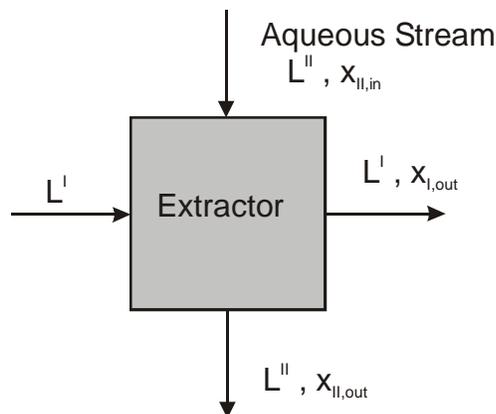
Figure 5.10-5 Single stage equilibrium liquid-liquid extraction.

Figure 5.10-5 shows a single stage liquid extractor where a pure flowing solvent stream at molar flow rate L^I is contacted with an aqueous stream flowing at L^{II} with a solute of mole fraction $x_{\text{II,in}}$. We assume that the solvent and water are immiscible and there is no change in

flowrates of L^I or L^{II}. The streams leaving the liquid extractor are at equilibrium so that $x_{I,out} = Kx_{II,out}$. Making a mole balance on the solute gives

$$L^{II} x_{II,in} = L^I x_{I,out} + L^{II} x_{II,out} = L^I K x_{II,out} + L^{II} x_{II,out}$$

$$L^{II} x_{II,in} = (L^I K + L^{II}) x_{II,out} \tag{5.10-20}$$

Solving for $x_{II,out} / x_{I,out}$ we obtain

$$\frac{x_{II,out}}{x_{II,in}} = \frac{L^{II}}{KL^I + L^{II}} = \frac{1}{1 + \dfrac{KL^I}{L^{II}}} = \frac{1}{1 + E} \tag{5.10-21}$$

In equation (5.10-21), E is defined as the extraction factor, $\dfrac{KL^I}{L^{II}}$. The amount of solute entering the extractor is $L^{II} x_{II,in}$. The amount of solute extracted from the aqueous phase II is $L^{II} x_{II,in} - L^{II} x_{II,out}$. The % extraction of the solute from phase II is then given by

$$\% \text{ extraction} = \left(\frac{L^{II} x_{II,in} - L^{II} x_{II,out}}{L^{II} x_{II,in}} \right) \times 100 = \left(1 - \frac{x_{II,out}}{x_{II,in}} \right) \times 100$$

Example 5.10-4.[25] --
A drug is in an aqueous (phase II) stream flowing at 100 moles/min at a drug mole fraction of 0.01. The aqueous stream is then contacted with an extractor with a pure solvent (phase I) flowing at 200 moles/min. The distribution coefficient for this particular drug is given by

$$K_i = \frac{x_i^I}{x_i^{II}} = 6$$

Determine the equilibrium mole fraction of the drug in the streams exiting the extractor and the % extraction of the drug from the aqueous stream.

Solution ---

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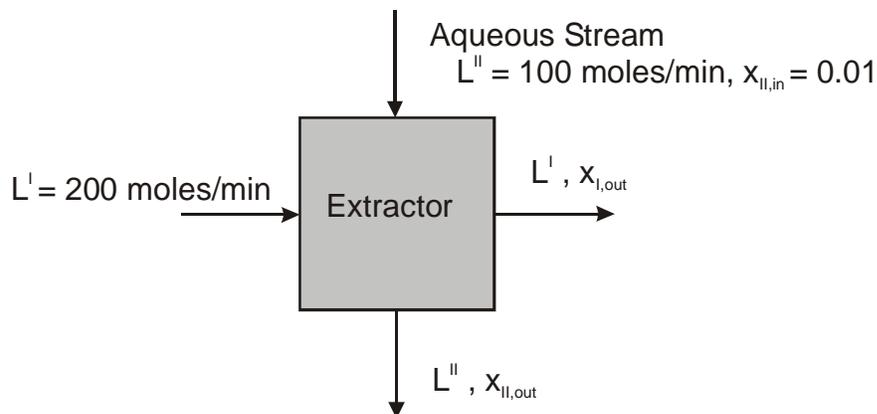
[25] Fournier, R. L., "Basic Transport Phenomena in Biomedical Engineering", Taylor & Francis, 2007, p. 72

Making a mole balance on the solute gives

$$L^{II} x_{II,in} = L^I x_{I,out} + L^{II} x_{II,out} = L^I K x_{II,out} + L^{II} x_{II,out}$$

$$L^{II} x_{II,in} = (L^I K + L^{II}) x_{II,out}$$

Solving for $x_{II,out} / x_{I,out}$ we obtain

$$\frac{x_{II,out}}{x_{II,in}} = \frac{L^{II}}{KL^I + L^{II}} = \frac{1}{1 + \dfrac{KL^I}{L^{II}}} = \frac{1}{1 + E} = \frac{1}{1 + \dfrac{(6)(200)}{100}} = 0.0769$$

$$x_{II,out} = (0.01)(0.0769) = \mathbf{7.69 \times 10^{-4}}, \quad x_{I,out} = (6)(7.69 \times 10^{-4}) = \mathbf{4.62 \times 10^{-3}}$$

$$\% \text{ extraction} = \left(\frac{L^{II} x_{II,in} - L^{II} x_{II,out}}{L^{II} x_{II,in}} \right) \times 100 = \left(1 - \frac{x_{II,out}}{x_{II,in}} \right) \times 100 = (1 - 0.0769) \times 100 = \mathbf{92.3 \ \%}$$

Chapter 6

Chemical Equilibrium

6.1 Introduction

Chemical reaction engineering and separation processes are the two fields unique to chemical engineering. The design of chemical reactor often requires extensive repetitive calculations with the help of sophisticated computer models now available to design engineer. Analysis of chemical reactions is central to the design of chemical reactor. We will first review the stoichiometry of the reactions.

Consider the following reaction in which α moles of species A react with β moles of species B to produce ρ moles of R and v moles of S.

$$\alpha A + \beta B \Leftrightarrow \rho R + vS$$

or $$\rho R + \gamma S - \alpha A - \beta B = 0$$

or $$\sum_{i=1}^{4} v_i I_i = 0$$
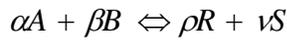
where v_i = stoichiometric coefficient of species I_i
v_i is positive if I_i is a product
v_i is negative if I_i is a reactant
v_i is zero if I_i is an inert

For example, consider the reaction $A + 2B \Leftrightarrow C$ or $C - A - 2B = 0$, then $v_C = 1$, $v_A = -1$, and $v_C = -2$. At any time the moles N_i of species I_i can be related to the initial moles N_{io} of species I_i by the following relation

$$N_i = N_{io} + v_i \zeta$$

where the quantity ζ, which has the same unit as N_i, is called the molar extent of reaction. The definition of ζ

$$\zeta = \frac{N_i - N_{io}}{v_i}$$

is not the same as the definition for the fractional conversion f

$$f = \frac{N_{io} - N_i}{N_{io}} = \frac{\text{moles reacted}}{\text{moles fed}}$$

The relation between the molar extent of reaction and the fractional conversion is

$$\zeta = -\frac{N_{io} - N_i}{\nu_i} = -\frac{fN_{io}}{\nu_i}$$

ζ is not restricted to lie between 0 and 1. In fact, the molar extent of reaction may be negative if the reaction proceeds in the reverse direction to that indicated (e. g., if C is dissociated to form A and B).

Example 6.1-1. --
 Consider the following gas phase reaction at 400°K and 2 atm.

$$A + 2B \Leftrightarrow C$$

The mole fractions of the reactive species at equilibrium satisfy the relation

$$\frac{y_C}{y_A y_B^2} = 1.1124$$

Starting with equimolar quantities of A and B, and no C, calculate y_A, y_B, and y_C, the molar extent of reaction, and the fractional conversion of A and B if the reaction proceeds to equilibrium.

Solution --

	A	B	C	Total
Initial	1	1	0	2
Final	$1 - \zeta$	$1 - 2\zeta$	ζ	$2(1 - \zeta)$

Since $N_A = N_{Ao} - \zeta$ and $N_B = N_{Bo} - 2\zeta$. The mole fraction of each species is then calculated

$$y_A = \frac{1 - \zeta}{2(1 - \zeta)} = 0.5, \; y_B = \frac{1 - 2\zeta}{2(1 - \zeta)}, \text{ and } y_C = \frac{\zeta}{2(1 - \zeta)}$$

From the equilibrium relation $y_C = 1.1124 \; y_A \, y_B^2$ or

$$\frac{\zeta}{2(1 - \zeta)} = 1.1124 \times 0.5 \left(\frac{1 - 2\zeta}{2(1 - \zeta)} \right)^2$$

$$2\zeta(1 - \zeta) = 0.5562(1 - 2\zeta)^2$$

$$4.2248\ \zeta^2 - 4.2248\zeta + 0.5562 = 0$$

There are two roots: $\zeta_1 = 0.156$ and $\zeta_2 = 0.844$

If $\zeta = 0.844$ then $N_B = N_{Bo} - 2\zeta = 1 - 2\zeta < 0$: not possible

Therefore the molar extent of reaction ζ must be equal to 0.156, and

$$y_B = \frac{1 - 2\zeta}{2(1 - \zeta)} = 0.408, \text{ and } y_C = \frac{\zeta}{2(1 - \zeta)} = 0.092$$

$$f_A = \frac{N_{Ao} - N_A}{N_{Aio}} = \frac{\zeta}{N_{Aio}} = 0.156, \text{ and } f_B = \frac{N_{Bo} - N_B}{N_{Bio}} = \frac{2\zeta}{N_{Bio}} = 0.312$$

****

From the relation $N_i = N_{io} + \nu_i\zeta$, the rate of change of the number of moles of species i can be written as follows:

$$\frac{dN_i}{dt} = \nu_i \frac{d\zeta}{dt}$$

For chemists and chemical engineers, the rate of change of the number of moles is usually written in terms of the reaction rate per unit volume r:

$$\frac{dN_i}{dt} = \nu_i \frac{d\zeta}{dt} = r_i V$$

where V is the reactor volume.

Order of Reactions

When reaction rates are determined experimentally, is often found that the expression for the reaction rate can be expressed in the following way:

$$r_i = \frac{\nu_i}{V} \frac{d\zeta}{dt} = k C_A^\alpha C_B^\beta$$

In this equation C_A and C_B are the reactant concentration, and the constant of proportionality k is the reaction rate constant. The exponents of the concentrations, α and β, are called the orders of the reaction. In this case the reaction would be called "of order α" with respect to A, "of order β" with respect to B, or "of order α plus β" overall. For a reaction with stoichiometry $A \rightarrow$ products, a first order reaction will give the rate of consumption of A per unit reactor volume as $r_A = kC_A$, and a second order reaction will give $r_A = k(C_A)^2$

Sometimes the rate of consumption of A is independent of the concentration of A, or

$$r_A = k$$

Note that the unit of k is dependent on the order of the reaction. The zero-order reaction is controlled by something other than the concentration of A. In fact, zero-order kinetics are very common in the case of catalyzed reactions.

Type of Reactors

Batch reactor: There is neither inflow of reactants nor outflow of products while the reaction is being carried out.

Semibatch reactor: While the reaction is being carried out, there is either inflow of reactants or outflow of products but not both.

Continuous-stirred tank reactor CSTR: While the reaction is being carried out, there are inflow of reactants and outflow of products. Except for startup and shutdown, the CSTR is normally run at steady state, and is well mixed. As a result of mixing, the temperature and concentration are assumed to be identical everywhere within the reactor including the exit point.

Tubular reactor: It consists of a cylindrical pipe and is normally operated at steady state. For the systems in which the flow is highly turbulent, the flow field may be modeled by that of plug flow. The reactor is then called continuous plug-flow reactor PFR. The reactants are continuously consumed as they flow down the length of the reactor. The concentrations vary continuously only in the axial direction through the reactor but not in the radial direction.

BATCH   SEMIBATCH

Filling   Draining

CSTR

PFR
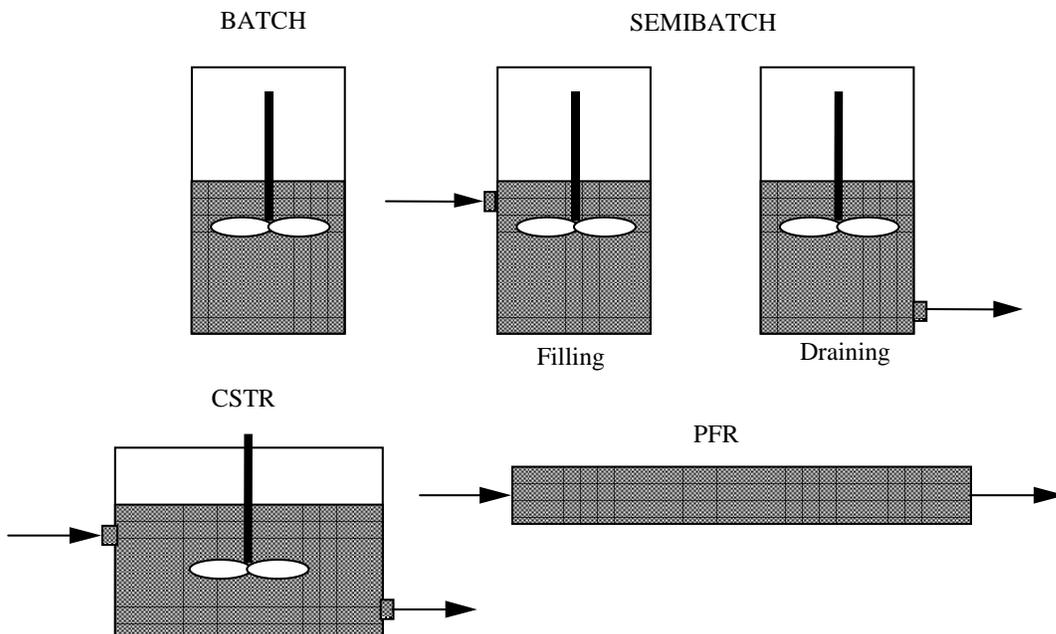
Figure 6.1-1. Common reactor types

Example 6.1-2. ---
The following second order, irreversible gas phase reaction

$$AB \rightarrow A + B, \text{ where } k = 2.0 \times 10^4 \text{ cm}^3/\text{mol·min}$$
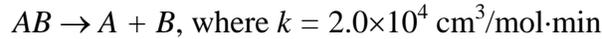
is allowed to decompose isothermally in a constant pressure batch reactor. The reactor initially contains pure AB with a volume of 2.0 m³ at 2.5 atm and 500°C. Assuming ideal behavior, determine the time for the reaction to reach 90% conversion.

Solution ---

Let X = fractional conversion, n_o = initial moles of AB in the reactor. The moles of A and B in the reactor at any time are given by

$$n_A = n_B = n_o X$$

We have

	AB	A	B	Total
Initial	n_o	0	0	n_o
Final	$n_o(1 - X)$	$n_o X$	$n_o X$	$n_o(1 + X)$

Applying the mass balance for AB in the reactor gives

$$\frac{d}{dt}[n_o(1 - X)] = - k(C_{AB})^2 V = - \frac{kn_o^2(1 - X)^2}{V} \tag{E-1}$$

Since the pressure is a constant, the volume must change since the number of moles change. From the ideal gas law

$$\frac{PV}{PV_0} = \frac{n_o(1 + X)RT}{n_o RT} \Rightarrow V = V_0(1 + X)$$

Equation (E-1) becomes

$$- n_o \frac{dX}{dt} = - \frac{kn_o^2(1 - X)^2}{V_0(1 + X)} \Rightarrow t = \frac{V_0}{kn_o} \int_0^X \frac{1 + X}{(1 - X)^2} dX$$

We can use partial fraction to obtain

$$\frac{1 - X}{(1 + X)^2} = \frac{a}{1 - X} + \frac{b}{(1 + X)^2} = \frac{-1}{1 - X} + \frac{2}{(1 + X)^2}$$

Therefore,

$$t = \frac{V_0}{kn_o} \left[- \int_0^{0.9} \frac{dX}{1 - X} + 2 \int_0^{0.9} \frac{dX}{(1 - X)^2} \right] = \frac{V_0}{kn_o} \left[\ln(1 - X) + \frac{2}{1 - X} \right]_0^{0.9}$$

$$t = \frac{V_0}{kn_o}\left[\ln(0.1) + 2(\frac{1}{.9} - 1)\right] = \frac{V_0}{kn_o}\left[\ln(0.1) + 18\right]$$

From the ideal gas law

$$\frac{V_0}{n_o} = \frac{RT}{P} \Rightarrow t = \frac{RT}{kP}\left[\ln(0.1) + 18\right]$$

Substituting the numerical values gives

$$t = \frac{82.05 \times 773}{2 \times 10^4 \times 2.5}\left[\ln(0.1) + 18\right] = 1.2685\left[\ln(0.1) + 18\right] = \textbf{19.91 min}$$

We use the ideal gas constant $R = 82.05$ atm·cm^3/mol·°K

6.2 Chemical Reaction and Gibbs Energy

We apply the same principle to solve phase equilibrium problems to chemical equilibrium. Consider the following ideal gas reaction at a total pressure of 1 bar[1].

$$A_2 + B_2 \Leftrightarrow 2AB \tag{6.2-1}$$

For a system in which we initially have 1 mole of A_2 and 1 mole of B_2, the moles of A_2 and B_2 in the reactor at any time are given by

$$n_{A2} = n_{B2} = 1 - \zeta \tag{6.2-2}$$

In this expression ζ is the molar extent of reaction. We have

	A_2	B_2	AB	Total
Initial	1	1	0	2
Final	$1 - \zeta$	$1 - \zeta$	2ζ	2

The total Gibbs energy is given by

$$G = \sum n_i \overline{G}_i = \sum n_i \mu_i = n_{A2}\mu_{A2} + n_{B2}\mu_{B2} + n_{AB}\mu_{AB} \tag{6.2-3}$$

The chemical potential of each component in an ideal gas mixture is given by

$$\mu_i = g_i^o + RT\ln\left(\frac{P_i}{1\,bar}\right) \tag{6.2-4}$$

---

[1] Koretsky M.D., Engineering and Chemical Thermodynamics, Wiley, 2004, pg. 435

In this expression, the reference state is the ideal gas state at the temperature of the reaction and a partial pressure of 1 bar. Since we specified the pressure of the reference state, g_i^o is a function of only temperature. Substitution of equation (6.2-4) into equation (6.2-3) yields

$$G = n_{A2}g_{A2}^o + n_{B2}g_{B2}^o + n_{AB}g_{AB}^o + RT[n_{A2}\ln P_{A2} + n_{B2}\ln P_{B2} + n_{AB}\ln P_{AB}] \quad (6.2\text{-}5)$$

In this expression, the partial pressures must have units of bar. Since $P_i = y_iP$, we have

$$G = n_{A2}g_{A2}^o + n_{B2}g_{B2}^o + n_{AB}g_{AB}^o + RT[n_{A2}\ln y_{A2} + n_{B2}\ln y_{B2} + n_{AB}\ln y_{AB}]$$

$$+ RT(n_{A2} + n_{B2} + n_{AB})\ln P$$

In terms of the molar extent of reaction, we have

$$G = (1 - \zeta)(g_{A2}^o + g_{B2}^o) + 2\zeta g_{AB}^o + RT[(1 - \zeta)\ln y_{A2} + (1 - \zeta)\ln y_{B2} + 2\zeta \ln y_{AB}] + 2RT \ln P$$

We will consider the system with the following numerical values: $T = 1000^oK$, $P = 1$ bar, $g_{A2}^o = g_{B2}^o = 0$, and $g_{AB}^o = -9.5$ kJ/mol. With a gas constant value $R = 8.314$ J/mol·^oK, we have $RT = 8.314$ kJ/mol. The Gibbs energy is plotted as a function of ζ in Figure 6.2-1. The pure species Gibbs energy is labeled "Term 1".

$$\text{Term 1} = (1 - \zeta)(g_{A2}^o + g_{B2}^o) + 2\zeta g_{AB}^o$$
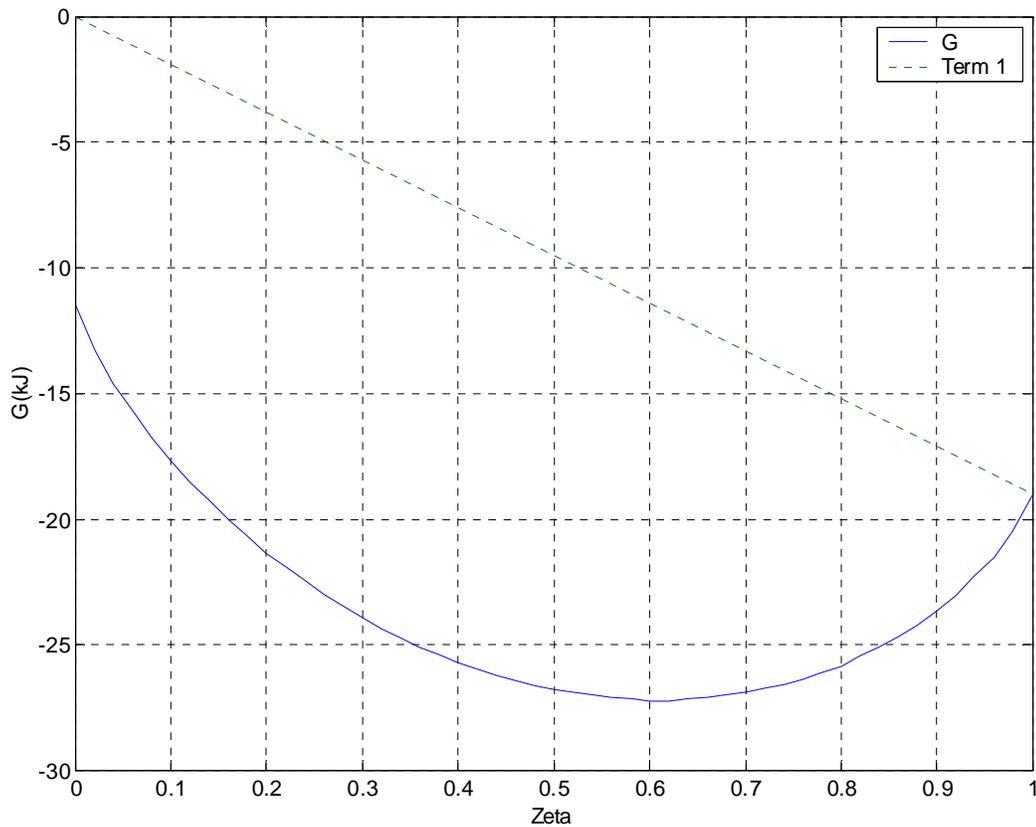
Figure 6.2-1 Gibbs energy of the system $A_2 + B_2 \Leftrightarrow 2AB$.

Table 6.2-1 lists the Matlab program used to plot Figure 6.2-1.

