CHEMICAL ENGINEERING THERMODYNAMICS

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Symbol Dictionary

The following is a list of symbols and their definitions used in this review guide. One common trend used in this guide is that lower-case symbols typically refer to intensive quantities while their corresponding upper-case symbols refer to extensive quantities. Also, an overhead dot indicates a quantity that is a function of time.

Symbol	Definition
A	Area
$a, \mathcal{A}$	Helmholtz free energy
c_p	Heat capacity at constant pressure
c_v	Heat capacity at constant volume
c_i	Molal concentration of species i
C_i	Mass concentration of species i
$|i|$	Molar concentration of species i
e, E	Energy
F	Force
$\mathcal{F}$	Degrees of freedom
f_i	Fugacity of pure species i
$\hat{f}_i$	Fugacity of species i in a mixture
f	Fugacity of solution
f, G	Gibbs free energy
h, H	Enthalpy
$\mathcal{H}_i$	Henry's law constant of solute i
k	Boltzmann's constant
k_{CP}	Heat capacity ratio
K	Equilibrium constant
m	Mass
n	Number of moles
N_A	Avogadro's number
P	Pressure
P_i	Partial pressure of species i
P_i^{sat}	Saturation pressure of species i
q, Q	Heat
r	Distance between two molecules
R	Ideal gas constant
s, S	Entropy
t	Time
T	Temperature
u, U	Internal energy
v, V	Volume
w, W	Work
w_i	Weight fraction of species i
x_i	Mole fraction of liquid species i
X_i	Mole fraction of solid species i
y_i	Mole fraction of vapor species i
z	Compressibility factor
φ_i	Fugacity coefficient of pure species i
$\hat{\varphi}_i$	Fugacity coefficient of species i in a mixture
φ	Fugacity coefficient of solution

γ_i	Activity coefficient of species i
η	Efficiency factor
μ_i	Chemical potential of species i
Π	Osmotic pressure
ρ	Density
ν_i	Stoichiometric coefficient
ω	Pitzer acentric factor
ξ	Extent of reaction

1. MEASURED THERMODYNAMIC PROPERTIES AND OTHER BASIC CONCEPTS

1.1 PRELIMINARY CONCEPTS – THE LANGUAGE OF THERMODYNAMICS

In order to accurately and precisely discuss various aspects of thermodynamics, it is essential to have a well-defined vernacular. As such, a list of some foundational concepts and their definitions are shown below:

- **Universe** – all measured space
- **System** – space of interest
- **Surroundings** – the space outside the system
- **Boundary** – the system is separated by the surroundings via a boundary
- **Open System** – a system that can have both mass and energy flowing across the boundary
- **Isolated System** – a system that can have neither mass nor energy flowing across the boundary
- **Closed System** – a system that can have energy but not mass flowing across the boundary
- **Extensive Property** – a property that depends on the size of the system
- **Intensive Property** – a property that does not depend on the size of the system
- **State** – the condition in which one finds a system at any given time (defined by its intensive properties)
- **Process** – what brings the system from one state to another
- **Adiabatic Process** – a process that has no heat transfer ($Q = 0$)
- **Isothermal Process** – a process that has a constant temperature ($\Delta T = 0$)
- **Isobaric Process** – a process that has a constant pressure ($\Delta P = 0$)
- **Isochoric Process** – a process that has a constant volume ($\Delta V = 0$)
- **Isenthalpic Process** – a process that has a constant enthalpy ($\Delta H = 0$)
- **Isentropic Process** – a process that has a constant entropy ($\Delta S = 0$)
- **State Function** – a quantity that depends only on the current state of a system
- **Path Function** – a quantity that depends on the path taken

1.2 MEASURED THERMODYNAMIC PROPERTIES

With this set of clearly defined vocabulary, we can now discuss how thermodynamic properties are measured.

1.2.1 VOLUME

Even though volume, V, is an extensive property, we can define intensive forms. If we divide the volume by the number of moles, n, we get a *molar* volume

$$v \equiv \frac{V}{n}$$

whereas dividing by mass, m, yields a *specific* volume

$$\hat{v} \equiv \frac{V}{m} = \frac{1}{\rho}$$

which is simply the inverse of density, ρ.

1.2.2 TEMPERATURE

Temperature, T, is an intensive property and is proportional to the average kinetic energy of the individual atoms or molecules in a system. Over time, the speed of all molecules in a given system becomes a well-

defined distribution; this is referred to as the Maxwell-Boltzmann distribution, an example of which is shown in Figure 1.
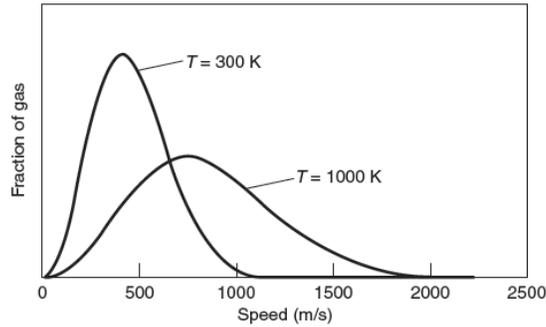
Figure 1. A schematic showing a Maxwell-Boltzmann distribution.

From the kinetic theory of gases, one can show that

$$\overline{e_k^{\text{molecular}}} = \frac{1}{2} m \overline{\vec{V}}^2$$

and

$$\overline{e_k^{\text{molecular}}} = \frac{3}{2} k_B T$$

where m is the mass of an individual molecule, $\overline{\vec{V}}$ is the mean velocity, and k_B is the Boltzmann constant. This means that

$$\overline{\vec{V}} \approx \sqrt{\frac{3 k_B T}{m}}$$

Thinking about temperature in terms of molecular motion, we can define an absolute temperature scale where 0 is equivalent to no molecular motion. One such absolute scale is the Kelvin scale, which is related to the temperature in Celsius via

$$T[\text{K}] = T[\text{°C}] + 273.15$$

Another absolute temperature scale – the Rankine scale – can be used to convert between SI and English systems:

$$T[\text{°R}] = \frac{9}{5} T[\text{K}]$$

$$T[\text{°R}] = T[\text{°F}] + 459.67$$

Of course, one can then write that

$$T[\