Table 6.2-1 --
```
% Figure 6.2-1:1 = A2, 2 = B2, and 3 = AB
%
g3=-9.5; RT=8.314;
zeta=.02:.02:.98;
y1=(1-zeta)/2;y2=y1;
y3=zeta;
G=2*zeta*g3+RT*((1-zeta).*log(y1)+(1-zeta).*log(y2)+2*zeta.*log(y3));
G1=2*RT*log(.5);Gn=2*g3;
zetap=[0 zeta 1];Gp=[G1 G Gn];
plot(zetap,Gp,[0 1],[0 Gn],':')
grid on
xlabel('Zeta');ylabel('G(kJ)');
legend('G','Term 1')
```

The product, species *AB*, has lower Gibbs energy than the reactants, species A_2 and B_2. However, the equilibrium conversion is not pure species *AB*, but rather the composition at which the Gibbs energy is a minimum. This is due to the fact that a mixture has much higher entropy than a pure component. The system can lower the Gibbs energy if the reaction is not completed. Starting with pure reactants or product, the system will have a minimum Gibbs energy when all three species are present. The contribution to the Gibbs energy of the system due to mixing is given by the expression

$$\Delta G_{\text{mix}} = RT[(1 - \zeta)\ln y_{A2} + (1 - \zeta)\ln y_{B2} + 2\zeta \ln y_{AB}]$$

We only need to specify the amount of each of the elements that are present and the system temperature and pressure to predict the equilibrium state of the system. The change in Gibbs energy with respect to temperature, pressure, and the number of moles is given by

$$dG = VdP - SdT + \sum_{i=1}^{C} \mu_i \, dn_i \qquad (6.2-6)$$

When the composition change is the result of a single chemical reaction we have

$$n_i = n_{io} + v_i\zeta \Rightarrow dn_i = v_i d\zeta$$

At constant temperature and pressure, the change in Gibbs energy is given by

$$dG_{T,P} = \sum \mu_i v_i \, d\zeta$$

There is no change in Gibbs energy at equilibrium: $dG_{T,P} = 0 \Rightarrow \left(\dfrac{\partial G}{\partial \zeta}\right)_{T,P} = \sum v_i \mu_i = 0$

Chapter 6

6.3 The Condition of Equilibrium for a Chemical Reaction

At constant temperature and pressure, the system comes to chemical equilibrium when the Gibbs energy is a minimum.

$$dG_{T,P} = \sum \mu_i \nu_i \, d\zeta \tag{6.3-1}$$

At equilibrium: $dG_{T,P} = 0 \Rightarrow \left(\dfrac{\partial G}{\partial \zeta} \right)_{T,P} = \sum \nu_i \mu_i = 0$ (6.3-2)

Equation (6.3-2) is the condition of equilibrium for a chemical reaction that can be solved if we relate chemical potential to fugacity. From the definition of the fugacity in a mixture we have

$$d\mu_i = RT \, d \ln \hat{f}_i \tag{6.3-3}$$

Integrating this equation between a standard state, denoted by the superscript ^{o}, and the equilibrium state yields

$$\mu_i = g_i^{\,o} + RT \ln \frac{\hat{f}_i}{f_i^{\,o}} \tag{6.3-4}$$

In this equation, the standard state is defined as the pure species at the temperature of the reaction and a pressure of 1 bar (or 1 atm, when appropriate). Since the Gibbs energy is not a strong function of pressure we will freely interchange 1 atm and 1 bar as the reference state pressure. We should note the difference between a standard state and a reference state. In a standard state, only pressure and physical form (gas, liquid, or crystal structure for solid) are specified while in reference state **temperature**, pressure and physical form are specified. For the reference state the temperature can be specified to be different from the reaction temperature. For the standard state the temperature must be the temperature of the reaction. Since the pressure is specified in the standard state, the pure species molar Gibbs energy, $g_i^{\,o}$, is a function of temperature only. Substituting equation (6.3-4) into equation (6.3-2) gives

$$\sum \nu_i g_i^{\,o} + RT \sum \nu_i \ln \frac{\hat{f}_i}{f_i^{\,o}} = 0 \tag{6.3-5}$$

The ratio of fugacities is called activity $\hat{a}_i$, a new thermodynamic function:

$$\hat{a}_i = \frac{\hat{f}_i}{f_i^{\,o}} \tag{6.3-6}$$

While the fugacity f_i depends only on the state of the system, the numerical value of the activity also depend on the choice of standard state. Rearranging equation (6.3-5) and using the mathematical identity that the sum of logarithms is equal to the log of the products gives

$$\ln \Pi \left(\frac{\hat{f}_i}{f_i^o} \right)^{\nu_i} = - \frac{\sum \nu_i g_i^o}{RT} = - \frac{\Delta g_{rxn}^o}{RT} \tag{6.3-7}$$

We have defined a new term, $\Delta g_{rxn}^o = \sum \nu_i g_i^o$, which is called the standards Gibbs free energy change of reaction or simply the Gibbs energy of reaction. The product on the left hand side of equation (6.3-7) is called the equilibrium constant K

$$K = \Pi \left(\frac{\hat{f}_i}{f_i^o} \right)^{\nu_i} \tag{6.3-8}$$

Equation (6.3-7) can now be written as

$$\ln K = - \frac{\Delta g_{rxn}^o}{RT} \tag{6.3-9}$$

The reaction equation for a single reaction may be written as

$$\sum \nu_i I_i = 0 \tag{6.3-10}$$

When more than one chemical reaction is required to describe chemical equilibrium in a system we need one equation for each reaction j or

$$\sum \nu_{ij} I_{ij} = 0 \tag{6.3-11}$$

The change in Gibbs energy of the system is then

$$dG = \sum_j \left(\sum_i \mu_{ij} \nu_{ij} \right) d\zeta_j \tag{6.3-12}$$

At equilibrium G is a minimum, and all partial derivatives with respect to extent of reaction ζ must equal zero

$$\left(\frac{\partial G}{\partial \zeta_j} \right)_{T,P} = \sum_i \mu_{ij} \nu_{ij} = 0 \tag{6.3-13}$$

Equation (6.3-13) applies to each reaction, and at equilibrium the equilibrium constant for each reaction must be satisfied.

6.4 Calculation of Equilibrium Constant from Data

The Gibbs energy of reaction may be obtained from the Gibbs energy of formation which is the Gibbs energy of reaction when the species of interested is formed from its pure elements, as found in nature, that is,

$$\text{Elements} \overset{\Delta g_f}{\longleftrightarrow} \text{Species } i$$
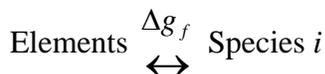
The Gibbs energy of formation of a pure element, as it is found in nature, is equal to zero. The Gibbs energy of formation is available for many species at 25^oC and 1 bar. The Gibbs energy of reaction is then given by

$$\Delta g^o{}_{rxn,298} = \sum \nu_i \Delta g^o{}_{f,298} \tag{6.4-1}$$

In this equation, the stoichiometric coefficients for products are positive and those for reactants are negative. The equilibrium constant is then evaluated:

$$\ln K = - \frac{\Delta g^o{}_{rxn,298}}{RT} \tag{6.4-2}$$

Example 6.4-1.[2] --
Calculate the equilibrium constant for the following reaction using the data at 298^oK

$$H_2O(g) + CH_3OH(g) \Leftrightarrow CO_2(g) + 3H_2(g)$$
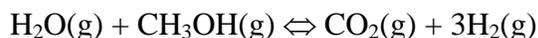
	$H_2O(g)$	$CH_3OH(g)$	$CO_2(g)$	$H_2(g)$
$\Delta g^o{}_f$ (kJ/mol)	-228.57	-161.96	-394.36	0

Solution --

$$\Delta g^o{}_{rxn,298} = \sum \nu_i \Delta g^o{}_{f,298}$$

$$\Delta g^o{}_{rxn,298} = (\Delta g^o{}_f)_{CO2} + 3(\Delta g^o{}_f)_{H2} - (\Delta g^o{}_f)_{H2O} - (\Delta g^o{}_f)_{CH3OH}$$

$$\Delta g^o{}_{rxn,298} = (-394.36)_{CO2} + 3(0)_{H2} - (-228.57)_{H2O} - (-161.96)_{CH3OH}$$

$$\Delta g^o{}_{rxn,298} = -3.83 \text{ kJ/mol}$$

The equilibrium constant is then

$$K = \exp\left(-\frac{\Delta g^o{}_{rxn,298}}{RT}\right) = \exp\left(-\frac{-3,830}{(8.314)(298.15)}\right) = 4.69$$

---

[2] Koretsky M.D., Engineering and Chemical Thermodynamics, Wiley, 2004, pg. 444

Example 6.4-2. ---

Find the equilibrium concentration of $N_2O_4(g)$ [Nitrogen nitroxide] due to the chemical reaction at 25°C and 1 atm.

$$N_2O_4(g) \Leftrightarrow 2NO_2(g)$$

The following data are available:

(1)	$N_2O_4(g) \Leftrightarrow N_2(g) + 2O_2(g)$	$\Delta g^o{}_{rxn,1} = -\Delta g^o{}_{f,N2O4} = -23.41$ kcal/mol
(2)	$0.5N_2(g) + O_2(g) \Leftrightarrow NO_2(g)$	$\Delta g^o{}_{rxn,2} = \Delta g^o{}_{f,NO2} = 12.24$ kcal/mol
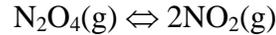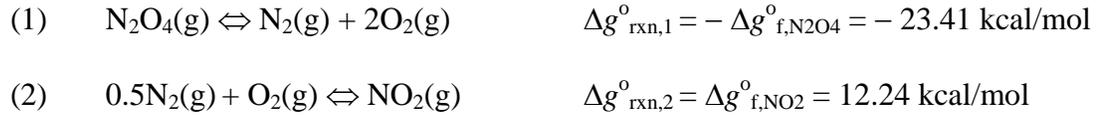
Solution ---

The reaction $N_2O_4(g) \Leftrightarrow 2NO_2(g)$ may be obtained by combining reactions (1) and (2)

$$(1) + 2(2) \Rightarrow \quad N_2O_4(g) \Leftrightarrow 2NO_2(g)$$

Therefore

$$\Delta g^o{}_{rxn} = \Delta g^o{}_{rxn,1} + 2\Delta g^o{}_{rxn,2} = -\Delta g^o{}_{f,N2O4} + 2\Delta g^o{}_{f,NO2} = -23.41 + 2(12.24)$$

$$\Delta g^o{}_{rxn} = 1.11 \text{ kcal/mol} = 4644 \text{ J/mol} = -RT \ln K$$

$$K = \exp\left(-\frac{\Delta g^o{}_{rxn,298}}{RT}\right) = \exp\left(-\frac{4,644}{(8.314)(298.15)}\right) = 0.1563$$

The equilibrium constant K can also be expressed in terms of the activities:

$$K = \frac{a^2_{NO_2}}{a_{N_2O_4}} = \frac{\left(\dfrac{\hat{f}_{NO_2}}{f^0_{NO_2}}\right)^2}{\left(\dfrac{\hat{f}_{N_2O_4}}{f^0_{N_2O_4}}\right)} \tag{E-1}$$

Assume ideal gas $\hat{f}_i = P_i$, $f_i^0 = P^o{}_{NO2} = P^o{}_{N2O4} = 1$ atm, equation (E-1) becomes

$$K = \frac{\left(\dfrac{\hat{f}_{NO_2}}{f^0_{NO_2}}\right)^2}{\left(\dfrac{\hat{f}_{N_2O_4}}{f^0_{N_2O_4}}\right)} = \frac{\left(\dfrac{P_{NO_2}}{P^0_{NO_2}}\right)^2}{\left(\dfrac{P_{N_2O_4}}{P^0_{N_2O_4}}\right)} = \frac{\left(\dfrac{y_{NO_2}P}{1 \text{ atm}}\right)^2}{\left(\dfrac{y_{N_2O_4}P}{1 \text{ atm}}\right)} \tag{E-2}$$

Since $P = 1$ atm, equation (E-2) becomes

$$K = \frac{\left(\dfrac{y_{NO_2} P}{1\text{ atm}}\right)^2}{\left(\dfrac{y_{N_2O_4} P}{1\text{ atm}}\right)} = \frac{y_{NO_2}^2}{y_{N_2O_4}} = 0.1563 \qquad\qquad (E\text{-}3)$$

We have

	N_2O_4	NO_2	Total
Initial	1	0	1
Final	$1 - \zeta$	2ζ	$1 + \zeta$

The mole fractions of N_2O_4 and NO_2 are given by

$$y_{N2O4} = \frac{1-\zeta}{1+\zeta} \qquad\qquad\qquad y_{NO2} = \frac{2\zeta}{1+\zeta}$$

Substituting y_{N2O4} and y_{NO2} into equation (E-3) gives

$$\frac{\left(\dfrac{2\zeta}{1+\zeta}\right)^2}{\dfrac{1-\zeta}{1+\zeta}} = 0.1563 \Rightarrow \frac{4\zeta^2}{(1-\zeta)(1+\zeta)} = 0.1563$$

$$4\zeta^2 = 0.1563(1-\zeta^2) \Rightarrow \zeta^2 = \frac{0.1536}{4.1536} \Rightarrow \zeta = 0.1923$$

The equilibrium concentration of $N_2O_4(g)$ is then

$$y_{N2O4} = \frac{1-\zeta}{1+\zeta} = \mathbf{0.6774}$$

If the Gibbs energies of formation are available at the reaction temperature, the equilibrium constant can be calculated directly from

$$K = \exp\left(-\frac{\Delta g^o{}_{rxn}}{RT}\right)$$

However most reactions we want to study are at temperatures different than 25°C where data are not available. We need an expression to determine the equilibrium constant at any temperature from one set of Gibbs energy data.

6.5 Variation of Equilibrium Constant with Temperature

Since $c_p = \left(\dfrac{\partial h}{\partial T}\right)_P$ and expressions for c_p as a function of temperature are available for many species, if we could relate Gibbs energy to enthalpy we might found an equation to determine the temperature dependence of the equilibrium constant.
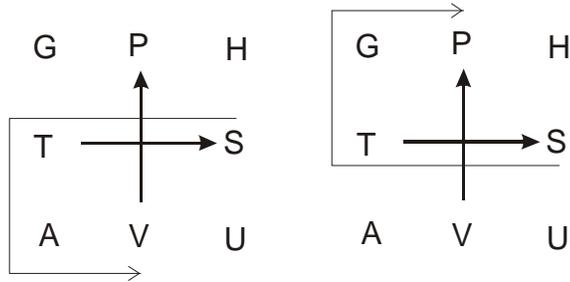
From the thermodynamic diagram we have $S = -\left(\dfrac{\partial G}{\partial T}\right)_P$ or

$$s^o_i = -\left(\frac{\partial g^o_i}{\partial T}\right)_P \tag{6.5-1}$$

Taking the derivative of g^o_i/T with respect to T yields

$$\frac{\partial}{\partial T}\left(\frac{g^o_i}{T}\right) = \frac{1}{T}\frac{\partial g^o_i}{\partial T} - \frac{g^o_i}{T^2} \tag{6.5-2}$$

Substituting $\left(\dfrac{\partial g^o_i}{\partial T}\right)_P = -s^o_i$ into equation (6.5-2) gives

$$\frac{\partial}{\partial T}\left(\frac{g^o_i}{T}\right) = -\frac{s^o_i}{T} - \frac{g^o_i}{T^2} \tag{6.5-3}$$

Since $g^o_i = h^o_i - Ts^o_i$, we have

$$\frac{g^o_i}{T^2} = \frac{h^o_i}{T^2} - \frac{s^o_i}{T} \Rightarrow -\frac{s^o_i}{T} - \frac{g^o_i}{T^2} = -\frac{h^o_i}{T^2} \tag{6.5-4}$$

Comparing equations (6.5-3) and (6.5-4) yields

$$\frac{\partial}{\partial T}\left(\frac{g^o_i}{T}\right) = -\frac{h^o_i}{T^2} \tag{6.5-5}$$

Since
$$\ln K = -\frac{\sum v_i g_i^{\,o}}{RT} = -\frac{\Delta g_{rxn}^{\,o}}{RT} \tag{6.5-6}$$

$$\frac{\partial}{\partial T}\left(\frac{\Delta g_{rxn}^{\,o}}{RT}\right) = \frac{1}{R}\sum v_i \frac{\partial}{\partial T}\left(\frac{g_i^{\,o}}{T}\right) = -\frac{\partial(\ln K)}{\partial T} \tag{6.5-7}$$

$$\frac{\partial(\ln K)}{\partial T} = \frac{1}{R}\sum v_i \frac{h_i^{\,o}}{T^2} = \frac{\Delta h_{rxn}^{\,o}}{RT^2} \tag{6.5-8}$$

In equation (6.5-8) we have defined the enthalpy of reaction $\Delta h_{rxn}^{\,o} = \sum v_i h_i^{\,o}$. For exothermic reaction ($\Delta h_{rxn}^{\,o} < 0$), the equilibrium constant decreases as temperature increases, since RT^2 is always positive. For endothermic reaction ($\Delta h_{rxn}^{\,o} < 0$), the equilibrium constant increases as temperature increases. The enthalpy of reaction can be determined at any temperature based on the enthalpy of reaction at 298°K and heat capacity data from the equation

$$\Delta h_{rxn}^{\,o} = \Delta h_{rxn,298}^{\,o} + \int_{298}^{T}\left(\sum v_i c_{pi}\right)dT \tag{6.5-9}$$

Let $\dfrac{c_{pi}}{R} = A_i + B_i T + C_i T^2$, equation (6.5-9) becomes

$$\Delta h_{rxn}^{\,o} = \Delta h_{rxn,298}^{\,o} + R\int_{298}^{T}\left(\sum v_i A_i + \sum v_i B_i T + \sum v_i C_i T^2\right)dT \tag{6.5-10}$$

Integrating equation (6.5-10) yields

$$\Delta h_{rxn}^{\,o} = \Delta h_{rxn,298}^{\,o} + R[\Delta A(T-298) + \frac{\Delta B}{2}(T^2-298^2) + \frac{\Delta C}{3}(T^3-298^3)\,] \tag{6.5-11}$$

In this equation we have defined $\Delta A = \sum v_i A_i$, $\Delta B = \sum v_i B_i$, and $\Delta C = \sum v_i C_i$. Equation (6.5-11) can also be written as

$$\Delta h_{rxn}^{\,o} = \Delta h_{con} + R[\Delta A T + \frac{\Delta B}{2}T^2 + \frac{\Delta C}{3}T^3] \tag{6.5-12}$$

where

$$\Delta h_{con} = \Delta h_{rxn,298}^{\,o} - R[298\Delta A + 298^2\frac{\Delta B}{2} + 298^3\frac{\Delta C}{3}] \tag{6.5-13}$$

Substituting $\Delta h_{rxn}^{\,o} = \Delta h_{con} + R[\Delta A T + \frac{\Delta B}{2}T^2 + \frac{\Delta C}{3}T^3]$ into equation (6.5-8)

$$\frac{\partial (\ln K)}{\partial T} = \frac{\Delta h^o_{rxn}}{RT^2} \qquad (6.5\text{-}8)$$

We obtain

$$\frac{\partial (\ln K)}{\partial T} = \frac{\Delta h_{con}}{RT^2} + \frac{\Delta A}{T} + \frac{\Delta B}{2} + \frac{\Delta C}{3}T \qquad (6.5\text{-}14)$$

Integrating equation (6.5-14) from 298°K (or any temperature T_1) to T yields

$$\ln\left(\frac{K_T}{K_{T_1}}\right) = - \frac{\Delta h_{con}}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right) + \Delta A \ln\left(\frac{T}{T_1}\right) + \frac{\Delta B}{2}(T - T_1) + \frac{\Delta C}{6}(T^2 - T_1^2) \quad (6.5\text{-}15)$$

If the heat capacity has the form $\dfrac{c_{pi}}{R} = A_i + B_iT + C_iT^2 + D_iT^{-2}$, equation (6.5-9) becomes

$$\Delta h^o_{rxn} = \Delta h^o_{rxn,298} + R\int_{298}^{T}\left(\Delta A + \Delta BT + \Delta CT^2 + \Delta DT^{-2}\right)dT \qquad (6.5\text{-}16)$$

Integrating equation (6.5-16) yields

$$\Delta h^o_{rxn} = \Delta h^o_{rxn,298} + R[\Delta A(T - 298) + \frac{\Delta B}{2}(T^2 - 298^2) + \frac{\Delta C}{3}(T^3 - 298^3) - \Delta D\left(\frac{1}{T} - \frac{1}{298}\right)]$$

Let $\Delta h_{con} = \Delta h^o_{rxn,298} - R[298\Delta A + 298^2\dfrac{\Delta B}{2} + 298^3\dfrac{\Delta C}{3} - \dfrac{\Delta D}{298}]$, the expression for heat of reaction is then

$$\Delta h^o_{rxn} = \Delta h_{con} + R[\Delta AT + \frac{\Delta B}{2}T^2 + \frac{\Delta C}{3}T^3 - \frac{\Delta D}{T}]$$

We need to integrate the following equation

$$\frac{\partial (\ln K)}{\partial T} = \frac{\Delta h_{con}}{RT^2} + \frac{\Delta A}{T} + \frac{\Delta B}{2} + \frac{\Delta C}{3}T - \frac{\Delta D}{T^3}$$

The equation for equilibrium constant as a function of temperature is finally

$$\ln\left(\frac{K_T}{K_{T_1}}\right) = - \frac{\Delta h_{con}}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right) + \Delta A \ln\left(\frac{T}{T_1}\right) + \frac{\Delta B}{2}(T - T_1) + \frac{\Delta C}{6}(T^2 - T_1^2) + \frac{\Delta D}{2}\left(\frac{1}{T^2} - \frac{1}{T_1^2}\right)$$

Chapter 6

Example 6.5-1.[3] ---

Calculate the equilibrium constant for the following reaction at 60°C using the data at 298°K

$$H_2O(g) + CH_3OH(g) \Leftrightarrow CO_2(g) + 3H_2(g)$$
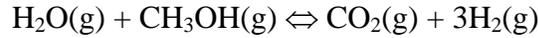
	$H_2O(g)$	$CH_3OH(g)$	$CO_2(g)$	$H_2(g)$
$\Delta g^o_{f,298}$ (kJ/mol)	− 228.57	− 161.96	− 394.36	0
$\Delta h^o_{f,298}$ (kJ/mol)	− 241.82	− 200.66	− 393.51	0

Solution ---

The equilibrium constant as a function of temperature is given by

$$\frac{\partial(\ln K)}{\partial T} = \frac{\Delta h^o_{rxn}}{RT^2} \tag{E-1}$$

Since the data are available at 25°C and K is needed at 60°C, we can integrate equation (E-1) assuming constant Δh^o_{rxn}

$$\Delta h^o_{rxn} = \Delta h^o_{rxn,298} = \sum \nu_i \Delta h^o_{f,298}$$

$$\Delta h^o_{rxn,298} = (\Delta h^o_f)_{CO2} + 3(\Delta h^o_f)_{H2} - (\Delta h^o_f)_{H2O} - (\Delta h^o_f)_{CH3OH}$$

$$\Delta h^o_{rxn,298} = (- 393.51)_{CO2} + 3(0)_{H2} - (- 241.82)_{H2O} - (- 200.66)_{CH3OH}$$

$$\Delta h^o_{rxn} = \Delta h^o_{rxn,298} = 48.97 \text{ kJ/mol}$$

The equilibrium constant K at 298°K is evaluated

$$\Delta g^o_{rxn,298} = (\Delta g^o_f)_{CO2} + 3(\Delta g^o_f)_{H2} - (\Delta g^o_f)_{H2O} - (\Delta g^o_f)_{CH3OH}$$

$$\Delta g^o_{rxn,298} = (- 394.36)_{CO2} + 3(0)_{H2} - (- 228.57)_{H2O} - (- 161.96)_{CH3OH}$$

$$\Delta g^o_{rxn,298} = - 3.83 \text{ kJ/mol}$$

The equilibrium constant at 298°K is then

$$K = \exp\left(- \frac{\Delta g^o_{rxn,298}}{RT}\right) = \exp\left(- \frac{-3,830}{(8.314)(298.15)}\right) = 4.69$$

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[3] Koretsky M.D., <u>Engineering and Chemical Thermodynamics</u>, Wiley, 2004, pg. 445

Integrating equation (E-1) from 298°K to 333°K yields

$$\ln \frac{K_{333}}{K_{298}} = -\frac{\Delta h_{rxn}^{o}}{R}\left(\frac{1}{T} - \frac{1}{298}\right)$$

$$\ln \frac{K_{333}}{4.69} = -\frac{48,970}{8.314}\left(\frac{1}{333} - \frac{1}{298}\right) = 2.08$$

$$K_{333} = \textbf{37.44}$$

Example 6.5-2.[4] --
Formaldehyde, CH_2O, is produced by the gas-phase pyrolysis of methanol, CH_3OH, according to the reaction

$$CH_3OH(g) \Leftrightarrow CH_2O(g) + H_2(g)$$

1) Determine the equilibrium constant at room temperature.
2) Determine the equilibrium constant at 600°C and 1 bar assuming (a) Δh_{rxn}^{o} = constant, and
(b) $\Delta h_{rxn}^{o} = \Delta h_{rxn}^{o}(T)$.

The heat capacity has the form: $\dfrac{c_{pi}}{R} = A_i + B_i T + C_i T^2 + D_i T^{-2}$

	$CH_2O(g)$	$CH_3OH(g)$	$H_2(g)$
$\Delta g^{o}_{f,298}$ (kJ/mol)	− 110.0	− 162.0	0
$\Delta h^{o}_{f,298}$ (kJ/mol)	− 116.0	− 200.7	0
ν_i	1	− 1	1
A_i	2.264	2.211	3.249
B_i	7.022×10^{-3}	1.222×10^{-2}	0.422×10^{-3}
C_i	-1.877×10^{-6}	-3.45×10^{-6}	0
D_i	0	0	0.083×10^{5}

Solution ---

1) <u>Determine the equilibrium constant at room temperature.</u>

$$\Delta g^{o}_{rxn,298} = \sum \nu_i \Delta g^{o}_{f,298}$$

$$\Delta g^{o}_{rxn,298} = (\Delta g^{o}_{f})_{CH2O} + (\Delta g^{o}_{f})_{H2} - (\Delta g^{o}_{f})_{CH3OH}$$

$$\Delta g^{o}_{rxn,298} = (-110.0)_{CH2O} + 3(0)_{H2} - (-162.0)_{CH3OH}$$

$$\Delta g^{o}_{rxn,298} = 52 \text{ kJ/mol}$$

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[4] Koretsky M.D., Engineering and Chemical Thermodynamics, Wiley, 2004, pg. 447

The equilibrium constant is then

$$K = \exp\left(-\frac{\Delta g^o_{rxn,298}}{RT}\right) = \exp\left(-\frac{-52,000}{(8.314)(298.15)}\right) = 7.75\times10^{-10}$$

Since $K = \dfrac{a_{CH_2O}a_{H_2}}{a_{CH_3OH}}$, very little formaldehyde will form at 298°K.

2a) <u>Determine the equilibrium constant at 600°C and 1 bar assuming Δh^o_{rxn} = constant</u>

The equilibrium constant as a function of temperature is given by

$$\frac{\partial(\ln K)}{\partial T} = \frac{\Delta h^o_{rxn}}{RT^2} \tag{E-1}$$

We need the enthalpy of reaction Δh^o_{rxn} to calculate K at 600°C.

$$\Delta h^o_{rxn} = \Delta h^o_{rxn,298} = \sum v_i \Delta h^o_{f,298}$$

$$\Delta h^o_{rxn,298} = (\Delta h^o{}_f)_{CH2O} + (\Delta h^o{}_f)_{H2} - (\Delta h^o{}_f)_{CH3OH}$$

$$\Delta h^o_{rxn,298} = (-116.0)_{CH2O} + (0)_{H2} - (-200.7)_{CH3OH}$$

$$\Delta h^o_{rxn} = \Delta h^o_{rxn,298} = 84.7 \text{ kJ/mol}$$

Integrating equation (E-1) from 298°K to 873°K yields

$$\ln\frac{K_{873}}{K_{298}} = -\frac{\Delta h^o_{rxn}}{R}\left(\frac{1}{T} - \frac{1}{298}\right)$$

$$\ln\frac{K_{873}}{7.75\times10^{-10}} = -\frac{84,700}{8.314}\left(\frac{1}{873} - \frac{1}{298}\right) = 22.5$$

$$K_{873} = \mathbf{4.66}$$

2b) <u>Determine the equilibrium constant at 600°C and 1 bar assuming $\Delta h^o_{rxn} = \Delta h^o_{rxn}(T)$</u>

The equilibrium constant at 600°C can be evaluated from

$$\ln\left(\frac{K_T}{K_{T_1}}\right) = -\frac{\Delta h_{con}}{R}\left(\frac{1}{T}-\frac{1}{T_1}\right) + \Delta A\ln\left(\frac{T}{T_1}\right) + \frac{\Delta B}{2}(T - T_1) + \frac{\Delta C}{6}(T^2 - T_1{}^2) + \frac{\Delta D}{2}\left(\frac{1}{T^2}-\frac{1}{T_1{}^2}\right)$$

In this expression

$$\frac{\Delta h_{con}}{R} = \frac{\Delta h^{o}_{con,298}}{R} - [298\Delta A + 298^2\frac{\Delta B}{2} + 298^3\frac{\Delta C}{3} - \frac{\Delta D}{298}] \qquad \text{(E-2)}$$

$$\Delta A = \sum v_i A_i = 3.302, \qquad\qquad \Delta B = \sum v_i B_i = -4.776\times10^{-3},$$

$$\Delta C = \sum v_i C_i = 1.57\times10^{-6}, \qquad\qquad \Delta D = \sum v_i D_i = 0.083\times10^{5}$$

Substituting the numerical values into equation (E-2)

$$\frac{\Delta h_{con}}{R} = \frac{84700}{8.314} - [(298)(3.302) + (298^2)\left(\frac{-4.776\times10^{-3}}{3}\right) + (298^3)\left(\frac{1.57\times10^{-6}}{3}\right) - \frac{8.3\times10^{3}}{298}]$$

$$\frac{\Delta h_{con}}{R} = 9.43\times10^{3}\ {}^{o}K$$

Performing the calculation for the equilibrium constant gives

$$\ln\left(\frac{K_{873}}{K_{298}}\right) = 23.15 \Rightarrow K_{873} = 7.75\times10^{-10}\exp(23.15) = \mathbf{8.8}$$

6.6 Homogeneous Gas Phase Reaction

The equilibrium constant is given by the expression

$$K = \Pi\left(\frac{\hat{f}_i}{f_i^{o}}\right)^{v_i} \qquad\qquad (6.6\text{-}1)$$

For gas phase we choose the standard state pressure to be ideal gas at 1 bar, therefore

$$f_i^{o} = 1\ \text{bar} \qquad\qquad (6.6\text{-}2)$$

The fugacity in equation (6.6-1) must have unit of bar and becomes

$$K = \Pi\left(\hat{f}_i[bar]\right)^{v_i} = \Pi\left(y_i\hat{\varphi}_i\ P[bar]\right)^{v_i} \qquad\qquad (6.6\text{-}3)$$

For the calculation of the equilibrium concentration we usually assume $\hat{\varphi}_i = \varphi_i$ so that equation (6.6-3) can be written as

$$K = \Pi\left(y_i \varphi_i P\right)^{\nu_i} \tag{6.6-4}$$

For an ideal gas $\hat{\varphi}_i = 1$, equation (6.6-3) can be simplified to

$$K = \Pi\, y_i^{\nu_i} P^{\nu_i} \tag{6.6-4}$$

Example 6.6-1.[5] ---
Ethylene is produced from the decomposition of ethane according to the reaction

$$C_2H_6(g) \Leftrightarrow C_2H_4(g) + H_2(g)$$

Determine the equilibrium composition at 1000°C and 1 bar assuming Δh^o_{rxn} = constant.

	C_2H_6(g)	C_2H_4(g)	H_2(g)
$\Delta g^o_{f,298}$ (kJ/mol)	− 32.84	68.15	0
$\Delta h^o_{f,298}$ (kJ/mol)	− 84.68	52.26	0
ν_i	− 1	1	1

Solution ---

Determine the equilibrium constant at room temperature

$$\Delta g^o_{rxn,298} = \sum \nu_i \Delta g^o_{f,298}$$

$$\Delta g^o_{rxn,298} = (\Delta g^o_f)_{C2H4} + (\Delta g^o_f)_{H2} - (\Delta g^o_f)_{C2H6}$$

$$\Delta g^o_{rxn,298} = (68.15)_{C2H4} + 3(0)_{H2} - (- 32.84)_{C2H6}$$

$$\Delta g^o_{rxn,298} = 100.99 \text{ kJ/mol}$$

The equilibrium constant is then

$$K = \exp\left(-\frac{\Delta g^o_{rxn,298}}{RT}\right) = \exp\left(-\frac{100,990}{(8.314)(298.15)}\right) = 2.0246\times10^{-18}$$

The equilibrium constant as a function of temperature is given by

$$\frac{\partial(\ln K)}{\partial T} = \frac{\Delta h^o_{rxn}}{RT^2} \tag{E-1}$$

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[5] Koretsky M.D., Engineering and Chemical Thermodynamics, Wiley, 2004, pg. 451

We need the enthalpy of reaction Δh^o_{rxn} to calculate K at 1000^oC.

$$\Delta h^o_{rxn} = \Delta h^o_{rxn,298} = \sum v_i \Delta h^o_{f,298}$$

$$\Delta h^o_{rxn,298} = (\Delta h^o_f)_{C2H4} + (\Delta h^o_f)_{H2} - (\Delta h^o_f)_{C2H6}$$

$$\Delta h^o_{rxn,298} = (52.26)_{C2H4} + (0)_{H2} - (-84.68)_{C2H6}$$

$$\Delta h^o_{rxn} = \Delta h^o_{rxn,298} = 136.94 \text{ kJ/mol}$$

Integrating equation (E-1) from 298^oK to 873^oK yields

$$\ln \frac{K_{1273}}{K_{298}} = -\frac{\Delta h^o_{rxn}}{R}\left(\frac{1}{T} - \frac{1}{298}\right)$$

$$\ln \frac{K_{873}}{2.0246 \times 10^{-18}} = -\frac{136{,}940}{8.314}\left(\frac{1}{1273} - \frac{1}{298}\right) = 42.3331$$

$$K_{1273} = \textbf{4.9133}$$

The equilibrium constant K can also be expressed in terms of the activities:

$$K = \frac{a_{C_2H_4}a_{H_2}}{a_{C_2H_6}} = \frac{\left(\dfrac{\hat{f}_{C_2H_4}}{f^o_{C_2H_4}}\right)\left(\dfrac{\hat{f}_{H_2}}{f^o_{H_2}}\right)}{\left(\dfrac{\hat{f}_{C_2H_6}}{f^o_{C_2H_6}}\right)} \qquad \text{(E-2)}$$

Assume ideal gas $\hat{f}_i = P_i$, $f^o_i = P^o_{C2H6} = P^o_{C2H4} = P^o_{H2} = 1$ bar, equation (E-2) becomes

$$K = \frac{\left(\dfrac{\hat{f}_{C_2H_4}}{f^o_{C_2H_4}}\right)\left(\dfrac{\hat{f}_{H_2}}{f^o_{H_2}}\right)}{\left(\dfrac{\hat{f}_{C_2H_6}}{f^o_{C_2H_6}}\right)} = \frac{\left(\dfrac{P_{C_2H_4}}{P^o_{C_2H_4}}\right)\left(\dfrac{P_{H_2}}{P^o_{H_2}}\right)}{\left(\dfrac{P_{C_2H_6}}{P^o_{C_2H_6}}\right)} = \frac{\left(\dfrac{y_{C_2H_4}P}{1\text{ bar}}\right)\left(\dfrac{y_{H_2}P}{1\text{ bar}}\right)}{\left(\dfrac{y_{C_2H_6}P}{1\text{ bar}}\right)} \qquad \text{(E-3)}$$

Since $P = 1$ bar, equation (E-3) becomes

$$K = \frac{\left(\dfrac{y_{C_2H_4}P}{1\,\text{bar}}\right)\left(\dfrac{y_{H_2}P}{1\,\text{bar}}\right)}{\left(\dfrac{y_{C_2H_6}P}{1\,\text{bar}}\right)} = \frac{y_{C_2H_4}\,y_{H_2}}{y_{C_2H_6}} = 4.9133 \qquad\qquad \text{(E-4)}$$

We have $\qquad C_2H_6(g) \Leftrightarrow C_2H_4(g) + H_2(g)$

	C_2H_6	C_2H_4	H_2	Total
Initial	1	0	0	1
Final	$1-\zeta$	ζ	ζ	$1+\zeta$

The mole fractions of C_2H_6, C_2H_4, and H_2 are given by

$$y_{C2H6} = \frac{1-\zeta}{1+\zeta}, \; y_{C2H4} = \frac{\zeta}{1+\zeta}, \text{ and } y_{H2} = \frac{\zeta}{1+\zeta}$$

Substituting the mole fractions in terms of extent of reaction into equation (E-4) gives

$$\frac{\left(\dfrac{\zeta}{1+\zeta}\right)^2}{\dfrac{1-\zeta}{1+\zeta}} = 4.9133 \Rightarrow \frac{\zeta^2}{(1-\zeta)(1+\zeta)} = 4.9133$$

$$\zeta^2 = 4.9133(1-\zeta^2) \Rightarrow \zeta^2 = \frac{4.9133}{5.9133} = 0.8309$$

$$\zeta = 0.9115$$

The equilibrium concentration of $C_2H_4(g)$ is then

$$y_{C2H4} = \frac{\zeta}{1+\zeta} = \mathbf{0.4769}$$

Example 6.6-2. --
Calculate the partial pressure of monatomic hydrogen in hydrogen gas at 2000°K and 1 atm for

$$0.5H_2(g) \Leftrightarrow H(g)$$
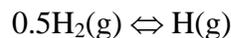
Data: $\Delta h^o_{rxn,298} = 217{,}990$ J/mol, $\Delta s^o_{rxn,298} = 49.35$ J/mol·°K, heat capacity of H(g) = 1.5R, and heat capacity of $H_2(g) = 31$ J/mol·°K.

Solution ---

$$\Delta g^{\circ}{}_{rxn,2000} = \Delta h^{\circ}{}_{rxn,2000} - T\Delta s^{\circ}{}_{rxn,2000}$$

The heat of reaction $\Delta h^{\circ}{}_{rxn,2000}$ and the entropy of reaction $\Delta s^{\circ}{}_{rxn,2000}$ can be calculated using the heat capacity data as follows:

$$\Delta h^{\circ}{}_{rxn,2000} = 0.5c_{p,H2}(298 - 2000) + \Delta h^{\circ}{}_{rxn,298} + c_{p,H}(2000 - 298)$$

$$\Delta h^{\circ}{}_{rxn,2000} = \Delta h^{\circ}{}_{rxn,298} + 1702(c_{p,H} - 0.5c_{p,H2}) = 217{,}990 + 1702(1.5 \times 8.314 - 0.5 \times 31) = 212{,}830 \text{ J}$$

$$\Delta s^{\circ}{}_{rxn,2000} = 0.5c_{p,H2}\int_{2000}^{298}\frac{dT}{T} + \Delta s^{\circ}{}_{rxn,298} + c_{p,H}\int_{298}^{2000}\frac{dT}{T} = \Delta s^{\circ}{}_{rxn,298} + (c_{p,H} - 0.5c_{p,H2})\ln\frac{2000}{298}$$

$$\Delta s^{\circ}{}_{rxn,2000} = 39.35 + (1.5 \times 8.314 - 0.5 \times 31)\ln\frac{2000}{298} = 43.58 \text{ J/mol}\cdot{}^{\circ}\text{K}$$

$$\Delta g^{\circ}{}_{rxn,2000} = \Delta h^{\circ}{}_{rxn,2000} - T\Delta s^{\circ}{}_{rxn,2000} = 212{,}830 - 2000(43.58) = 125{,}670 \text{ J/mol}$$

The equilibrium constant is given by

$$K = \exp\left(-\frac{\Delta g^{\circ}{}_{rxn,2000}}{RT}\right) = \exp\left(-\frac{125{,}670}{(8.314)(2000)}\right) = 5.22 \times 10^{-4}$$

For ideal gas, the fugacity can be replaced by pressure with standard state pressure equal to 1 atm.

$$K = \frac{\dfrac{P_H}{1\text{ atm}}}{\left(\dfrac{P_{H_2}}{1\text{ atm}}\right)^{0.5}} = \frac{P_H}{\left(P_{H_2}\right)^{0.5}} = \frac{P_H}{\left(1 - P_H\right)^{0.5}} = 5.22 \times 10^{-4}$$

The partial pressure of monatomic hydrogen is then

$$P_H = 5.22 \times 10^{-4} \text{ atm}$$

Chapter 6

Example 6.6-1.[6] --

Ammonia is produced from a stoichiometric feed of nitrogen and hydrogen.

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$$
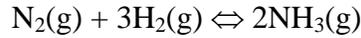
Determine the maximum possible conversion at 500^oC and 300 bar using (a) ideal gas law and (b) the Van der Waals equation of state.

The heat capacity has the form: $\dfrac{c_{pi}}{R} = A_i + B_iT + C_iT^2 + D_iT^2$

	NH$_3$(g)	N$_2$(g)	H$_2$(g)
$\Delta g^o_{f,298}$ (kJ/mol)	-16.45	0	0
$\Delta h^o_{f,298}$ (kJ/mol)	-46.11	0	0
ν_i	2	-1	-3
A_i	3.578	3.280	3.249
B_i	3.020×10^{-3}	0.593×10^{-3}	0.422×10^{-3}
C_i	0	0	0
D_i	-0.186×10^5	0.040×10^5	0.083×10^5

Solution --

Determine the equilibrium constant at room temperature

$$\Delta g^o_{rxn,298} = \sum \nu_i \Delta g^o_{f,298}$$

$$\Delta g^o_{rxn,298} = 2(\Delta g^o_f)_{NH3} - (\Delta g^o_f)_{N2} - 3(\Delta g^o_f)_{H2}$$

$$\Delta g^o_{rxn,298} = 2(-16.45)_{NH3} - (0)_{N2} - 3(0)_{H2} = -32.9 \text{ kJ/mol}$$

The equilibrium constant is then

$$K = \exp\left(-\frac{\Delta g^o_{rxn,298}}{RT}\right) = \exp\left(-\frac{-32,900}{(8.314)(298.15)}\right) = 5.81 \times 10^5$$

The standard heat of reaction is needed to evaluate equilibrium constant at 500^oC

$$\Delta h^o_{rxn,298} = \sum \nu_i \Delta h^o_{f,298}$$

$$\Delta h^o_{rxn,298} = 2(\Delta h^o_f)_{NH3} - (\Delta h^o_f)_{N2} - 3(\Delta h^o_f)_{H2}$$

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[6] Koretsky M.D., <u>Engineering and Chemical Thermodynamics</u>, Wiley, 2004, pg. 454

$$\Delta h^{o}_{rxn,298} = 2(-46.11)_{NH3} - (0)_{N2} - 3(0)_{H2} = -92.22 \text{ kJ/mol}$$

The equilibrium constant at 500°C can be evaluated from

$$\ln\left(\frac{K_T}{K_{T_1}}\right) = -\frac{\Delta h_{con}}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right) + \Delta A \ln\left(\frac{T}{T_1}\right) + \frac{\Delta B}{2}(T - T_1) + \frac{\Delta D}{2}\left(\frac{1}{T^2} - \frac{1}{T_1^2}\right) \qquad \text{(E-1)}$$

In this expression

$$\frac{\Delta h_{con}}{R} = \frac{\Delta h^{o}_{con,298}}{R} - [298\Delta A + 298^2\frac{\Delta B}{2} - \frac{\Delta D}{298}] \qquad \text{(E-2)}$$

$$\Delta A = \sum v_i A_i = -5.871, \qquad\qquad \Delta B = \sum v_i B_i = 4.180\times10^{-3},$$

$$\Delta C = \sum v_i C_i = 0, \qquad\qquad \Delta D = \sum v_i D_i = -0.661\times10^5$$

Substituting the numerical values into equation (E-2)

$$\frac{\Delta h_{con}}{R} = \frac{-92,220}{8.314} - [(298)(-5.871) + (298^2)\left(\frac{4.180\times10^{-3}}{3}\right) - \frac{-0.661\times10^5}{298}]$$

$$\frac{\Delta h_{con}}{R} = -9.75\times10^3 \text{ °K}$$

Performing the calculation for the equilibrium constant gives

$$\ln\left(\frac{K_{773}}{K_{298}}\right) = -24.39 \Rightarrow K_{773} = 5.81\times10^5\exp(-24.39) = 1.483\times10^{-5}$$

The equilibrium constant K can also be expressed in terms of the activities:

$$K = \frac{a^2_{NH_3}}{a_{N_2}a^3_{H_2}} = \frac{\left(\dfrac{\hat{f}_{NH_3}}{f^{o}_{NH_3}}\right)^2}{\left(\dfrac{\hat{f}_{N_2}}{f^{o}_{N_2}}\right)\left(\dfrac{\hat{f}_{H_2}}{f^{o}_{H_2}}\right)^3} \qquad \text{(E-3)}$$

We choose the standard state pressure to be ideal gas at 1 bar, therefore

$$f^{o}_i = 1 \text{ bar}$$

The fugacity of species i in the vapor phase can be expressed in terms of the mole fraction, y_i, fugacity coefficient, $\hat{\varphi}_i$, and total pressure, P, as

$$\hat{f}_i = y_i \hat{\varphi}_i P$$

Hence

$$K = \frac{y_{NH_3}^2 \hat{\varphi}_{NH_3}^2}{y_{N_2} \varphi_{N_2} y_{H_2}^3 \hat{\varphi}_{H_2}^3} P^{-2} \tag{E-4}$$

(a) <u>Ideal gas law</u>

For ideal gas, $\hat{\varphi}_i = 1$, the equilibrium constant is simplified to

$$K_{ideal} = \frac{y_{NH_3}^2}{y_{N_2} y_{H_2}^3} P^{-2} \tag{E-5}$$

We have $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$

	N_2	H_2	NH_3	Total
Initial	1	3	0	4
Final	$1 - \zeta$	$3(1 - \zeta)$	2ζ	$4 - 2\zeta$

The mole fractions of N_2, H_2, and NH_3 are given by

$$y_{N2} = \frac{1 - \zeta}{4 - 2\zeta}, \; y_{H2} = \frac{3 - 3\zeta}{4 - 2\zeta}, \; \text{and } y_{NH3} = \frac{2\zeta}{4 - 2\zeta}$$

Substituting the mole fractions in terms of extent of reaction into equation (E-5) yields

$$1.483 \times 10^{-5} = \frac{(2\zeta)^2 (4 - 2\zeta)^2}{(1 - \zeta)(3 - 3\zeta)^3} P^{-2}$$

For $P = 300$ bar, we have

$$(2\zeta)^2(4 - 2\zeta) = 1.3347(1 - \zeta)(3 - 3\zeta)^3$$

We can use the following Matlab statements to solve the nonlinear equation

```
>> ff=inline('(2*z)^2*(4-2*z)^2-1.3347*(1-z)*(3-3*z)^3');
>> zeta=fsolve(ff,.5,optimset('Display','off'))
zeta =
   0.3676
```

The extent of reaction at 500°K and 300 bar is $\zeta = 0.3676$.

(b) The Van der Waals equation of state.

We assume that $\hat{\varphi}_i = \varphi_1$ = fugacity of pure species that can be evaluated from the Van de Waals equation of state

$$\ln\varphi_1 = (Z - 1) - \frac{A}{Z} - \ln(Z - B) \tag{E-6}$$

From Example 4.2-2, the Van der Waals equation of state $P = \dfrac{RT}{v - b} - \dfrac{a}{v^2}$ can be written in terms of the compressibility factor $Z = \dfrac{Pv}{RT}$ as

$$Z^3 - (1 + B)Z^2 + AZ - AB = 0 \tag{E-7}$$

In this equation $B = \dfrac{bP}{RT}$ and $A = \dfrac{aP}{(RT)^2}$ where the constant a and b can be evaluated from the critical properties:

$$a = \frac{27}{64}\frac{(RT_c)^2}{P_c} \text{ and } b = \frac{RT_c}{8P_c} \tag{E-8}$$

Table E-1 lists the critical properties, the parameters a and b evaluated from equation (E-8), the compressibility from equation (E-7), and the fugacity coefficient from equation (E-6).

Table E-1 Summary of Fugacity Coefficient Calculation

	NH$_3$(g)	N$_2$(g)	H$_2$(g)
T_c [°K]	405.5	126.2	33.3
P_c [atm]	111.3	33.5	12.8
a [Pa·m^6/mol^2]	0.425	0.137	0.0249
b [m^3/mol]	3.74×10^{-5}	3.86×10^{-5}	2.67×10^{-5}
Z	0.897	1.105	1.11
φ_1	0.885	1.098	1.114

The fugacity coefficients can be substituted into equation (E-4)

$$K = \frac{y_{NH_3}^2 \hat{\varphi}_{NH_3}^2}{y_{N_2}\varphi_{N_2} y_{H_2}^3 \hat{\varphi}_{H_2}^3} P^{-2} \tag{E-4}$$

$$K = 0.516\frac{y_{NH_3}^2}{y_{N_2} y_{H_2}^3} P^{-2}$$

In terms of the extent of reaction the above equation becomes

$$1.483 \times 10^{-5} = 0.516 \frac{(2\zeta)^2 (4 - 2\zeta)^2}{(1 - \zeta)(3 - 3\zeta)^3} P^{-2}$$

For $P = 300$ bar, we have

$$(2\zeta)^2 (4 - 2\zeta) = 2.5868(1 - \zeta)(3 - 3\zeta)^3$$

We can use the following Matlab statements to solve the nonlinear equation

```
>> ff=inline('(2*z)^2*(4-2*z)^2-2.5868*(1-z)*(3-3*z)^3');
>> zeta=fsolve(ff,.5,optimset('Display','off'))
zeta =
   0.4311
```

The extent of reaction at 500°K and 300 bar is $\zeta = 0.4311$.

Table E-2 lists the Matlab program to evaluate the fugacity coefficient

Table E-2 --
```
% Example 6.6-1c, compressibility using Van der Waals EQS
%
R = 8.314; % Pa.m3/(mol.K)
Tc=[405.5 126.2 33.3] ; % Degree K
Pc=[111.3 33.5 12.8]*1.01325e5 ; %Pa
av=27*(R*Tc).^2./(64*Pc); % Pa.m6/mol2
bv=R*Tc./(8*Pc); % m3/mol
name='NH3*N2*H2';
%
P=3e7; % Pa
T=773; % K
for ic=1:3
   ib=3*(ic-1)+1;ie=ib+2;
   ni=name(ib:ie);
   a=av(ic);b=bv(ic);
%
disp(ni)
fprintf('a(Pa.m6/mol2) = %g, b(m3/mol) = %g\n',a,b)
A=a*P/(R*T)^2;B=b*P/(R*T);
fprintf('A = %8.5e, B = %8.5e\n',A,B)
b2=-(1+B);b1=A;b0=-A*B;
fprintf('b2 = %8.5e, b1 = %8.5e, b0 = %8.5e\n',b2,b1,b0)
Z=1;
for i=1:20
   fz=((Z+b2)*Z+b1)*Z+b0;
```

```
    dfz=(3*Z+2*b2)*Z+b1;
    eZ=fz/dfz;Z=Z-eZ;
    if abs(eZ)<.00001; break; end
end
foP=exp((Z-1)-A/Z-log(Z-B));
fprintf('Z = %8.5f, f/P = %8.5f\n',Z,foP)
end


>> e6d6d1c
NH3
a(Pa.m6/mol2) = 0.425181, b(m3/mol) = 3.73679e-005
A = 3.08828e-001, B = 1.74434e-001
b2 = -1.17443e+000, b1 = 3.08828e-001, b0 = -5.38700e-002
Z =  0.89713, f/P =  0.88484
*N2
a(Pa.m6/mol2) = 0.136824, b(m3/mol) = 3.86383e-005
A = 9.93810e-002, B = 1.80364e-001
b2 = -1.18036e+000, b1 = 9.93810e-002, b0 = -1.79247e-002
Z =  1.10511, f/P =  1.09792
*H2
a(Pa.m6/mol2) = 0.0249325, b(m3/mol) = 2.66832e-005
A = 1.81096e-002, B = 1.24557e-001
b2 = -1.12456e+000, b1 = 1.81096e-002, b0 = -2.25568e-003
Z =  1.11007, f/P =  1.11444
```

6.7 Heterogeneous Reaction

We will consider an equilibrium system with a gas phase and one or more condensed phases. The mole fractions in the equilibrium relations refer to the mole fraction in a given phase, not the total mole fraction. When the heterogeneous system is in equilibrium, there will be chemical equilibrium in the gas phase and also phase equilibrium between species in the gas phase and the pure condensed phases. When a pure condensed phase is present, the partial pressure of that component in the gas phase will equal the vapor or saturation pressure of the pure condensed phase. Hence a pure condensed phase cannot exist if the partial pressure of that component is less than the vapor pressure.

The activity of a pure condensed phase is given by

$$a = \frac{f}{f^o}$$

In this definition, f is the fugacity of the pure solid in the equilibrium system and f^o is the fugacity of the pure condensed phase at 1 bar. For a pure substance at given T and P, we have

$$d\mu = vdP - sdT \tag{6.7-1}$$

At constant temperature

$$d\mu = vdP = RTd(\ln f) \tag{6.7-2}$$

Integrating equation (6.7-2) from the standard pressure 1 bar to the pressure of the system yields

$$RT\int_{f_o}^{f} d(\ln f) = \int_{1}^{P} vdP$$

$$RT\ln\left(\frac{f}{f^o}\right) = RT\ln a = v(P - 1) \tag{6.7-3}$$

We have assumed incompressible for the volume of the condensed phase. The activity is given by

$$a = \exp\left[\frac{v(P - 1)}{RT}\right] \tag{6.7-3}$$

Except for very high pressures the activity is close to unity. The state of the pure condensed phase at equilibrium is not significantly different from the standard state.

Example 6.7-1[7] ---
Determine the activity of liquid water at 30°C and at the saturation pressure, 10 bar, and 100 bar.

Solution --

At 30°C, P^{sat} = 0.0424 bar. We will assume the volume of liquid water remains constant at the saturation temperature of 30°C.

$$v = 0.001004 \text{ m}^3/\text{kg} = (0.001004)(18.02) = 0.01809 \text{ m}^3/\text{kmol}$$

The activity of liquid water at 30°C and 0.0424 bar is

$$a = \exp\left[\frac{v(P - 1)}{RT}\right] = \exp\left\{\frac{0.01809(0.0424 - 1) \times 10^5}{(8314.3)(303.15)}\right\} = \mathbf{0.9993}$$

The activity of liquid water at 30°C and 10 bar is then

$$a = \exp\left\{\frac{0.01809(10 - 0.0424) \times 10^5}{(8314.3)(303.15)}\right\} = \mathbf{1.0065}$$

The activity of liquid water at 30°C and 100 bar is

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[7] Kyle, B.G., Chemical and Process Thermodynamics, Prentice Hall, 1999, pg. 257

$$a = \exp\left\{\frac{0.01809(100 - 0.0424) \times 10^5}{(8314.3)(303.15)}\right\} = \mathbf{1.0736}$$

Hence the fugacity of a pure liquid varies little over a moderate pressure range.

Example 6.7-2[8] ---
Determine the equilibrium conversion for the isomerization reaction of methylcyclopentane ($CH_3C_5H_9$) to cyclohexane (C_6H_{12}) at 298°K. Gibbs energies of formation are given at 298°K as: $\Delta g^o_{f,CH3C5H9} = 31.72$ [kJ/mol] and $\Delta g^o_{f,C6H12} = 26.89$ [kJ/mol]

Solution ---

Determine the equilibrium constant at room temperature

$$\Delta g^o_{rxn,298} = \sum v_i \Delta g^o_{f,298}$$

$$\Delta g^o_{rxn,298} = (\Delta g^o_f)_{C6H12} - (\Delta g^o_f)_{CH3C5H9} = 26.89 - 31.72 = -4.83 \text{ kJ/mol}$$

The equilibrium constant is then

$$K = \exp\left(-\frac{\Delta g^o_{rxn,298}}{RT}\right) = \exp\left(-\frac{-4,830}{(8.314)(298.15)}\right) = 7.0182$$

The equilibrium constant is also given by the expression

$$K = \Pi\left(\frac{\hat{f}_i}{f_i^o}\right)^{v_i} = \Pi\left(\frac{x_i \gamma_i f_i}{f_i^o}\right)^{v_i} \tag{E-1}$$

Except for very high pressure the ratio $\dfrac{f_i}{f_i^o} = \exp\left[\dfrac{v(P-1)}{RT}\right]$ is close to unity. Equation (E-1) becomes

$$K = \Pi(x_i \gamma_i)^{v_i} \tag{E-2}$$

For ideal solution: $K = \Pi(x_i)^{v_i} = \dfrac{x_{C_6H_{12}}}{x_{CH_3C_5H_9}} = \dfrac{\zeta}{1-\zeta} = 7.0182$

$$\zeta = \frac{7.0182}{8.0182} = 0.8753 \Rightarrow 87.5\% \text{ of the liquid exists as cyclohexane.}$$

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[8] Koretsky M.D., <u>Engineering and Chemical Thermodynamics</u>, Wiley, 2004, pg. 456

Chapter 6

Example 6.7-3[9] ---

Calcium carbonate can dissociate according to the following reaction:

$$CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$$

Determine the equilibrium pressure for a closed system with pure $CaCO_3$ in vacuum at $1000^\circ K$. Assume that the two solid phases are completely immiscible.

	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
$\Delta g^\circ_{f,1000}$ (kJ/mol)	-951.25	-531.09	-395.81

Solution ---

The equilibrium constant K can be expressed in terms of the activities:

$$K = \frac{a_{CaO} a_{CO_2}}{a_{CaCO_3}} = \frac{\left(\dfrac{\hat{f}_{CaO}}{f^o_{CaO}}\right)\left(\dfrac{\hat{f}_{CO_2}}{f^o_{CO_2}}\right)}{\left(\dfrac{\hat{f}_{CaCO_3}}{f^o_{CaCO_3}}\right)} \qquad \text{(E-1)}$$

Since we have pure solid phases:

$$a_{CaO} = \frac{\hat{f}_{CaO}}{f^o_{CaO}} = \frac{f_{CaO}}{f^o_{CaO}} = \exp\left[\frac{v(P-1)}{RT}\right] \approx 1 \text{ at low pressure}$$

$$a_{CaCO_3} = \frac{\hat{f}_{CaCO_3}}{f^o_{CaCO_3}} = \frac{f_{CaCO_3}}{f^o_{CaCO_3}} = \exp\left[\frac{v(P-1)}{RT}\right] \approx 1 \text{ at low pressure}$$

For the gas phase

$$a_{CO_2} = \frac{\hat{f}_{CO_2}}{f^o_{CO_2}} = \frac{y_{CO_2} P}{1\, bar} = P_{CO_2}$$

Therefore $K = P_{CO_2} == \exp\left(-\dfrac{\Delta g^o_{rxn,1000}}{RT}\right)$

The Gibbs energy of reaction is given by

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[9] Koretsky M.D., <u>Engineering and Chemical Thermodynamics</u>, Wiley, 2004, pg. 457

$$\Delta g^o{}_{rxn,1000} = \sum \nu_i \Delta g^o{}_{f,1000}$$

$$\Delta g^o{}_{rxn,1000} = (\Delta g^o{}_f)_{CaO} + (\Delta g^o{}_f)_{CO2} - (\Delta g^o{}_f)_{CaCO3}$$

$$\Delta g^o{}_{rxn,1000} = (-531.09)_{CaO} + (-395.81)_{CO2} - (-951.25)_{CaCO3}$$

$$\Delta g^o{}_{rxn,1000} = 24.35 \text{ kJ/mol}$$

$$K = \exp\left(-\frac{\Delta g^o{}_{rxn,1000}}{RT}\right) = \exp\left(-\frac{24,350}{(8.314)(298.15)}\right) = 0.0535$$

Therefore, calcium carbonate will dissociate at 1000°K until the pressure reaches 0.0535 bar or until all the available $CaCO_3(s)$ reacted.

6.8 Thermodynamics of Pack Cementation

Pack cementation is a process where a pure element or master alloy is deposited on the surface of a superalloy to extend its life in corrosive and oxidizing environments at high temperature. There are four constituents to this process: a filler, a pure element or master alloy, an activator, and a substrate. The inert or filler provides a medium for vapor transport, e.g., aluminum oxide Al_2O_3. The pure element or master alloy will be deposited on the substrate. The activator is used to transport the master alloy through the filler to the substrate, which is the surface of the superalloy. We will consider the case where aluminum with AlF_3 activator will be mixed with aluminum oxide powder in a pack cementation process at 1400°K. A schematic of the process is shown in Figure 6.8-1 where the system is maintained at 1 atm in an environment of Argon gas. The bulk pack is the region where aluminum and activator exist within the filler. In the depleted zone, there is no aluminum or activator. For this process aluminum is transferred from the bulk pack to the substrate in the form of aluminum flouride vapor, under the action of the thermodynamic activity gradient that exists between the pack and substrate.
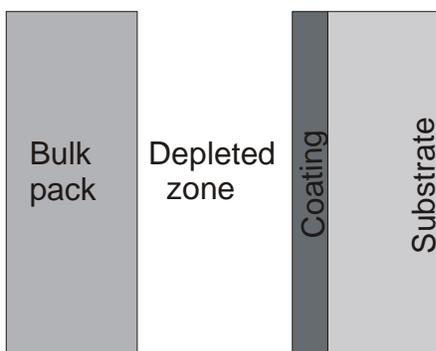
Figure 6.8-1 Schematic of pack aluminizing process.

At the bulk pack the following reactions will occur

$$AlF_3(s) = AlF_3(g) \tag{6.8-1}$$

$$2Al(l) + AlF_3(s) = 3AlF(g) \tag{6.8-2}$$

$$Al(l) + 2AlF_3(s) = 3AlF_2(g) \tag{6.8-3}$$

$$2AlF_3(g) = Al_2F_6(g) \tag{6.8-4}$$

Since the melting point of pure aluminum is 933.6^oK, aluminum will exist in the bulk pack as a liquid. The five partial pressures (P_{AlF}, P_{AlF2}, P_{AlF3}, P_{Al2F6}, and P_{Ar}) in the bulk pack can be obtained from the four equilibrium conditions above and the assumption that

$$P_{AlF} + P_{AlF2} + P_{AlF3} + P_{Al2F6} + P_{Ar} = 1 \text{ atm} \tag{6.8-5}$$

Table 6.8-1 provides data for the Gibbs energies of formation for the species present in the process.

Table 6.8-1 $\Delta g^o{}_{rxn,1400}$ in kcal/mol·^oK

Thermodynamic Data for Mineral Technology, L. B. Pankrats, J. M. Stuve, and N. A. Gokcen

Species	$AlF_3(c)$	$AlF(g)$	$AlF_2(g)$	$AlF_3(g)$	$Al(c,l)$	$Al_2F_6(g)$
$\Delta g^o{}_{rxn,1400}$	− 274.125	− 88.241	− 173.235	− 267.838	0	− 532.504

The equilibrium constant K is then calculated from

$$K = \exp(-\Delta g^o{}_{rxn,1400}/RT) \tag{6.8-6}$$

In this equation, $\Delta g^o{}_{rxn,1400} = \sum v_i \Delta g^o{}_{f,1400}$

The equilibrium constant K_1 for reaction (6.8-2): [$2Al(l) + AlF_3(s) = 3AlF(g)$] can be expressed in terms of the activities:

$$K = \frac{a_{AlF}^3}{a_{AlF_3} a_{Al}^2} \tag{6.8-7}$$

Since we have pure solid and liquid phase:

$$a_{AlF} = \frac{\hat{f}_{AlF}}{f^o_{AlF}} = \frac{f_{AlF}}{f^o_{AlF}} = \exp\left[\frac{v(P-1)}{RT}\right] = 1$$

$$a_{Al} = \frac{\hat{f}_{Al}}{f^o_{Al}} = \frac{f_{Al}}{f^o_{Al}} = \exp\left[\frac{v(P-1)}{RT}\right] = 1$$

For the gas phase

$$a_{AlF_3} = \frac{\hat{f}_{AlF_3}}{f^o_{AlF_3}} = \frac{y_{AlF_3} P}{1 \text{ atm}} = P_{AlF_3}$$

6-35

The equilibrium constants for the four reactions (6.8-1) - (6.8-4) are then related to the partial pressures by the following relations

$$K_1 = P_{AlF3} \tag{6.8-8}$$

$$K_2 = P_{AlF}{}^3 \tag{6.8-9}$$

$$K_3 = P_{AlF2}{}^3 \tag{6.8-10}$$

$$K_4 = \frac{P_{Al2F6}}{P_{AlF3}^2} \tag{6.8-11}$$

The five partial pressures can be easily determined from equations (6.8-8)-(6.8-11) and equation (6.8-5). The results are

$$P_{AlF3} = 0.1043, \; P_{AlF} = 0.3241, \; P_{AlF2} = 0.0327, \; P_{Al2F6} = 0.0035, \text{ and } P_{Ar} = 0.5353$$

The following Matlab program is used to evaluate the partial pressures

```
-------------------------------------------------------------------------------
% Aluminum packing with AlF3 activator
% T = 1400 K
R = 1.987;T = 1400;RT = R*T;P=1;
% Data at 1400 K
dGAIF3c = -274.125;dGAIF3 = -267.838;
dGAIF = -88.241; dGAIF2 = -173.235;
dGHF = -67.047; dGAl2F6 = -532.504;
%
dGr = dGAIF3 - dGAIF3c; K1 = exp(-1000*dGr/RT);
dGr = 3*dGAIF- dGAIF3c; K2 = exp(-1000*dGr/RT);
dGr = 3*dGAIF2 - 2*dGAIF3c; K3 = exp(-1000*dGr/RT);
dGr = dGAl2F6 - 2*dGAIF3; K4 = exp(-1000*dGr/RT);
% Evaluate the partial pressure at the bulk pack
%
PAIF3 = K1; PAIF = K2^(1/3); PAIF2 = K3^(1/3); PAl2F6 = K4*PAIF3^2;
PAr = 1 - (PAIF3 + PAIF + PAIF2 + PAl2F6);
disp('Partial pressure in atm, diffusion in argon')
disp('PAIF3        PAIF       PAIF2       PAl2F6       PAr')
fprintf('%10.3e %10.3e %10.3e %10.3e %10.3e
%10.3e\n',PAIF3,PAIF,PAIF2,PAl2F6,PAr)

>> c6d8
Partial pressure in atm, diffusion in argon
PAIF3        PAIF       PAIF2       PAl2F6      PAr
1.043e-001  3.241e-001  3.270e-002  3.481e-003  5.353e-001
-------------------------------------------------------------------------------------------------
```

6.9 Equilibrium in Electrochemical Systems

In electrochemical systems we can obtain work by applying an electric potential to two electrodes. A **galvanic cell** is an electrochemical cell that uses a spontaneous reaction to produce useful work. When copper and iron pipes are connected, a galvanic cell is created as shown in Figure 6.9-1. Electron will flow from iron with lower electron affinity to copper with higher affinity until a few volts counterbalancing electrical potential is established between them. An electrochemical cell also needs an electrolytic solution in contact with the two metals that allows ions to be transported from one metal to the other. Water is an electrolyte since it contains H^+, OH^-, and other ions.
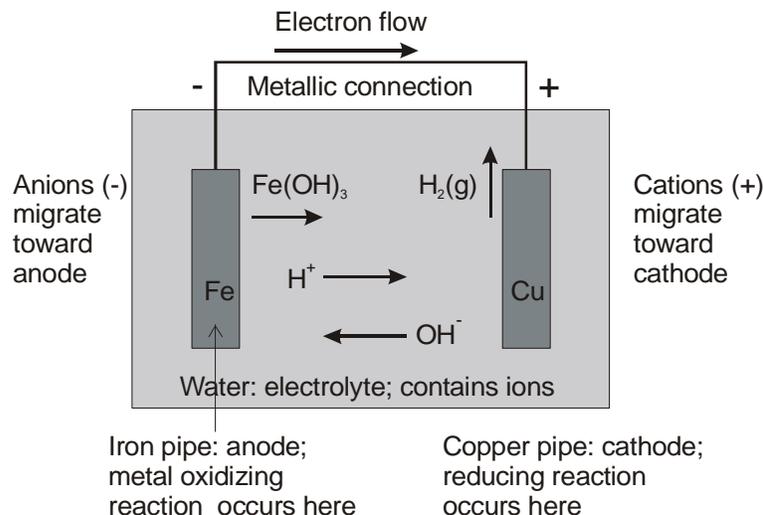
Figure 6.9-1 Schematic of a galvanic cell.

An **electrolytic cell** is an electrochemical cell that requires electrical work to induce a reaction that would not occur spontaneously. An example of an electrolytic cell is shown in Figure 6.9-2 where both electrodes are immersed in a common electrolyte.
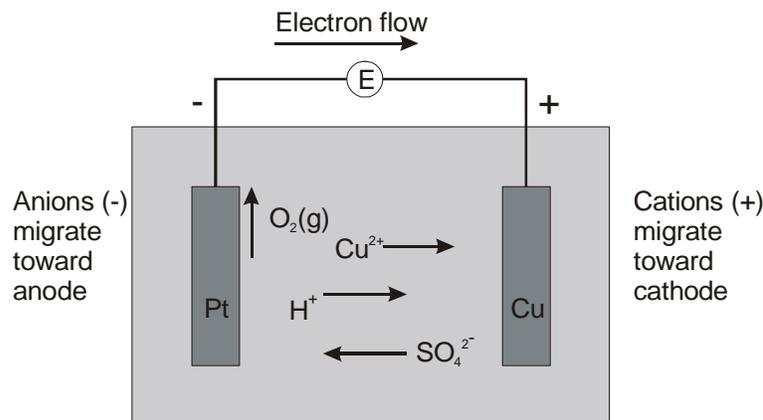
Figure 6.9-2 Schematic of an electrolytic cell.

At the cathode we have reduction of cupric ions to grow solid copper:

$$Cu^{2+}(l) + 2e^- \rightarrow Cu(s) \qquad (6.9\text{-}1)$$

At the anode we have oxidation of the water:

$$H_2O(l) \rightarrow 0.5O_2(g) + 2H^+(l) + 2e^- \qquad (6.9\text{-}2)$$
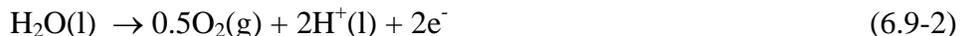
The reaction (6.9-1) occurring on the cathode and reaction (6.9-2) occurring on the anode are called half-cell reactions. The overall reaction is obtained by adding the oxidation and reduction half reactions:

$$H_2O(l) + Cu^{2+}(l) \rightarrow 0.5O_2(g) + 2H^+(l) + Cu(s) \qquad (6.9\text{-}3)$$
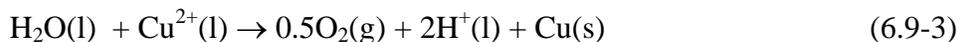
Electrochemical cells can contain different electrolyte compositions at the anode and the cathode. An example shown in Figure 6.9-3 is an alternative electroplating process for copper in which zinc is oxidized at the anode and goes into solution as Zn^{2+}. This cell is galvanic since the copper growth occurs spontaneously without the input of electrical work. The two electrolytes are separated by a salt bridge that allows a net charge to be transferred from one electrolyte solution to the other but does not allow undesired mixing of the electrolyte. A salt bridge in impermeable to the ions. It can be a simple porous disk or a gel saturated with a strong electrolyte such as KCl.
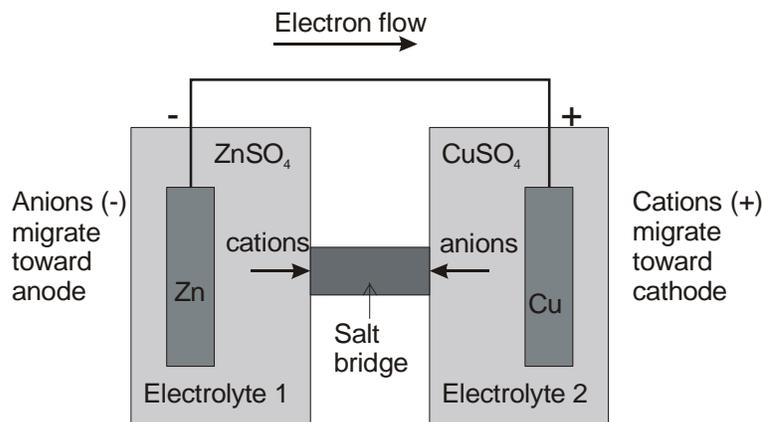
Figure 6.9-3 A galvanic cell with a salt bridge.

A shorthand notation has been developed to describe electrochemical cells. Starting at the anode, we pass through the electrolyte to the cathode and indicate the active species in chemical notation. A vertical bar separates two phases, that is, phase 1| phase 2. A double bar indicates a salt bridge or an impermeable separation of the phases, that is, phase 1|| phase 2. The short hand notation for the electrolytic cell shown in Figure 6.9-2 is:

$$Pt|O_2(g)|H_2SO_4(l), CuSO_4(l)|Cu(s) \qquad (6.9\text{-}4)$$

The short hand notation for the galvanic cell shown in Figure 6.9-3 is:

$$Zn(s)|ZnSO_4(l)||CuSO_4(l)|Cu(s) \qquad (6.9\text{-}5)$$

The differential electrical work, δW^*, can be related to the electric potential difference between the cathode and the anode, E, and the differential amount of charge transferred, dQ, by the equation:

$$\delta W^* = -\,EdQ \tag{6.9-6}$$

The sign convention for equation (6.9-6) is chosen so that when the cathode has a positive potential with respect to the anode, the process is spontaneous, while a negative potential indicates that work is required for the process to proceed. The oxidation half-reaction at the anode causes a flow of electrons in the external circuit; therefore the differential charge transferred can be related to the extent of reaction as follows:

$$\{\text{charge transferred}\} = \left\{\frac{\text{mole e}^-\ \text{liberated}}{\text{mole species reacting}}\right\}\left\{\frac{\text{charge}}{\text{mole e}^-}\right\}\{\text{extent of reaction}\}$$

$$dQ = zFd\zeta \tag{6.9-7}$$

In this equation, z is the number of moles of electron liberated per mole of species that reacts and F is Faraday's constant, 96,485 C/(mole e$^-$), which represents the charge of 1 mole of electrons. Substituting dQ from equation (6.9-7) into equation (6.9-6) yields

$$\delta W^* = -\,zEFd\zeta \tag{6.9-8}$$

For reversible reaction with non-Pv work we have

$$\delta W^* = (dG)_{T,P} = \sum \mu_i \nu_i\, d\zeta \tag{6.9-9}$$

Comparing equations (6.9-8) and (6.9-9) we obtain

$$-zEF = \sum \mu_i \nu_i = \sum \left(g_i^o + RT \ln \frac{\hat{f}_i}{f_i^o} \right)\nu_i \tag{6.9-10}$$

Assuming the activity of the solids in equation (6.9-10) is unity, we obtain

$$-zEF = \Delta g_{rxn}^o + RT\ln\left[\prod_{vapors}\left(y_i \hat{\varphi}_i P\right)^{\nu_i} \right]\prod_{liquids}\left(x_i \gamma_i\right)^{\nu_i} \tag{6.9-11}$$

Electrochemical cells typically operate at low pressure so we can assume $\hat{\varphi}_i = 1$. For the liquid in the electrolyte, the standard state is 1-m solution where m denotes molality (moles per kg of solvent). Equation (6.9-11) becomes

$$-zEF = \Delta g_{rxn}^o + RT\ln\left[\prod_{vapors}\left(P_i\right)^{\nu_i} \right]\prod_{liquids}\left(c_i \gamma_i\right)^{\nu_i} \tag{6.9-12}$$

In this equation, the concentration c_i is in molality. If a species in the liquid concentration of 1 mole per kg of solvent and its interactions corresponding to an ideal solution, it has $c_i\gamma_i = 1$. Dividing equation (6.9-12) by zF yields

$$E = E_{rxn}^o - \frac{RT}{zF} \ln \left[\prod_{vapors} (P_i)^{\nu_i} \right] \prod_{liquids} (c_i\gamma_i)^{\nu_i} \qquad (6.9\text{-}12)$$

In this equation, the standard potential of reaction is defined as

$$E_{rxn}^o = - \frac{\Delta g_{rxn}^o}{RT} \qquad (6.9\text{-}13)$$

The standard potential of reaction is obtained from thermochemical data and is measured with reference to hydrogen-hydrogen ion oxidation reaction, whose potential is defined as zero:

$$H_2(g) \rightarrow 2H^+(l) + 2e^- \qquad E^o = 0.0 \text{ V} \qquad (6.9\text{-}14)$$

Example 6.7-3[10] --
The reverse copper disproportion reaction has been proposed to etch solid copper:

$$Cu + Cu^{2+}(l) \rightarrow 2Cu^+(l)$$
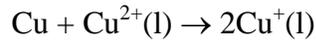
Determine the equilibrium constant of the disproportionation reaction using the following half-cell reactions:

$$Cu^{2+}(l) + e^- \rightarrow Cu^+(l) \qquad E^o = 0.153 \text{ V}$$

$$Cu \rightarrow Cu^+(l) + e^- \qquad E^o = -0.521 \text{ V}$$
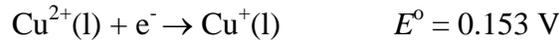
Solution --

The sum of the half-cell reactions gives the copper disproportion reaction, therefore

$$E_{rxn}^o = 0.153 - 0.521 = -0.368 \text{ V}$$

$$\Delta g_{rxn}^o = -zF E_{rxn}^o = (-1)(96,485)(-0.368) = 35.5 \text{ kJ/mol}$$

Since $\Delta g_{rxn}^o > 0$, this reaction will not occur spontaneously. The equilibrium K constant is then

$$K = K = \exp\left(-\frac{\Delta g_{rxn}^o}{RT} \right) = \exp\left(-\frac{35,500}{(8.314)(298.15)} \right) = 6.01 \times 10^{-7}$$

---

[10] Koretsky M.D., <u>Engineering and Chemical Thermodynamics</u>, Wiley, 2004, pg. 466

Chapter 6

6.10 Complex Chemical Equilibrium

We want to determine the number of intensive variables that must be specified to define a system consisting of m identifiable chemical species distributed among π phases. To describe each phase we need $m-1$ independent compositions, T, and P to a total of $m+1$ intensive variables. The total number of variables required to specify π phases is $\pi(m+1)$. For phase equilibrium we have the following set of equations:

$$T^\alpha = T^\beta = \ldots = T^\pi$$

$$P^\alpha = P^\beta = \ldots = P^\pi$$

$$\mu_1^\alpha = \mu_1^\beta = \ldots = \mu_1^\pi$$

$$\mu_2^\alpha = \mu_2^\beta = \ldots = \mu_2^\pi$$

$$\vdots$$

$$\mu_m^\alpha = \mu_m^\beta = \ldots = \mu_m^\pi$$

Each row in the set of equations above contains $(\pi-1)$ independent equations. Thus there are a total of $(\pi-1)(m+2)$ independent equations between the variables. In addition to these equations there are R equations from the number of independent reactions

$$\sum_i \mu_{ij} \nu_{ij} = 0 \quad (j = 1 \ldots R)$$

There might be additional equations, expressible in terms of intensive variables, which apply to the system. These equations will be called additional constraints and their number will be designated s. The total number of independent equations involving intensive variables is therefore

$$(\pi-1)(m+2) + R + s$$

The number of variables we can independently pick (the so-called degree of freedom, F) is obtained by subtracting the total $\pi(m+1)$ variables we need to specify by the $[(\pi-1)(m+2) + R + s]$ independent equations.

$$F = \pi(m+1) - [(\pi-1)(m+2) + R + s] = m + 2 - \pi - R - s$$

We can independently specify $(m + 2 - \pi - R - s)$ to complete define a system with m components and π phases. The combination of $(m - R - s)$ is called the phase rule components, C. We now need to determine the number of independent reaction, R, among

the chemical species in a system. The procedure will be illustrated by the following examples.

Example 6.10-1.[11] --
In a reacting system at equilibrium, the following species are considered to be present: CO_2, CO, C, CH_4, H_2, H_2O, and N_2. Determine the number of phase rule components and the number of independent reactions.

Solution ---

We will first create a coefficient matrix called the β matrix as follows:

	C	O	H	N
CO_2	1	2	0	0
CO	1	1	0	0
C	1	0	0	0
CH_4	1	0	4	0
H_2	0	0	2	0
N_2	0	0	0	2
H_2O	0	1	2	0

The number of phase rule components, C, is equal to the rank of the β matrix. The rank of a matrix is the order of the largest determinant having a nonzero value that can be created from the matrix. The order of a determinant, or a square matrix, is the number of rows or columns. For this example, the rank of the matrix is equal to or less than 4. A fourth order nonzero determinant can be formed from the β matrix. Therefore $C = 4$. The rank of the β matrix can also be founded from the following Matlab statement:

```
>> rank([1 2 0 0;1 1 0 0;1 0 0 0;1 0 4 0;0 0 2 0;0 0 0 2;0 1 2 0])
ans =
   4
```

Since $C = m - R - s$, and $s = 0$. The number of independent reaction R is

$$R = m - C = 7 - 4 = 3$$

We now need to find the three independent reactions. First we write the formation reaction for each of the 4 molecular species (CO_2, CO, CH_4, and H_2O).

$$\begin{array}{ll} C + O_2 = CO_2 & (1) \\ C + 0.5O_2 = CO & (2) \\ C + 2H_2 = CH_4 & (3) \\ H_2 + 0.5O_2 = H_2O & (4) \end{array}$$

Since free oxygen is not among the m species, we can eliminate O_2 from the above set by using the second equation

---

[11] Kyle, B.G., Chemical and Process Thermodynamics, Prentice Hall, 1999, pg. 535

$$C + 0.5O_2 = CO \Rightarrow 0.5O_2 = CO - C$$

Equation (1) becomes

$$C + 2CO - 2C = CO_2 \Rightarrow 2CO = C + CO_2$$

Equation (4) becomes

$$H_2 + CO - C = H_2O \Rightarrow H_2 + CO = C + H_2O$$

We now have a set of three independent reactions

$$2CO = C + CO_2 \qquad\qquad\qquad\qquad\qquad\qquad (E\text{-}1)$$
$$C + 2H_2 = CH_4 \qquad\qquad\qquad\qquad\qquad\qquad (E\text{-}2)$$
$$H_2 + CO = C + H_2O \qquad\qquad\qquad\qquad\qquad (E\text{-}3)$$

It should be noted that there are more than one set of 3 independent reactions.

Example 6.10-2. --
In a reacting system at equilibrium, the following species are considered to be present: H_2, ethane (C_2H_6), CO, H_2O, and methanol (CH_3OH). Determine the number of phase rule components and the number of independent reactions.

Solution ---

The β matrix is created as follows

	H_2	C_2H_6	CO	H_2O	CH_3OH
C	0	2	1	0	1
H	2	6	0	2	4
O	0	6	0	1	1

The rank of the β matrix is $3 = C$ (number of phase rule components)

Since $C = m - R - s$, and $s = 0$. The number of independent reaction R is

$$R = m - C = 5 - 3 = 2$$

Appendix A

Solving Algebraic Equations

A.1 The Newton-Raphson Method

The *Newton-Raphson* method and its modification is probably the most widely used of all root-finding methods. Starting with an initial guess x_1 at the root, the next guess x_2 is the intersection of the tangent from the point $[x_1, f(x_1)]$ to the *x*-axis. The next guess x_3 is the intersection of the tangent from the point $[x_2, f(x_2)]$ to the *x*-axis as shown in Figure A.1. The process can be repeated until the desired tolerance is attained.
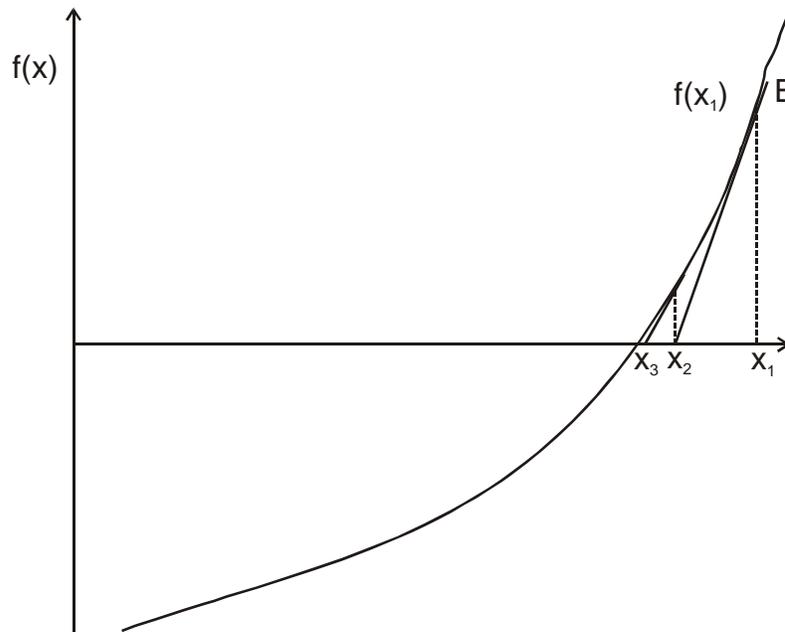
Figure A.1 Graphical depiction of the *Newton-Raphson* method.

The *Newton-Raphson* method can be derived from the definition of a slope

$$f'(x_1) = \frac{f(x_1) - 0}{x_1 - x_2} \Rightarrow x_2 = x_1 - \frac{f(x_1)}{f'(x_1)}$$

In general, from the point $[x_n, f(x_n)]$, the next guess is calculated as

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$$

The derivative or slope $f(x_n)$ can be approximated numerically as

$$f'(x_n) = \frac{f(x_n + \Delta x) - f(x_n)}{\Delta x}$$

Example A.1-1 --

Solve $f(x) = x^3 + 4x^2 - 10$ using the *Newton-Raphson* method for a root in [1, 2].

Solution ---

From the formula $x_{n+1} = x_n - \dfrac{f(x_n)}{f'(x_n)}$

$$f(x_n) = x_n^3 + 4x_n^2 - 10 \Rightarrow f'(x_n) = 3x_n^2 + 8x_n$$

$$x_{n+1} = x_n - \frac{x_n^3 + 4x_n^2 - 10}{3x_n^2 + 8x_n}$$

Using the initial guess, $x_n = 1.5$, x_{n+1} is estimated as

$$x_{n+1} = 1.5 - \frac{1.5^3 + 4 \times 1.5^2 - 10}{3 \times 1.5^2 + 8 \times 1.5} = 1.3733$$

A Matlab program for the *Newton-Raphson* method is listed in Table A.1 where the function $f(x)$ is an input to the program. The statement eval(f) is used to evaluate the function at a given value of x. The derivative is evaluated numerically using $f'(x_n) = \dfrac{f(x_n + \Delta x) - f(x_n)}{\Delta x}$

with $\Delta x = 0.01$. A sample result is given at the end of the program.

Table A.1 ---
```
% Example A.1: Newton method with numerical derivative
%
f=input('f(x)=','s');
tol=input('error tolerance =1e-5, new tolerance=');
if length(tol)==0,tol=1e-5;end
x1=input(' First guess=');
x=x1; fx=eval(f);
for i=1:100
  if abs(fx)<tol, break,end
  x=x+.01;
  ff=eval(f);
  fdx=(ff-fx)/.01;
  x1=x1-fx/fdx;
  x=x1;
  fx=eval(f);
  fprintf('i = %g, x = %g, fx = %g\n',i,x,fx)
end
```

```
>> e1d1
f(x)=x^3+4*x^2-10
error tolerance =1e-5, new tolerance=
 First guess=1.5
i = 1, x = 1.37391, fx = 0.143874
i = 2, x = 1.36531, fx = 0.00129871
i = 3, x = 1.36523, fx = 6.39291e-006
```

A.2 Newton's Method for Systems of Nonlinear Algebraic Equations

Consider two equations $f_1(x_1, x_2)$ and $f_2(x_1, x_2)$ for which the roots are desired. Let p_1^0, p_2^0 be the guessed values for the roots. $f_1(x_1, x_2)$ and $f_2(x_1, x_2)$ can be expanded about point (p_1^0, p_2^0) to obtain

$$f_1(x_1, x_2) = f_1(p_1^0, p_2^0) + \frac{\partial f_1}{\partial x_1}(x_1 - p_1^0) + \frac{\partial f_1}{\partial x_2}(x_2 - p_2^0) = 0$$

$$f_2(x_1, x_2) = f_2(p_1^0, p_2^0) + \frac{\partial f_2}{\partial x_1}(x_1 - p_1^0) + \frac{\partial f_2}{\partial x_2}(x_2 - p_2^0) = 0$$

Let $y_1^0 = (x_1 - p_1^0)$ and $y_2^0 = (x_2 - p_2^0)$, the above set can be written in the matrix form

$$\begin{bmatrix} \dfrac{\partial f_1}{\partial x_1} & \dfrac{\partial f_1}{\partial x_2} \\ \dfrac{\partial f_2}{\partial x_1} & \dfrac{\partial f_2}{\partial x_2} \end{bmatrix} \begin{bmatrix} y_1^0 \\ y_2^0 \end{bmatrix} = - \begin{bmatrix} f_1(p_1^0, p_2^0) \\ f_2(p_1^0, p_2^0) \end{bmatrix}$$

or

$$J(p^{(0)})y^{(0)} = - F(p^{(0)})$$

In general, the superscript (0) can be replaced by (k−1)

$$J(p^{(k-1)})y^{(k-1)} = - F(p^{(k-1)})$$

$J(p^{(k-1)})$ is the *Jacobian* matrix of the system. The new guessed values x at iteration k are given by

$$x = p^{(k)} = p^{(k-1)} + y^{(k-1)}$$

Example A.2-1

Use Newton's method with the initial guess $x = [0.1\ 0.1\ -0.1]$ to obtain the solutions to the following equations[1]

$$f_1(x_1, x_2, x_3) = 3x_1 - \cos(x_2\, x_3) - \frac{1}{2} = 0$$

$$f_2(x_1, x_2, x_3) = x_1^2 - 81(x_2 + 0.1)^2 + \sin x_3 + 1.06 = 0$$

$$f_2(x_1, x_2, x_3) = e^{-x_1 x_2} + 20x_3 + \frac{10\pi - 3}{3} = 0$$

Solution

The following two formulas can be applied to obtain the roots

$$J(p^{(k-1)})y^{(k-1)} = -F(p^{(k-1)})$$

$J(p^{(k-1)})$ is the *Jacobian* matrix of the system.

$$J(p^{(k-1)}) = \begin{bmatrix} \dfrac{\partial f_1}{\partial x_1} & \dfrac{\partial f_1}{\partial x_2} & \dfrac{\partial f_1}{\partial x_3} \\ \dfrac{\partial f_2}{\partial x_1} & \dfrac{\partial f_2}{\partial x_2} & \dfrac{\partial f_2}{\partial x_3} \\ \dfrac{\partial f_3}{\partial x_1} & \dfrac{\partial f_3}{\partial x_2} & \dfrac{\partial f_3}{\partial x_3} \end{bmatrix}$$

$F(p^{(k-1)})$ is the column vector of the given functions

$$F(p^{(k-1)}) = \begin{bmatrix} f_1(x_1, x_2, x_3) \\ f_2(x_1, x_2, x_3) \\ f_3(x_1, x_2, x_3) \end{bmatrix}$$

The new guessed values x at iteration k are given by

$$x = p^{(k)} = p^{(k-1)} + y^{(k-1)}$$

Table A.2-1 lists the Matlab program to evaluate the roots from the given initial guesses.

Table A.2-1 Matlab program for Example A.2-1 -------------
```
% Newton Method for set of nonlinear equations
%
f1='3*x(1)-cos(x(2)*x(3))-.5';
f2='x(1)*x(1)-81*(x(2)+.1)^2+sin(x(3))+1.06';
f3= 'exp(-x(1)*x(2))+20*x(3)+10*pi/3-1' ;
```

[1] Numerical Analysis by Burden and Faires

```
% Initial guess
%
x=[0.1 0.1 -0.1];
for i=1:5
f=[eval(f1) eval(f2) eval(f3)];
Jt=[3               2*x(1)        -x(2)*exp(-x(1)*x(2))
   x(3)*sin(x(2)*x(3))  -162*(x(2)+.1)   -x(1)*exp(-x(1)*x(2))
   x(2)*sin(x(2)*x(3))  cos(x(3))      20]';
%
dx=Jt\f';
x=x-dx';
fprintf('x = ');disp(x)
end

>> e1d5d1
x =    0.4999   0.0195  -0.5215
x =    0.5000   0.0016  -0.5236
x =    0.5000   0.0000  -0.5236
x =    0.5000   0.0000  -0.5236
x =    0.5000   0.0000  -0.5236
```

Matlab can also evaluate the *Jacobian* matrix of the system analytically as shown in Table A.2-2

 Table A.2-2 Matlab program for Example A.2-1 -------------
```
% Newton Method with Jacobian matrix evaluated analytically by Matlab
%
syms x1 x2 x3
F=[3*x1-cos(x2*x3)-.5
   x1^2-81*(x2+.1)^2+sin(x3)+1.06
   exp(-x1*x2)+20*x3+(10*pi-3)/3];
Jac=[diff(F,x1) diff(F,x2) diff(F,x3)];
x1=.1;x2=.1;x3=-.1;
k=0;
disp('  k    x1            x2            x3')
fprintf('%3.0f %10.7f %10.7f %10.7f\n',k,x1,x2,x3)
for k=1:10
Am=eval(Jac);Bc=eval(F);
yk=Am\Bc;
x1=x1-yk(1);
x2=x2-yk(2);
x3=x3-yk(3);
fprintf('%3.0f %10.7f %10.7f %10.7f\n',k,x1,x2,x3)
if max(abs(yk))<.00001, break, end
end

>> e1d5d1b
```

Jac =
```
[          3,   sin(x2*x3)*x3,   sin(x2*x3)*x2]
[        2*x1,    -162*x2-81/5,        cos(x3)]
[ -x2*exp(-x1*x2), -x1*exp(-x1*x2),       20]
```

k	x_1	x_2	x_3
0	0.1000000	0.1000000	-0.1000000
1	0.4998697	0.0194668	-0.5215205
2	0.5000142	0.0015886	-0.5235570
3	0.5000001	0.0000124	-0.5235985
4	0.5000000	0.0000000	-0.5235988
5	0.5000000	0.0000000	-0.5235988

Solving set of nonlinear equations with Excel

Use the initial guess x = [0.1 0.1 −0.1] to obtain the solutions to the following equations

$$f_1(x_1, x_2, x_3) = 3x_1 - \cos(x_2\,x_3) - \frac{1}{2} = 0$$

$$f_2(x_1, x_2, x_3) = x_1^2 - 81(x_2 + 0.1)^2 + \sin x_3 + 1.06 = 0$$

$$f_2(x_1, x_2, x_3) = e^{-x_1 x_2} + 20x_3 + \frac{10\pi - 3}{3} = 0$$

Microsoft Excel - Nonlinear.xls

File Edit View Insert Format Tools Data Window Help Acrobat

D8 =

	A	B	C	D	E
1			x	y	z
2			0.1	0.1	-0.1
3		f1	-1.19995		
4		f2	-2.26983		
5		f3	8.46202		
6		Obj. func	78.1977		

Appendix B

Curve Fitting

B.1 Nonlinear Curve Fitting

A sample consists of a layer of aluminum and a layer of a composite coating is tested in a vacuum chamber by measuring its temperature as a function of time. The behavior of the sample temperature has a nonlinear dependence on the emissivity ε of the sample and the heat transfer coefficient h between the coating and the vacuum air.
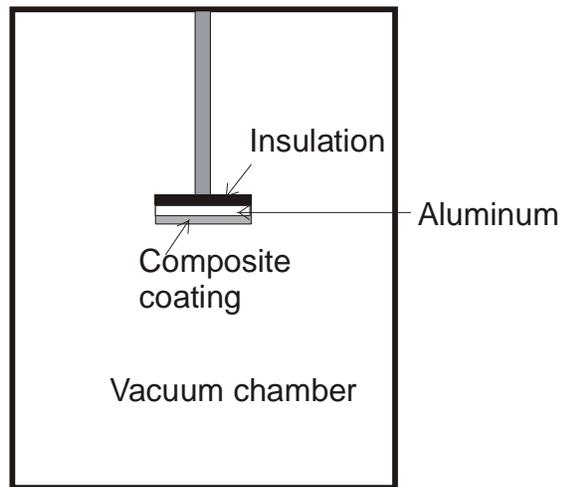
Figure B.1-1. A sample enclosed within a testing chamber.

The unknown parameters h and ε may be obtained by fitting the model equation to experimental data as shown in Figure B.1.2 where the curve represents the model equation and the circles represent the data.
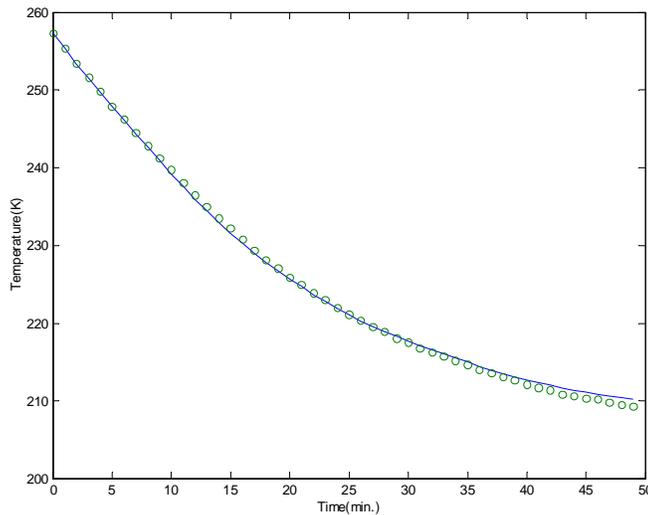
Figure B.1-2. Transient temperature of a typical sample.

To illustrate how this is done, first consider a portion of the graph in Figure B.1-2 that is re-plotted in Figure B.1-3. The relationship between the temperature T_i obtained from the model equation and the experimental value $T_{i,exp}$ can be expressed generally as

$$T_{i,exp} = T_i (t; \varepsilon, h) + e_i \qquad \text{(B.1-2)}$$

where e_i is a random error that can be negative or positive. T_i is a function of the independent variable t_i and the parameters h and ε. The random error is also called the residual, which is the difference between the calculated and measured values.
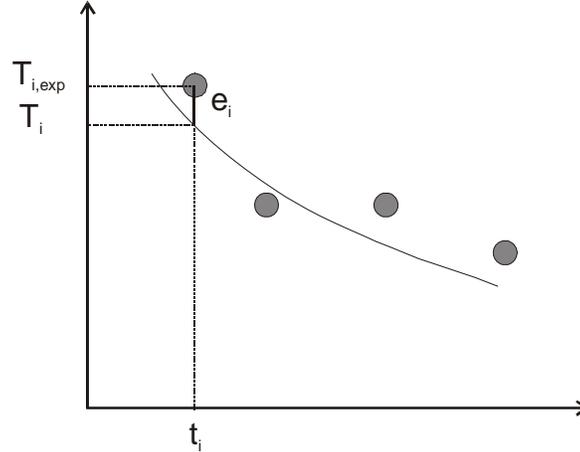
Figure B.1-3. Relationship between the model equation and the data

Nonlinear regression is based on determining the values of the parameters that minimize the sum of the squares of the residuals called an objective function F_{obj}.

$$F_{obj} = \sum_{i=1}^{N} e_i^2 = \sum_{i=1}^{N} \left(T_{i,exp} - T_i \right)^2 = \sum_{i=1}^{N} \left(T_i - T_{i,exp} \right)^2 \qquad \text{(B.1-3)}$$

Where N is the number of data points or measured temperatures in this case. The temperature from equation B.1-2 can be expanded in a Taylor series around h and ε and curtailed after the first derivative.

$$T_{i,j+1} = T_{i,j} + \frac{\partial T_{i,j}}{\partial \varepsilon} \Delta \varepsilon + \frac{\partial T_{i,j}}{\partial h} \Delta h \qquad \text{(B.1-4)}$$

Where j is the guess and $j+1$ is the prediction, $\Delta \varepsilon = \varepsilon_{j+1} - \varepsilon_j$, and $\Delta h = h_{j+1} - h_j$. We have linearized the original model with respect to the parameters h and ε. Equation (B.1-4) can be substituted into Eq. (B.1-2) to yield

$$T_{i,exp} - T_{i,j} = \frac{\partial T_{i,j}}{\partial \varepsilon} \Delta \varepsilon + \frac{\partial T_{i,j}}{\partial h} \Delta h + e_i \qquad \text{(B.1-5a)}$$

or in matrix form

$$\{D\} = [Z_j]\{\Delta A\} + \{E\} \qquad\qquad\qquad\qquad \text{(B.1-5b)}$$

where $[Z_j]$ is the matrix of partial derivatives of the function (called the *Jacobian* matrix) evaluated at the guess j, the vector $\{D\}$ contains the differences between the measure temperature and the calculated temperature at the guess j, the vector $\{\Delta A\}$ contains the changes in the parameter values, and the vector $\{E\}$ contains the residuals. It should be noted that as the final values of the parameters are obtained after the iterations vector $\{D\}$ is the same as vector $\{E\}$.

$$[Z_j] = \begin{bmatrix} \dfrac{\partial T_1}{\partial \varepsilon} & \dfrac{\partial T_1}{\partial h} \\ \dfrac{\partial T_2}{\partial \varepsilon} & \dfrac{\partial T_2}{\partial h} \\ \vdots & \vdots \\ \dfrac{\partial T_N}{\partial \varepsilon} & \dfrac{\partial T_N}{\partial h} \end{bmatrix}, \{D\} = \begin{Bmatrix} T_{1,\exp} - T_{1,j} \\ T_{2,\exp} - T_{2,j} \\ \vdots \\ T_{N,\exp} - T_{N,j} \end{Bmatrix}, \{\Delta A\} = \begin{Bmatrix} \Delta \varepsilon \\ \Delta h \end{Bmatrix}, \{E\} = \begin{Bmatrix} e_1 \\ e_2 \\ \vdots \\ e_N \end{Bmatrix}$$

We minimize the objective function

$$F_{\text{obj}} = \sum_{i=1}^{N} e_i^2 = \sum_{i=1}^{N} \left(T_{i,\exp} - T_i \right)^2 \qquad\qquad\qquad\qquad \text{(B.1-3)}$$

by taking its derivative with respect to each of the parameters and setting the resulting equation to zero.

$$\frac{\partial F_{obj}}{\partial \varepsilon} = -2 \sum_{i=1}^{N} \left(T_{i,\exp} - T_i \right) \frac{\partial T_i}{\partial \varepsilon} = 0 \qquad\qquad\qquad\qquad \text{(B.1-6a)}$$

$$\frac{\partial F_{obj}}{\partial h} = -2 \sum_{i=1}^{N} \left(T_{i,\exp} - T_i \right) \frac{\partial T_i}{\partial h} = 0 \qquad\qquad\qquad\qquad \text{(B.1-6b)}$$

This algorithm is *Gauss-Newton* method for minimizing the sum of the squares of the residuals between data and nonlinear functions. Equations (B.1-6a) and (B.1-6b) can be combined in a matrix form

$$[Z_j]^{\text{T}}\{E\} = 0 \qquad\qquad\qquad\qquad \text{(B.1-7)}$$

where $[Z_j]^{\text{T}}$ is the transpose of $[Z_j]$. Let consider $N = 3$ so we can see the combination from (B.1-6a) and (B.1-6b) to (B.1-7).

$$\begin{bmatrix} \dfrac{\partial T_1}{\partial \varepsilon} & \dfrac{\partial T_2}{\partial \varepsilon} & \dfrac{\partial T_3}{\partial \varepsilon} \\ \dfrac{\partial T_1}{\partial h} & \dfrac{\partial T_2}{\partial h} & \dfrac{\partial T_3}{\partial h} \end{bmatrix} \begin{Bmatrix} T_{1,\exp} - T_1 \\ T_{2,\exp} - T_2 \\ T_{3,\exp} - T_3 \end{Bmatrix} = 0$$

Substitute $\{E\} = \{D\} - [Z_j]\{\Delta A\}$ from Eq. (B.1-5b) into (B.1-7)

$$[Z_j]^T\{\{D\} - [Z_j]\{\Delta A\}\} = 0$$

or

$$[Z_j]^T[Z_j]\{\Delta A\} = \{[Z_j]^T\{D\}\} \tag{B.1-8}$$

The *Jacobian* matrix $[Z_j]$ may be evaluated numerically for the model equation (B.1-1).

$$\frac{\partial T_i}{\partial \varepsilon} \approx \frac{T_i(\varepsilon + \delta\varepsilon, h) - T_i(\varepsilon, h)}{\delta\varepsilon} \tag{B.1-9a}$$

$$\frac{\partial T_i}{\partial h} \approx \frac{T_i(\varepsilon, h + \delta h) - T_i(\varepsilon, h)}{\delta h} \tag{B.1-9b}$$

Typically, $\delta\varepsilon$ can be chosen to be 0.01 and δh can be chosen to be 0.01 W/m$^2\cdot$K. Thus, the *Gauss-Newton* method consists of solving Eq. (B.1-8) for $\{\Delta A\}$, which can be employed to compute improved values for the parameters h and ε.

$$\varepsilon_{j+1} = \varepsilon_j + \Delta\varepsilon \, (\text{from } \{\Delta A\})$$

$$h_{j+1} = h_j + \Delta h \, (\text{from } \{\Delta A\})$$

This procedure is repeated until the solution converges that is until $\Delta\varepsilon$ and Δh fall below an acceptable criterion. The *Gauss-Newton* method is a common algorithm that can be found in many numerical method texts. However, this description follows the notations and development by Chapra and Canale.

Example B.1-1

Fit the function $T(t; \varepsilon, h) = \varepsilon(1 - e^{-ht})$ to the data.

t	0.25	0.75	1.25	1.75	2.25
T	0.28	0.75	0.68	0.74	0.79

Use initial guesses of $h = 1$ and $\varepsilon = 1$ for the parameters.

Solution

The partial derivatives of the function with respect to the parameters h and ε are

$$\frac{\partial T}{\partial \varepsilon} = 1 - e^{-ht} \text{ and } \frac{\partial T}{\partial h} = \varepsilon t e^{-ht}$$

$$[Z_j] = \begin{bmatrix} \dfrac{\partial T_1}{\partial \varepsilon} & \dfrac{\partial T_1}{\partial h} \\[2mm] \dfrac{\partial T_2}{\partial \varepsilon} & \dfrac{\partial T_2}{\partial h} \\[1mm] \vdots & \vdots \\[1mm] \dfrac{\partial T_N}{\partial \varepsilon} & \dfrac{\partial T_N}{\partial h} \end{bmatrix} = \begin{bmatrix} 0.2212 & 0.1947 \\ 0.5276 & 0.3543 \\ 0.7135 & 0.3581 \\ 0.8962 & 0.3041 \\ 0.8946 & 0.2371 \end{bmatrix}$$

The matrix multiplied by its transpose results in

$$[Z_j]^T[Z_j] = \begin{bmatrix} 0.2212 & 0.5276 & 0.7135 & 0.8962 & 0.8946 \\ 0.1947 & 0.3543 & 0.3581 & 0.3041 & 0.2371 \end{bmatrix} \begin{bmatrix} 0.2212 & 0.1947 \\ 0.5276 & 0.3543 \\ 0.7135 & 0.3581 \\ 0.8962 & 0.3041 \\ 0.8946 & 0.2371 \end{bmatrix}$$

$$[Z_j]^T[Z_j] = \begin{bmatrix} 2.3194 & 0.9489 \\ 0.9489 & 0.4404 \end{bmatrix}$$

The vector $\{D\}$ consists of the differences between the measurements T and the model predictions $T(t; \varepsilon, h) = \varepsilon(1 - e^{-ht})$

$$\{D\} = \begin{bmatrix} 0.28 - 0.2212 \\ 0.57 - 0.5276 \\ 0.68 - 0.7135 \\ 0.74 - 0.8262 \\ 0.79 - 0.8946 \end{bmatrix} = \begin{bmatrix} 0.0588 \\ 0.0424 \\ -0.0335 \\ -0.0862 \\ -0.1046 \end{bmatrix}$$

The vector $\{D\}$ is pre-multiplied by $[Z_j]^T$ to give

$$[Z_j]^T\{D\} = \begin{bmatrix} 0.2212 & 0.5276 & 0.7135 & 0.8962 & 0.8946 \\ 0.1947 & 0.3543 & 0.3581 & 0.3041 & 0.2371 \end{bmatrix} \begin{bmatrix} 0.0588 \\ 0.0424 \\ -0.0335 \\ -0.0862 \\ -0.1046 \end{bmatrix} = \begin{bmatrix} -0.1533 \\ -0.0365 \end{bmatrix}$$

The vector $\{\Delta A\}$ can be calculated by using MATLAB statement dA=ZjTZj\ZjTD ($\{\Delta A\} = \{[Z_j]^T[Z_j] \setminus [Z_j]^T\{D\}\}$)

$$\{\Delta A\} = \begin{bmatrix} -0.2714 \\ 0.5019 \end{bmatrix}$$

The next guesses for the parameters ε and h are

$$\varepsilon = 1 - 0.2715 = 0.7285$$

$$h = 1 + 0.5019 = 1.5019$$

Table B.1-1 lists the MATLAB program with the results of two iterations.

Table B.1-1 _____

```
% Gauss-Newton method
%
t=[0.25 0.75 1.25 1.75 2.25]';
T=[0.28 0.57 0.68 0.74 0.79]';
e=1;h=1;
Tmodel='e*(1-exp(-h*t))';
dTde='1-exp(-h*t)';dTdh='e*t.*exp(-h*t)';
for i=1:2
 Zj=[eval(dTde) eval(dTdh)];
 ZjTZj=Zj'*Zj
 D=T-eval(Tmodel)
 ZjTD=Zj'*D
 dA=ZjTZj\ZjTD
 e=e+dA(1);
 h=h+dA(2);
 fprintf('Iteration #%g: e = %8.4f, h = %8.4f\n',i,e,h)
end

>> Gauss
ZjTZj =
   2.3194   0.9489
   0.9489   0.4404
D =
   0.0588
   0.0424
  -0.0335
  -0.0862
  -0.1046
ZjTD =
  -0.1534
  -0.0366
dA =
  -0.2715
   0.5019
Iteration #1: e =   0.7285, h =   1.5019
ZjTZj =
   3.0660   0.4162
   0.4162   0.0780
```

```
D =
   0.0519
   0.0777
   0.0629
   0.0641
   0.0863
ZjTD =
   0.2648
   0.0397
dA =
   0.0625
   0.1758
Iteration #2: e =   0.7910, h =   1.6777
```

Table B.1-2 lists the Matlab program that solves for the two parameters ε and h until the maximum change of the parameters between two successive iterations is less than 0.01. The standard error and the correlation coefficient of the fitted values are also evaluated. The standard error stde is determine from

$$\text{stde} = \frac{1}{N-2} \sum_{i=1}^{N} (T_{i,\text{exp}} - T_i)^2 = \frac{S}{N-2}, \qquad \text{where } S = \sum_{i=1}^{N} (T_{i,\text{exp}} - T_i)^2$$

The standard error quantifies the spread around the regression curve. A crude measure of the goodness-of-fit is given by the correlation coefficient r

$$r = \sqrt{1 - \frac{S}{S_t}}, \qquad \text{where } S_t = \sum_{i=1}^{N} (T_{i,\text{exp}} - \overline{T}_{i,\text{exp}})^2$$

In this expression $\overline{T}_{i,\text{exp}}$ is the mean of the experimental dependent variable.

_____ **Table B.1-2** Gauss Newton method for nonlinear curve fitting _____

```
% Gauss-Newton method
%
t=[0.25 0.75 1.25 1.75 2.25]';
T=[0.28 0.57 0.68 0.74 0.79]';
e=1;h=1;
Tmodel='e*(1-exp(-h*t))';
dTde='1-exp(-h*t)';dTdh='e*t.*exp(-h*t)';
for i=1:20
 Zj=[eval(dTde) eval(dTdh)];
 ZjTZj=Zj'*Zj;
 D=T-eval(Tmodel);
 ZjTD=Zj'*D;
 dA=ZjTZj\ZjTD;
 e=e+dA(1);
 h=h+dA(2);
```

```
 if max(abs(dA))<.01,break, end
end
fprintf('# of Iteration = %g: e = %8.4f, h = %8.4f\n',i,e,h)
S=sum((T-eval(Tmodel)).^2);
stde=sqrt(S/(length(t)-2));
Tave=mean(T);Sdev=sum((T-Tave).^2);
cor=sqrt(1-S/Sdev);
fprintf('Standard error = %8.4f, Correlation coefficient = %8.4f\n',stde,cor)

>> gauss2
# of Iteration = 3: e =   0.7919, h =   1.6753
Standard error =   0.0149, Correlation coefficient =   0.9980
```

The Matlab function fminsearch can also be used to fit the data to an expression with more than one parameter, $T(t; \varepsilon, h) = \varepsilon(1 - e^{-ht})$. Table B.1-3 lists the function required by fminsearch. Table B.1-4 lists the program that calls fminsearch to find the two parameters $\varepsilon = 1$ and $h = 1$. The program also plots the fitted results with the experimental data shown in Figure B.1-4.

_____ **Table B.1-3** Matlab program to define the objective function _____

```
function y=nlin(p)
t=[.25 .75 1.25 1.75 2.25];
T=[.28 .57 0.68 0.74 0.79];
e=p(1);h=p(2);
Tc=e*(1-exp(-h*t));
y=sum((T-Tc).^2);
```

_____ **Table B.1-4** Matlab program to find ε and h _____

```
clf
t=[.25 .75 1.25 1.75 2.25];
T=[.28 .57 0.68 0.74 0.79];
p=fminsearch('nlin',[1 1])
tp=.25:.1:2.25;
e=p(1);h=p(2);
Tc=e*(1-exp(-h*tp));
plot(tp,Tc,t,T,'o')
grid on
xlabel('t');ylabel('T')
legend('Fitted','Data')

>> nlinear
p =
   0.7919    1.6751
```

Appendix C

Process Simulator

Process simulator is one of the most common types of software used in process design. It can be used to perform steady or unsteady materials and energy balances for a wide range of process equipment. A user usually must follow the following steps to set up a problem on a simulator[1]:

1. Select all of the chemical components that are required in the process from the component database.
2. Select the thermodynamic models required for the simulation. These may be different for different pieces of equipment. For example, the Peng Robinson equation of state can be used to simulate a pump. However, for a liquid-liquid extractor in the same process, it is necessary to use a thermodynamic model (e.g. Wilson model) that can predict liquid-phase activity coefficients and the existence of two liquid phases.
3. Select the topology of the flow sheet to be simulated by specifying the input and output streams for each piece of equipment.
4. Select the properties (temperature, pressure, flow rate, and composition) of the feed streams to the process.
5. Select the equipment specifications (parameters) for each piece of equipment in the process.
6. Select the format of the output results.
7. Select the convergence method and run the simulation.

There are basically three types of solution algorithm for process simulators: sequential modular, equation solving (simultaneous non-molar), and simultaneous modular. In the sequential modular approach the process is solved equipment piece by equipment piece. In the equation solving technique, all the equations for the process are written out together and then the resulting matrix of nonlinear simultaneous equations is solved to yield the solution. The final simultaneous modular technique combines the modularizing of the equations relating to specific equipment with the efficient solution algorithms for the simultaneous equation solving technique.

We will go over a sequence of events needed to simulate a two-stage compressor system using *Provision*. This process simulator uses the sequential modular algorithm in which each piece of equipment is solved in sequence, starting with the first then followed by the second, and so on. This method is not as efficient as the equation solving technique. However the user can easily detect the location where convergence is not obtained.

Example: A 1000 lb-mole per hour mixture of 5% methane, 20% ethane, 25% propane, 30% n-butane, and 20% n-pentane at 14.7 psia and 90°F is to be compressed first to 50 psia, then to 200 psia using a two-stage compressor system. An inner-stage cooler is used to cool the compressed gas from the first stage to its original temperature by passing the gas stream through a heat exchanger in which water is used as a coolant. This is done to maintain a lower energy requirement for the second stage compressor. A knockout drum is installed after the first cooler to remove any liquid present in the compressed gas before feeding it to the second compressor. If you have liquid present in a gas stream, it will damage the impeller of the compressor[2].

---

[1] Turton et al, Analysis, Synthesis, and Design of Chemical Processes, Prentice Hall, 1998, pg. 480
[2] Dr. Pang's Provision Student Manual

To open Provision, go to the *Start* menu, click on *Programs*, *Simsci*, and then *ProII 8.0*. The following screen should appear:
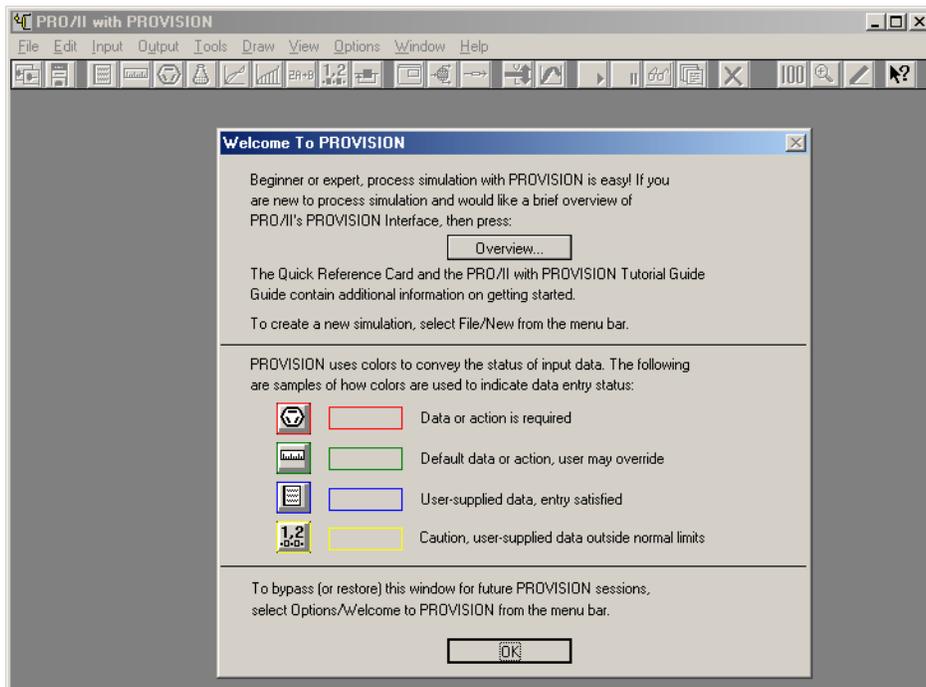
Note the different colored boxes and their meanings. They will be very important to remember later on in the simulation. Click on *OK* at the bottom of the box to continue into the simulation environment. Next, click on *File* and then *New*. This should bring you to the following screen:
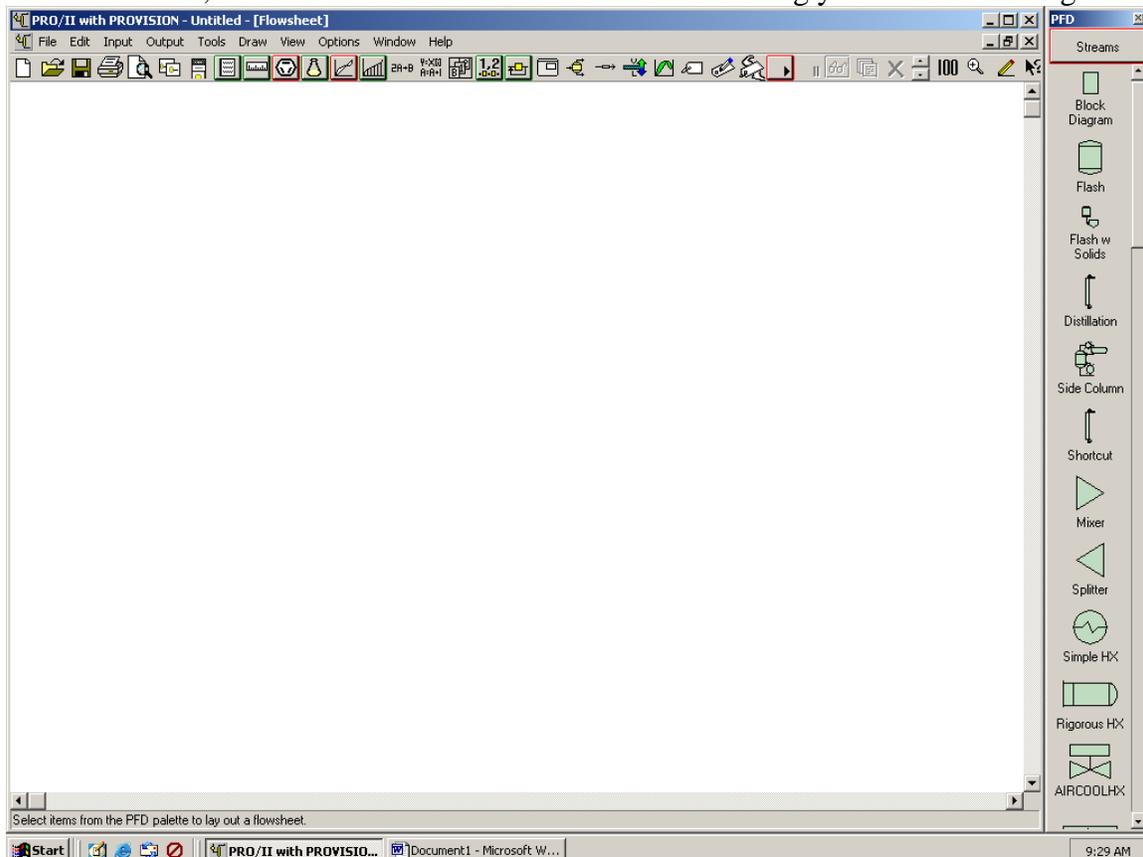
This is the basic simulation environment from which you will begin each time you use Provision. It is called the PFD screen. Before you begin with the procedure given to you in the assignment, you need to enter the components that you will be using and your equation of state. First click on the *Component Selection* button on the top toolbar. This button looks like this:

. The following screen should appear:
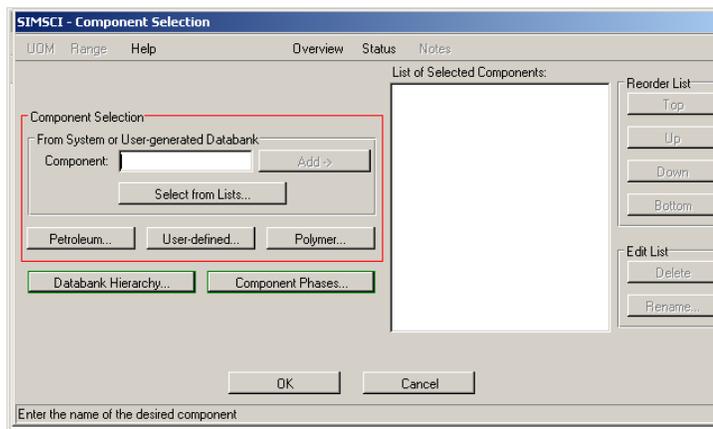
From here you can either type in the names of your desired components or you can select them from a list already inside Provision. We will select our components from a list by clicking on the *Select from Lists* button. The following screen should appear:
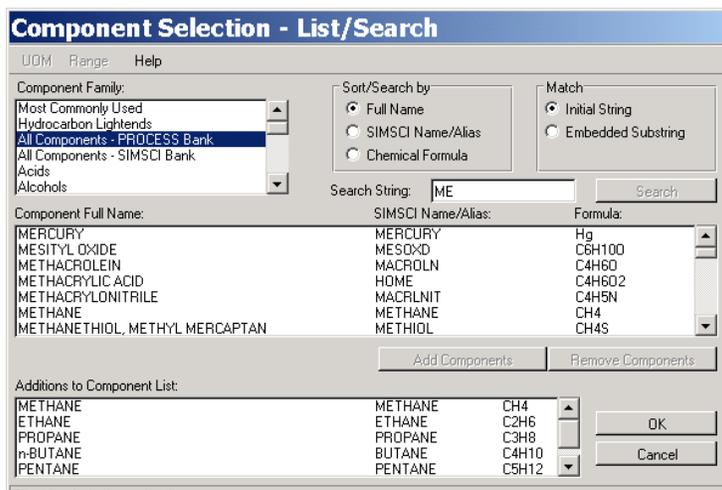
In this assignment, all of the needed components can be found in the *All Components - PROCESS Bank* file. Click on the desired species and click *Add Components*, the selected species will appear in the bottom text box *Additions to Component List*. After you selected all species (Methane, Ethane, Propane, N-butane, Pentane, and Water) click *OK* to return to the following screen.
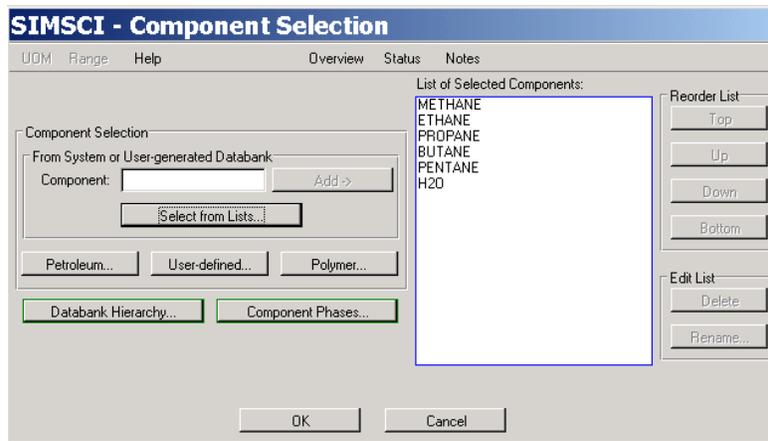
Click *OK* to return to the PFD screen. Next click on the *Thermodynamic Data* button,

.
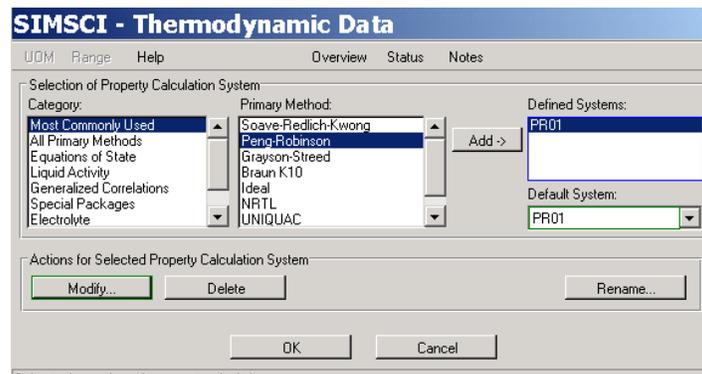
Once inside, click on *Most Commonly Used* and then click on *Peng-Robinson* in **Primary Method**: box. Then click *Add* and then *OK* to return back to the PFD screen. We are now ready to begin the procedure to simulate a Two-stage Compressor System.

Using your drawn PFD as a guide, select needed units and place them on the PFD screen one by one. All of the choices for equipment are located in the toolbar on the right side of the screen. It is the thin vertical toolbar titled "PFD". Click on the Compressor button and then click on the space in the PFD where you wish to place the compressor. Follow the same steps for *Simple* **HX (1),** *Flash*, *Compressor* (**2**), and *Simple* **HX (2)**. You will notice that each unit is named by PROVISION, automatically. You will also notice that each name has a red border meaning that some conditions have to be supplied.

Click on the *Stream* button on the build palette to draw the stream lines. All the possible EXIT ports appear on each unit as soon as the *Stream* button is selected. The required outlet port are colored red, while the optional exits are given in green.

Add streams by clicking on the origin of the stream (either a unit exit port or an external feed stream, on a unoccupied part of the PFD), then click again at the destination of the stream. For example: to apply a feed stream to **C1**, click on the PFD that is not occupied by any unit, and then click again at compressor. Notice the name is given as **S1**.

Connect all the streams in order shown in the Figure 1. Pay attention to the number of stream. Each stream is numbered in the order they are created.
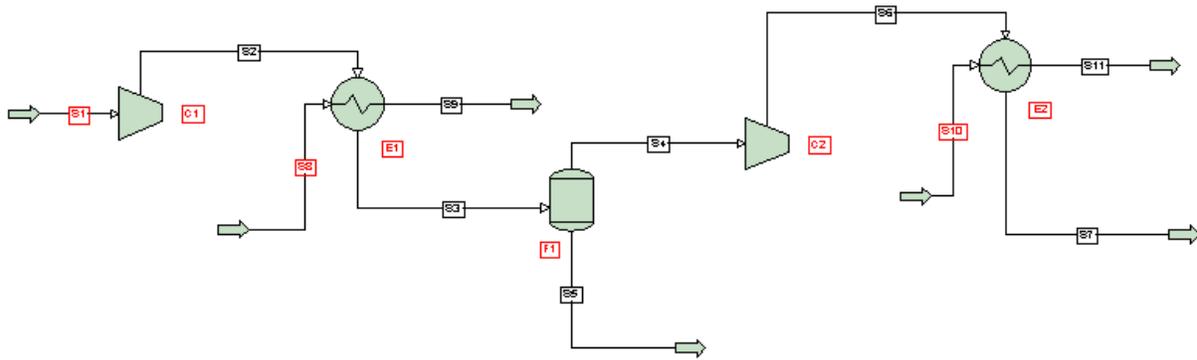
Figure 1 A two-stage compressor system

➢ It is always safe to save frequently. To save, click on *File* on the menu bar and click on *Save* on the *File* menu. Type in the file name, **Case1** or any name you like, and click on the *OK* button to go back to the PFD.

You now need to supply the required Stream and Unit Data.

Feed Stream S1: You can select a stream or unit by double clicking on the name in PFD. Let 's first start by completing the beginning feed stream, **S1**. Double click on **S1** to select that stream. You can give it a name, **Feed Stream**, by typing it in the box next to **Description:**

Click on the *Flowrate and Composition...* button to supply the flow rate and compositions. Since we know the total flow rate, click on *Total Fluid Flowrate* and type in 1000 lb-mol/hr. The border becomes blue as soon as you input the data. Fill in the composition since they have red borders (0.05, 0.2, 0.25, 0.3, 0.2). Click on *OK* button when done.

To satisfy the phase rule, you need two more variables. For this case you know temperature and pressure. To enter temperature, click on the red box named *First Specification*: choose *Temperature* and type in the temperature, 90°F. To enter the pressure, click on the red box named *Second Specification*: choose *Pressure* and type in 14.7 psia. Click on the *OK* button since all the requirements are met. **S1** now has a black border.

Compressor C1: Double click on the compressor, **C1**, on the PFD. Supply the *Outlet Pressure* as 50 PSIA in the red box. Change the *Adiabatic Efficiency* to 80%. Default is 100%. Notice the box is green, meaning that the user can input data. Click on the *OK* button to go back to the PFD.

Heat Exchanger E1: Double click on the heat exchanger, **E1**, on the PFD. You will see the **PRO/II-Heat Exchanger** window. Check for hot and cold streams by clicking on the *Process Stream...* button. **S2** and **S3** should be hot, and **S8** and **S9** should be cold streams. If the sides are not set correctly, you can correct it by clicking on the appropriate circle.

Click on the *OK* button to go back to **PRO/II-Heat Exchanger** window. Click on the *Specification...* button and click on the red box. Choose *Hot Product Temperature* which is the process stream going out of the heat exchanger and type in 90°F for the value.
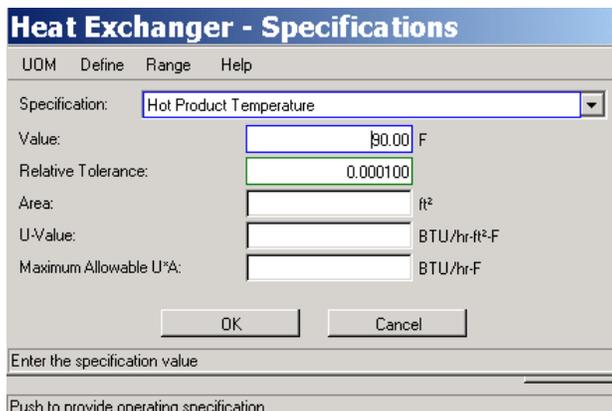
Click on the *OK* button to go back to **PRO/II-Heat Exchanger** window. Input 3 psi for *Hot Side Pressure Drop* and 2 psi for *Cold Side Pressure Drop*.
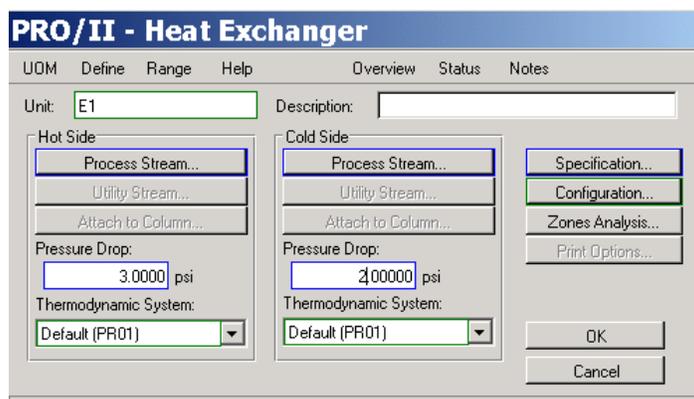
Click on the *OK* button to go back to the PFD.

Stream going to E1, S8: Double click on **S8** on the PFD. Click on the *Flowrate and Composition...* button to supply the flow rate and composition. Choose *Total Fluid Flowrate*. Since the set unit is lb-mol/hr, and you have mass flow rate, lb/hr, you must do the conversion.

Instead of doing it by yourself, you can click on the *UOM* button on the menu bar. Click on *Mass* and choose *lb*. Click on the *Change Units* button to change the unit.
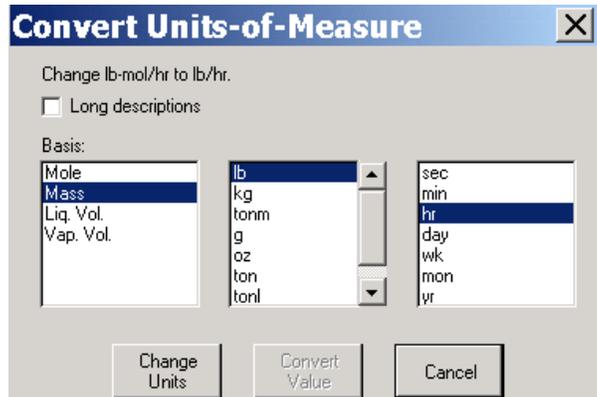
Now enter 420000 lb/hr for the flow rate. Enter 1.00 for the water composition. Click on *OK* button when done. Click on *First Specification*: choose *Temperature* and type in the temperature, 70°F. To enter the pressure, click on *Second Specification*: choose *Pressure* and type in 100 psia. Click on the *OK* button to go back to the PFD.

Flash F1: Select the flash drum, **F1**, by double clicking on it. Click on *Product Phase...* to make sure the phases of streams, **S4** and **S5**, are correctly set. **S4** should be **Vapor**, and **S5** should be **Liquid**. Make necessary changes by clicking on incorrect boxes and selecting the right phase. Click on the *OK* button to return to the **PRO/II-Flash Drum** window.
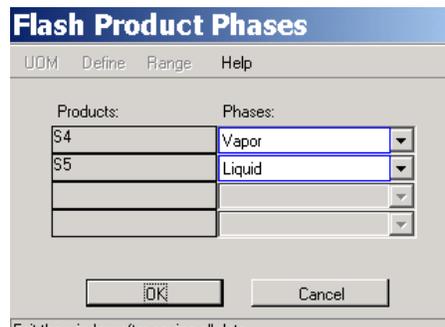
Input 3 psi for the *Pressure Drop*. Click in the *Unit Specification*: box. Select *Duty* and type in 0.00 for the value since it is an adiabatic flash drum. Click on the *OK* button when done.

Second Compressor C2: Double click on the compressor, **C2**, on the PFD. Supply the *Outlet Pressure* as 200 psia in the red box. Change the *Adiabatic Efficiency* to 80%. Click on the *OK* button to go back to the PFD.

Second Heat Exchanger E2: Double click on the heat exchanger, **E2**, on the PFD. Check for hot and cold streams by clicking on the *Process Stream...* button. **S6** and **S7** should be hot, and **S10** and **S11** should be cold streams. Click on the *OK* button when done.
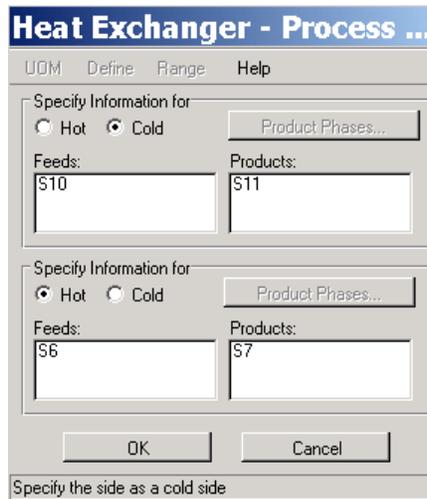
Click at the *Specification* and click on the red box. Choose *Hot Product Temperature* and type in 90°F for the value. Click on the *OK* button.
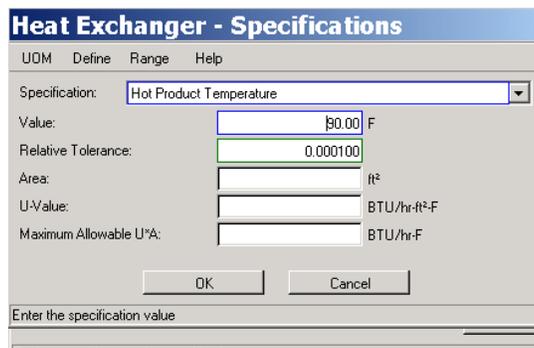
Input 3 psi for the *Hot Side Pressure Drop* and 2 psi for the *Cold Side Pressure Drop*. Click on the *OK* button to go back to the PFD.
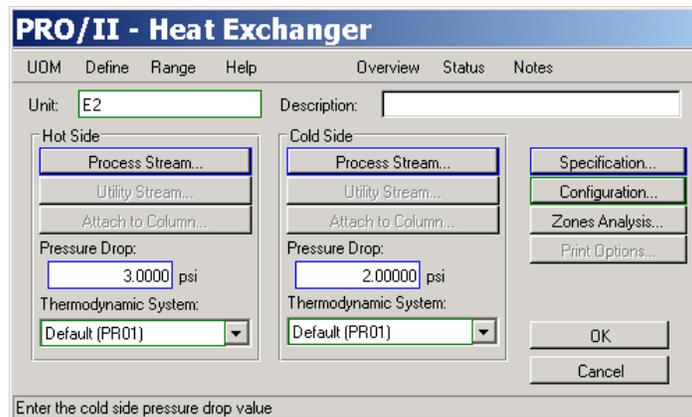
Stream going to E2, S10: Double click on **S10** on the PFD. Click on the *Flowrate and Composition...* button to supply the flow rate and composition. Choose *Total Fluid Flowrate*. You need to change the unit from lb/hr to lb-mol/hr. Click on the *UOM* button on the menu bar. Click on *Mass* and choose *lb*. Click on the *Change Units* button to change the unit.

Now enter 420000 lb/hr for the flow rate. Enter 1.00 for the water composition. Click on *OK* button when done. Click on *First Specification*: choose *Temperature* and type in the temperature,

70°F. To enter the pressure, click on *Second Specification*: choose *Pressure* and type in 100 psia. Click on the *OK* button to go back to the PFD.

It is now time to run your simulation. The button for running your simulation looks like this: . PROVISION starts the calculation from the beginning of the simulation and goes through every unit operation one by one. During the calculation, each unit goes through color changes.

Yellow — no calculation performed

Red — unit operation has not been solved

Green — calculation is being performed

Blue — unit operation has been solved

Dark Blue — unit operation has been calculated

Purple — indicate the break point

When the calculation is finished, all the unit operations should be blue, indicating that all the calculations are finished for the entire case. Once the calculations are performed, you do not need to run the calculations again as long as you do not change anything.

Reviewing and Printing the Results

Once the calculations are performed, you are ready to check the results by generating a report. To generate a report, follow these steps:

1) Click on *Output* from the menu bar in the main PFD.

2) Click on *Generate Report* on the *Output* menu and supply a name (*compressor* or any name you like) to save the output file. After you click on the *OK* button, the program will

bring up the *Programmer's File Editor* window. You can scroll up and down the report by using the scroll bars. The report lists information like PRO/II keyword input commands, component properties, unit operation results, and stream results. You can also edit the report by using the *Edit* menu.

You can print the entire report or part of the report by selecting *Print* in *File* menu.

3) To close the *Programmer's File Editor* window, double click on the bar located in the top right corner of the screen.

You can view the results of any stream or unit operation by clicking on the right button of your mouse when the cursor is pointing on it.

Printing Material and Energy Balance on PFD

In order to include material and energy balances on your PFD, you must define a property list first. The property list tells PROVISION what to include in the material and energy balance table. Let's define a property list that includes *Stream Name*, *Stream Phase*, *Total Molar Rate*, *Temperature*, *Pressure*, *Total Enthalpy*, and *Total Molar Comp. Fractions*.

Click on *Option* on the menu bar in the PFD window and choose *Stream Property Lists*. Click on *New* button in *Define Stream Property List* window to name the new list and type **case1** for the *List Name*.
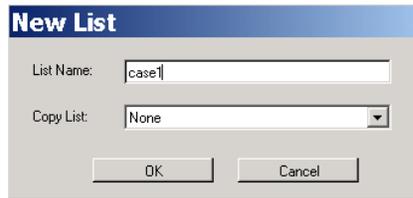
Click on the *OK* button to go back to *Define Stream Property List* window and choose the properties to include in the list from *Select Properties* box. Select *Stream Name* and click on *Add* button to include the selected property into the list. Repeat the procedure for *Stream Phase*, *Total Molar Rate*, *Temperature*, *Pressure*, *Total Enthalpy*, and *Total Molar Comp. Fractions*.
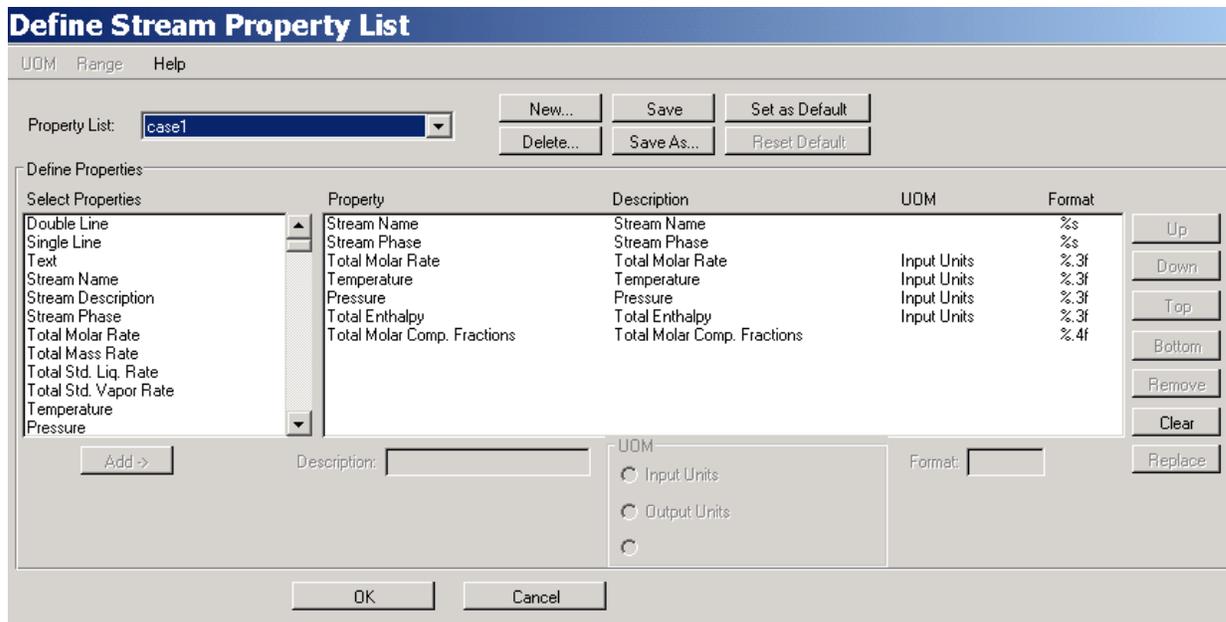
Save the list and click *OK*. Once the property list has been defined, you can now place the material and energy balance on the PFD. Follow these steps to place property table on the PFD:

1. Click on *Output* on the menu bar in the PFD window

2. Click on *Stream Property Table* on the *Output* menu

3. Click on the PFD where you want to place the property table

4. Double click on the property table to select the table

5. Choose **case1** in *Property List to be used*

6. You can select the streams you want by clicking on each stream or you could select all by clicking on *Add All*. Let's select all the streams by clicking on *Add All*.

C-13
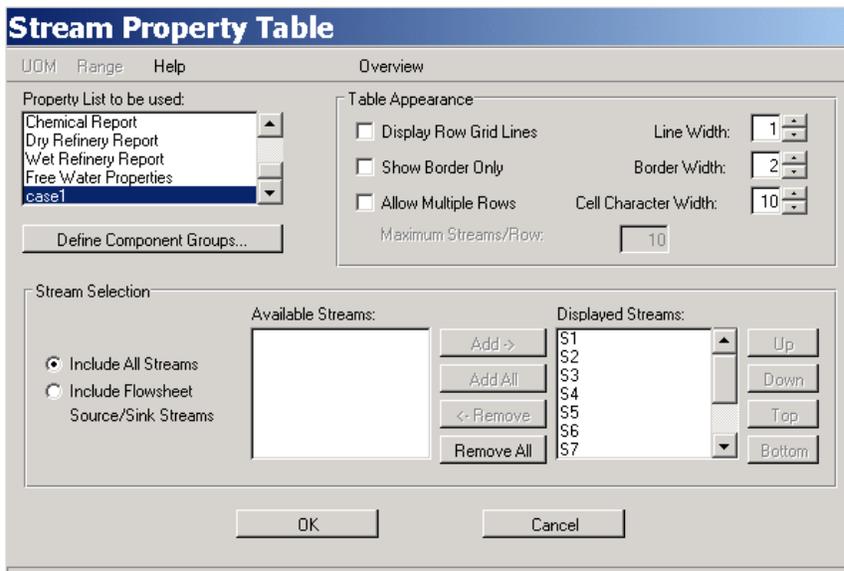
7. When you click on the *OK* button, the PFD should look like this:
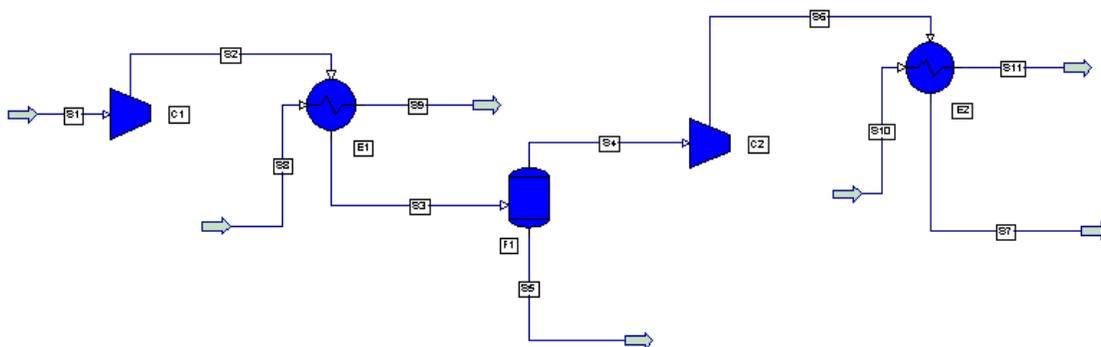
Stream Name		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
Stream Description		Feed Stream										
Phase		Vapor	Vapor	Mixed	Vapor	Liquid	Vapor	Mixed	Water	Water	Water	Water
Temperature	F	90.000	173.345	90.000	86.866	86.866	199.059	90.000	70.000	75.130	70.000	89.862
Pressure	PSIA	14.700	50.000	47.000	44.000	44.000	200.000	197.000	100.000	98.000	100.000	98.000
Flowrate	LB-MOL/HR	1000.000	1000.000	1000.000	974.964	25.036	974.964	974.964	23313.922	23313.922	23313.906	23313.906
Composition												
METHANE		0.050	0.050	0.050	0.051	0.001	0.051	0.051	0.000	0.000	0.000	0.000
ETHANE		0.200	0.200	0.200	0.205	0.019	0.205	0.205	0.000	0.000	0.000	0.000
PROPANE		0.250	0.250	0.250	0.255	0.072	0.255	0.255	0.000	0.000	0.000	0.000
BUTANE		0.300	0.300	0.300	0.300	0.293	0.300	0.300	0.000	0.000	0.000	0.000
PENTANE		0.200	0.200	0.200	0.189	0.615	0.189	0.189	0.000	0.000	0.000	0.000
H2O		0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000	1.000	1.000	1.000

Printing PFD: Click on *File* on the menu bar in the main PFD window and choose *Print*. Click on the *OK* button to start printing. You can draw or print text on the PFD by choosing *Draw/text* on the menu bar. After typing text in the box, use mouse to place on the PFD.

Appendix D Previous Exam

CHE 303 (Winter 2005)

_____
LAST NAME, FIRST

Quiz #1

Note: Your answers must be correct to 3 significant figures and have the appropriate units.

I. Circle the correct relation

(A) $\left(\dfrac{\partial h}{\partial P}\right)_T = T\left(\dfrac{\partial v}{\partial T}\right)_P + v$

(B) $\left(\dfrac{\partial h}{\partial P}\right)_T = T\left(\dfrac{\partial v}{\partial T}\right)_P - v$

(C) $\left(\dfrac{\partial h}{\partial P}\right)_T = -T\left(\dfrac{\partial T}{\partial v}\right)_P + v$

(D) $\left(\dfrac{\partial h}{\partial P}\right)_T = v - T\left(\dfrac{\partial v}{\partial T}\right)_P$

II. Circle the correct relation

(A) $\left(\dfrac{\partial T}{\partial P}\right)_s = \dfrac{T}{c_P}\left(\dfrac{\partial v}{\partial P}\right)_T$

(B) $\left(\dfrac{\partial T}{\partial P}\right)_s = \dfrac{T}{c_P}\left(\dfrac{\partial v}{\partial T}\right)_P$

(C) $\left(\dfrac{\partial T}{\partial P}\right)_s = \dfrac{T}{c_v}\left(\dfrac{\partial v}{\partial P}\right)_T$

(D) $\left(\dfrac{\partial T}{\partial P}\right)_s = -\dfrac{T}{c_P}\left(\dfrac{\partial v}{\partial T}\right)_P$

III. A gas mixture contains 30 mol % H_2O, 30 mole % N_2, and 40 mol % H_2.

Mass fraction of H_2O is   _____

IV. Nitrogen gas flowing at the rate of 400 kg/hr enters a compressor at 1 bar and 300°K and leaves at 10 bar and 450°K. Cooling water enters the compressor at 290°K and leaves at 340°K. Cooling water flow rate is 500 kg/hr. Nitrogen (MW = 28) is an ideal gas with Cp = 1.05 kJ/kg.°K. Heat capacity of water is 4.184 kJ/kg.°K. Gas constant R = 8.314 J/mol.°K.

1) (4 pts) The entropy change of nitrogen (kJ/hr·°K) is   _____
(**Show all the work**)

2) The entropy change of water (kJ/hr·°K) is   _____

3) The work provided by the compressor is   _____

4) If the entropy change of nitrogen is – 125 kJ/hr·°K and the entire process is reversible,

the temperature of the exit water is   _____

V. Consider the piston-cylinder assembly shown below; 200 moles of gas expand isothermally after the removal of a 10,000 kg block.

Assume that the PvT behavior can be described by the Van der Waals equation $\left(P = \dfrac{RT}{v-b} - \dfrac{a}{v^2} \right)$

with $a = 0.5$ [J·m³/mol²] and $b = 4 \times 10^{-5}$ [m³/mol] and that the ideal gas heat capacity has a constant value of $c_P = 35$ J/(mol·°K), $R = 8.314$ J/mol·°K.

Weightless, frictionless piston

Isothermal expansion

P_{atm}

$A = 0.1\ m^2$

10,000 kg

P_{atm}

$A = 0.1\ m^2$

0.4 m
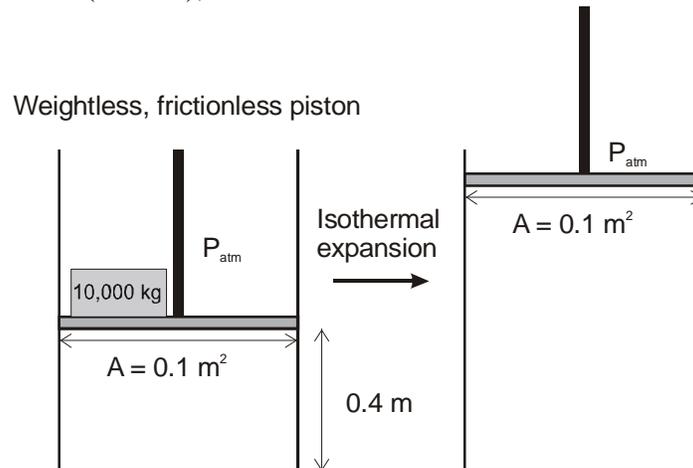
1) (4 pts) Determine the temperature of the system   _____
(**Show all the work**)

Quiz #2

Note: Your answers must be correct to 3 significant figures and have the appropriate units.

I. Circle the correct relation

(A) $ds = \dfrac{c_p}{T} dT + \left(\dfrac{\partial P}{\partial T}\right)_v dv$

(B) $ds = \dfrac{c_p}{T} dT - \left(\dfrac{\partial P}{\partial T}\right)_v dv$

(C) $ds = -\dfrac{c_p}{T} dT + \left(\dfrac{\partial P}{\partial T}\right)_v dv$

(D) $ds = \dfrac{c_v}{T} dT + \left(\dfrac{\partial P}{\partial T}\right)_v dv$

II. For the van der Waals equation: $P = \dfrac{RT}{v-b} - \dfrac{a}{v^2}$, we have

(A) $\left(\dfrac{\partial v}{\partial T}\right)_P = \dfrac{Rv^3(v-b)}{RTv^3 + 2a(v-b)^2}$

(B) $\left(\dfrac{\partial v}{\partial T}\right)_P = \dfrac{Rv^3(v-b)}{RTv^3 - a(v-b)^2}$

(C) $\left(\dfrac{\partial v}{\partial T}\right)_P = \dfrac{Rv^3(v-b)}{RTv^2 + 2a(v-b)^2}$

(D) $\left(\dfrac{\partial v}{\partial T}\right)_P = \dfrac{Rv^3(v-b)}{RTv^3 - 2a(v-b)^2}$

III. The following data are available at 25°C for graphite and diamond:

$\Delta g(25°C, 1\ atm) = g_{diamond} - g_{graphite} = 2866$ [J/mol], $\rho_{diamond} = 3.51$ [g/cm^3], and $\rho_{graphite} = 2.26$ [g/cm^3].

(3) The pressure at which these two forms of carbon are in equilibrium at 25°C can be determined from the following equation

(A) $2866 \left[\dfrac{J}{mol}\right] = (v_{graph} - v_{diam})(P - 1)$

(B) $2866 \left[\dfrac{J}{mol}\right] = (v_{diam} - v_{graph})(P - 1)$

(C) $2866 \left[\dfrac{J}{mol}\right] = (v_{graph} - v_{diam})P$

(D) $2866 \left[\dfrac{J}{mol}\right] = (v_{diam} - v_{graph})P$

(4) In the correct equation to determine the pressure in [Pa] where $\Delta g(25°C, 1\ atm) = 2866$ [J/mol], the numerical value of v_{graph} (with the correct unit) is

_____

IV. At 25°C, the vapor pressure of water is 3.169 kPa and at 35°C the vapor pressure of water is 5.628 kPa. Estimate the enthalpy of vaporization of water in kJ/mol.

Note: $\dfrac{dP}{dT} = \dfrac{h^v - h^l}{(v^v - v^l)T}$, gas constant $R = 8.314$ J/mol·°K

5) _____

V. (6) Calculate the power (kJ/hr) for compressing 5,000 kg/hr of methane from 0.8 Mpa, 210°K to 4 Mpa. The adiabatic efficiency of the compressor is 75%.
(*P-h* diagram is given for methane) _____

VI. (7) Saturated liquid methane at 3 MPa is reduced to 1 MPa through an expansion (let-down) valve. The vapor fraction of methane leaving the valve is
(*P-h* diagram is given for methane) _____

VII. The equilibrium conditions for two phases I and II of a single component are

    A) $T^I = T^{II}$, $P^I = P^{II}$, $h^I = h^{II}$ **B)** $T^I = T^{II}$, $P^I = P^{II}$, $s^I = s^{II}$

    C) $T^I = T^{II}$, $P^I = P^{II}$, $u^I = u^{II}$ **D)** None of the above
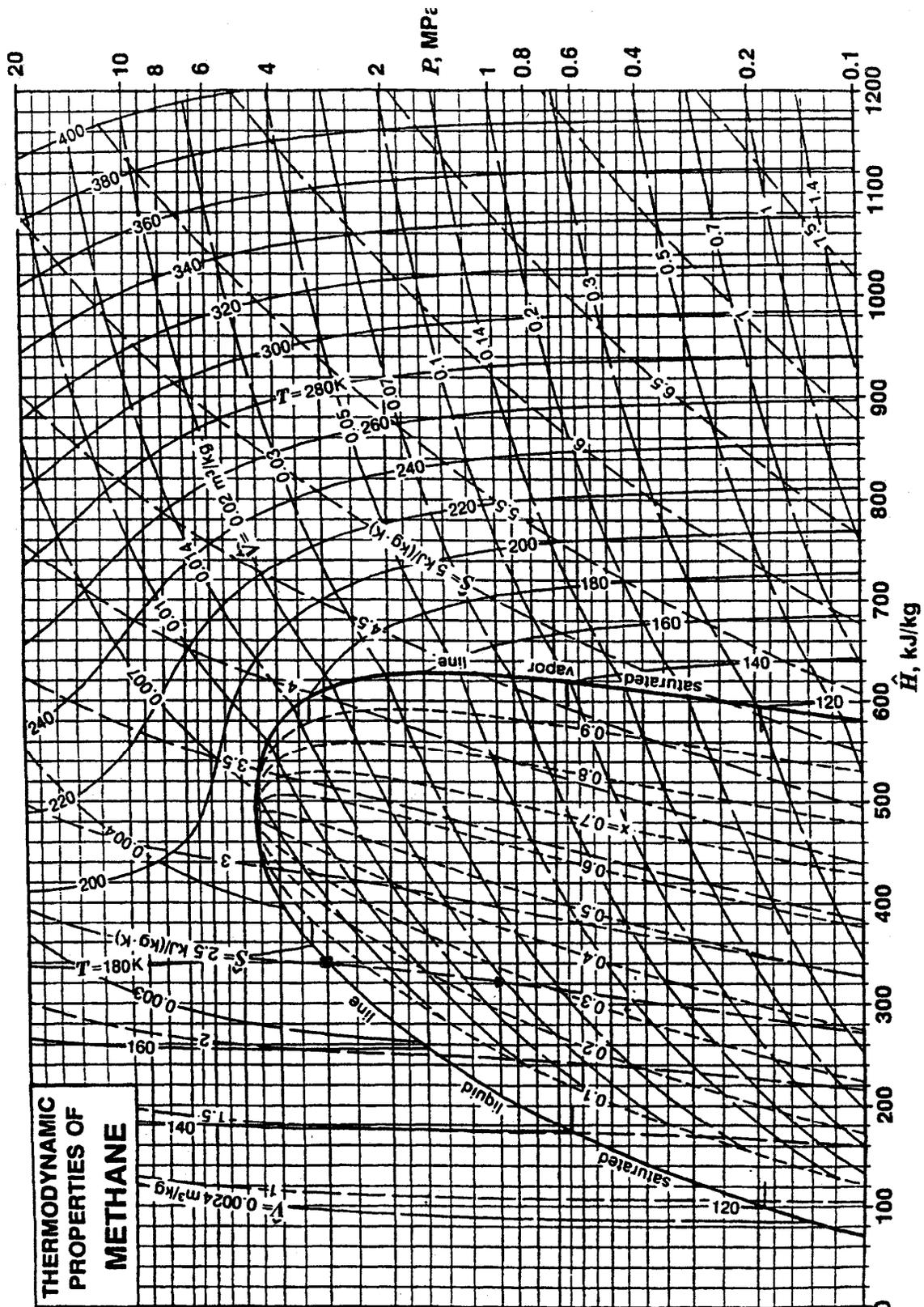
THERMODYNAMIC PROPERTIES OF METHANE

P, MPa

$\hat{H}$, kJ/kg

VIII.   Consider the piston-cylinder assembly shown below; 200 moles of gas expand isothermally after the removal of a 10,000 kg block.

Assume that the *PvT* behavior can be described by the Van der Waals equation $\left(P = \dfrac{RT}{v - b} - \dfrac{a}{v^2} \right)$
with $a = 0.5$ [J·m³/mol²] and $b = 4\times10^{-5}$ [m³/mol] and that the ideal gas heat capacity has a constant value of $c_P = 35$ J/(mol·°K), $R = 8.314$ J/mol·°K.

Weightless, frictionless piston

P_{atm}

P_{atm}

10,000 kg

$A = 0.1$ m²

Isothermal expansion

0.4 m

P_{atm}

$A = 0.1$ m²
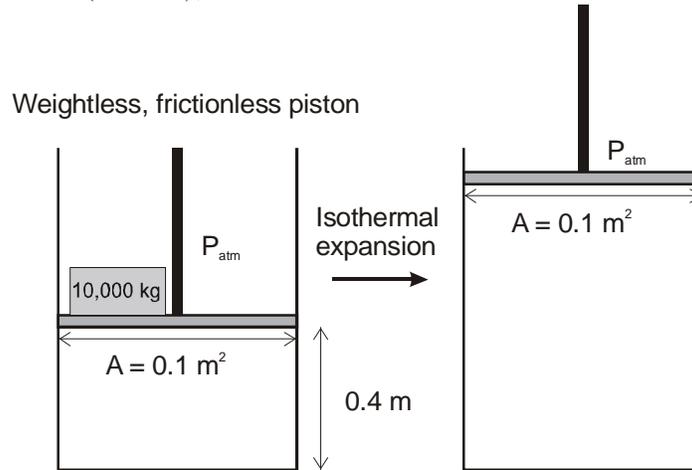
9) (4 pts) Determine the work [J] done by the gas on the surrounding   _____
(**Show all the work**)

Quiz #3

Note: Your answers must be correct to 3 significant figures and have the appropriate units.

I. Circle the correct relation

(A) $\left(\dfrac{\partial u}{\partial v}\right)_T = \left[T\left(\dfrac{\partial P}{\partial T}\right)_v + P\right]$

(B) $\left(\dfrac{\partial u}{\partial v}\right)_T = \left[P\left(\dfrac{\partial T}{\partial P}\right)_v - P\right]$

(C) $\left(\dfrac{\partial u}{\partial v}\right)_T = \left[T\left(\dfrac{\partial P}{\partial T}\right)_v - P\right]$

(D) $\left(\dfrac{\partial u}{\partial v}\right)_T = \left[P\left(\dfrac{\partial T}{\partial P}\right)_v + P\right]$

II. A vapor-compression refrigeration process using ammonia as the working fluid is to operate between 32°F and 86°F. In step (4) → (1) heat is supplied to the fluid at 32°F under the pressure P_1. The saturated vapor at P_1 is then compressed isentropically to P_2, where it becomes superheated vapor, state (2). Removal of heat from this vapor leads to cooling at constant pressure followed by condensation at 86°F, step (2) → (3). The cycle is closed by passing the saturated liquid at (3) through a let-down valve to the lower pressure at (4). The four states are given (not in any particular order) as follow

$T(°F)$	P(psia)	h(Btu/lb)	s(Btu/lb·°R)
32	63.1	621.5	1.2734
32			0.2941
86	171.5	139.0	0.2867
157.6		681.6	

1) The heat transferred (Btu/lb) in step (4) → (1) is $Q_L =$ _____

2) The heat transferred (Btu/lb) in step (2) → (3) is $Q_H =$ _____

3) The work supplied (Btu/lb) by the compressor is   W =   _____

4) The entropy (Btu/lb·°R) at state (2) is   _____

III. The free energy change for the following change in state is 685 cal/mol at 25°C

carbon (graphite, 1 atm) → carbon (diamond, 1 atm)

The pressure at which these two forms of carbon are in equilibrium at 25°C is 14,959 atm. The densities of graphite and diamond are 2.26 and 3.51 g/cm³, respectively, at 25°C independent of pressure. Determine Δg (cal/g) for the following processes at 25°C (cal = 41.3 cm³·atm)

1) carbon (graphite, 1 atm) → carbon (graphite, 14,959 atm)   _____

2) carbon (graphite, 14,959 atm) → carbon (diamond, 14,959 atm)   _____

IV. The vapor pressure of liquid water at 20°C is 0.0234 bar. Specific volume of water is 0.0180 m³/kmol. Gas constant R = 8314.3 Pa·m³/kmol·°K. 1 bar = 10⁵ Pa.

The fugacity of water at 20°C and 200 bar is   _____

V. (4 pts, show all your work) What fraction f of the volume of a rigid tube must be occupied by liquid water at 100°C (the remainder being water vapor) so that when the tube is heated the contents will pass through the critical state? Data: critical state $v^c = 3.155 \times 10^{-3}$ m³/kg, at 100°C: $v^G = 1.044 \times 10^{-3}$ m³/kg, $v^L = 1.673$ m³/kg.

$$f = _____$$

Quiz #4

Note: Your answers must be correct to 3 significant figures and have the appropriate units.

I. A. The fugacity of a component in a perfect gas mixture is equal to its partial pressure.
     B. At low pressure the fugacity of a liquid is equal to its vapor pressure.

1. A and B are true   2. Only A is true   3. Only B is true   4. A and B are false

II. Calculate the fugacity of steam at 450°C and 10 MPa. $f =$ _____

   Data: At 450°C and 0.01 MPa: $g = - 3672.8$ kJ/kg

       At 450°C and 10 MPa: $g = - 1399.9$ kJ/kg

       Gas constant $R = 8.314$ J/(mol·°K), molecular weight of water $= 18$

       $dg = RT \, d(\ln f)$

III. Two compounds A and B are known to form ideal liquid solutions. A vapor mixture containing 40 mol% of A and 60 mol% of B is initially at 100°F and 1 atm. The vapor pressures of A and B at this temperature are $P_A^{sat} = 0.90$ atm and $P_B^{sat} = 1.50$ atm. This mixture is compressed isothermally.

1. The dew point pressure is   _____

2. The bubble point pressure is   _____

IV. A vessel initially containing propane at 520°R is connected to a nitrogen cylinder, and the pressure is increased to 300 psia. The vapor pressure of propane at 520°R is 155 psia. Nitrogen is insoluble in liquid propane.

1. Assume ideal solution, mol fraction of propane in the vapor phase is _____

2. Using K value from table 1, mol fraction of propane in the vapor phase is _____

Table 1. Equilibrium K values for light hydrocarbon systems
(Ref: <u>Equilibrium Staged Separations</u> by Wankat)
==

(1) $\ln K = -A/T^2 + B - C \ln(P) + D/P^2$
(2) $\ln K = -A/T^2 + B - C \ln(P) + D/P$, where P is in psia, T is in °R

compound	A	B	C	D	Form

==

| Propane | 970688.6 | 7.15059 | .76984 | 6.90224 | (2) |
| n-Butane | 1280557 | 7.94986 | .96455 | 0 | (1) |

V. A liquid containing 60 mol% propane (C3) and 40 mol% n-butane (C4) is subjected to a flash vaporization process at a pressure of 20 psia where the temperature inside the flash drum is 475ºR. At these condition $K_{C3} = 2.4284$, $K_{C4} = 0.5405$ (from Table 1).

1. The exit mol fraction of propane in the vapor phase is   _____

2. If the exit mol fraction of propane in the liquid phase is 0.3, V/F =   _____

3. The boiling point of pure n-butane at 20 psia is   _____

VI. A. In a closed system at constant T and P, a spontaneous process will increase Gibbs free energy, G, until a maximum value for G is reached at equilibrium.

     B. For an isolated system, a process that would move the system to a less constrained equilibrium state will decrease the entropy of the system.

1. A and B are true   2. Only A is true   3. Only B is true   4. A and B are false

_____
LAST NAME, FIRST

Quiz #5

Note: Your answers must be correct to 3 significant figures and have the appropriate units.

I. At 25ºC a binary system containing components A and B is in a state of liquid-liquid vapor equilibrium. The mixture is not ideal however Raoult's and Henry's laws can be applied. The compositions of the saturated liquid phases are

$x^I_{As} = 0.02, x^I_{Bs} = 0.98$ and $x^{II}_{As} = 0.97, x^{II}_{Bs} = 0.03$

The vapor pressure at 25ºC are: $P^o_A = 0.2$ atm, $P^o_B = 0.8$ atm

1) The vapor mole fraction of A at three-phase equilibrium is   _____

2) The vapor mole fraction of A in equilibrium with $x_A = 0.01$ is   _____

3) The vapor mole fraction of A in equilibrium with $x_A = 0.99$ is   _____

4) At 25ºC a vapor containing 10 mol % A and 90 mol % B initially at 0.1 atm is compressed

isothermally until liquid phase I is formed. The dew point pressure is   _____

II. In the system A-B, activity coefficients can be expressed by $\ln \gamma_A = 0.5\, x_B^2$ and $\ln \gamma_B = 0.5\, x_A^2$. The vapor pressure of A and B at 80°C are: $P_A^o = 650$ mm Hg, $P_B^o = 900$ mmHg. There is an azeotrope in this system.

5) If the azeotrope mole fraction x_A is 0.17458 the azeotrope pressure is   _____

6) The azeotrope mole fraction x_A can be determine from
A) $\exp\{[\, x_A^2 - (1 - x_A)^2]\} = P_B^o / P_A^o$ B) $\exp\{[\, x_A^2 - (1 - x_A)^2]\} = P_A^o / P_B^o$
C) $\exp\{[\, x_A^2 - (1 - x_A^2)]\} = P_A^o / P_B^o$ D) None of the above

III. A system contains 40 mol % toluene, 30 mol % ethylbenzene, and 30 mol % water. Mixtures of ethylbenzene and toluene obey Raoult's law and the hydrocarbons are completely immiscible in water. The system pressure is 1 atm. (Note T = toluene, EB = ethylbenzene, W = water)

7) The bubble point temperature can be determine by solving the following equation:

A) $.3\, P_w^o + .4\, P_T^o + .3\, P_{EB}^o = 1$ atm   B) $P_w^o + .4\, P_T^o + .3\, P_{EB}^o = 1$ atm

C) $P_w^o + \dfrac{4}{7}\, P_T^o + \dfrac{3}{7}\, P_{EB}^o = 1$ atm   D) None of the above

8) If the hydrocarbon phase condenses first, the dew point temperature can be determine from

A) $\dfrac{.4atm}{P_T^o} + \dfrac{.3atm}{P_{EB}^o} = 1$ B) $\dfrac{.3atm}{P_W^o} + \dfrac{.4atm}{P_T^o} + \dfrac{.3atm}{P_{EB}^o} = 1$

C) $\dfrac{4atm}{7P_T^o} + \dfrac{3atm}{7P_{EB}^o} = 1$ C) None of the above

IV.(9) A solute diffuses through a membrane that separates two compartments A and B that have different initial concentrations. The solute concentrations in the two compartments as a function of time, C^A and C^B are shown in Figure 1. The volumes of the two compartments are V^A and V^B.

(A) $V^A < V^B$ **(B)** Solute diffuses from compartment B to A.

a. A and B are true   **b.** Only A is true   **c.** Only B is true   **d.** A and B are false
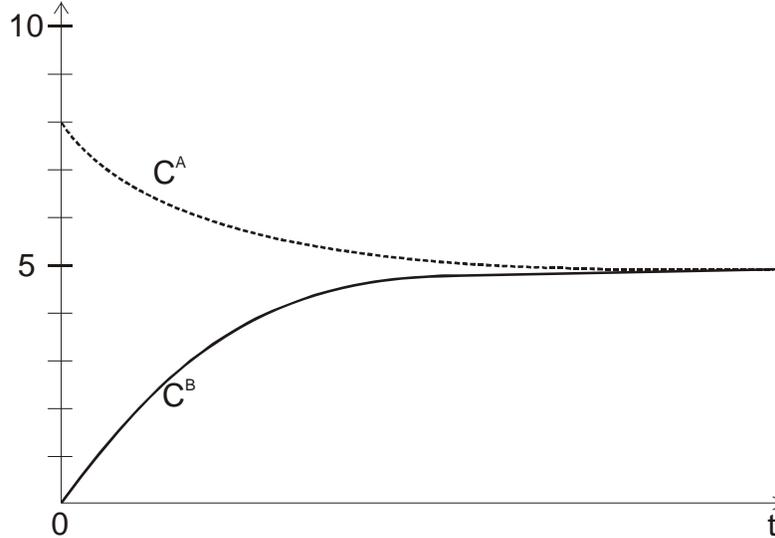
Figure 1. Concentration of solute as a function of time in compartments A and B.

V.(10) Measurements show that the osmolarity of human tears is 320 mosmol/L. Determine the value of the osmotic pressure of human tears in pascals at 300°K.
$$\pi = RT\sum_{i=1}^{N} C_{S,i} \text{, gas constant } R = 8.314\frac{Pa \cdot m^3}{mol \cdot K}$$

$$\pi = \underline{\hspace{2cm}}$$

Answers to CHE303 Quizzes 2005

Quiz #1
I.   (D)
II.   (B)
III.   0.37
IV.   1) − 103.19 kJ/hr·K   2) 332.76 kJ/hr·K   3) 167,600 kJ/hr   4) 307.9 K

Quiz #2
I.   (D)
II.   (D)
III.   3) (A)   4) 5.31×10^{-6} m^3/mol
IV.   43.87 kJ/mol
V. 1.33×10^6 kJ/hr
VI.   0.313
VII.   (D)
VIII. 4.31×10^5 J

Quiz #3
I.   (C)
II.   1) 482.5 Btu/lb   2) 542.6 Btu/lb   3) 60.1 Btu/lb   4) 1.2734 Btu/lb·^{o}R
III.   1) 106.3 cal/g   2) 0
IV.   0.0271 bar
V.   0.6695

Quiz #4
I.   (1)
II.   9.0209 MPa
III.   1) 1.1842 atm   2) 1.260 atm
IV.   1) 0.5167   2) 0.4461
V.   1) 0.591   2) 0.7001   3) 503oR
VI.   (4)

Quiz #5
I.   1) 0.1984   2) 0.10901   3) 0.431   4) 0.8808 atm
II.   5) 913.88 mmHg   6) (D)
III.   7) (C)   8) (A)
IV.   (d)
V. 7.98×10^5 Pa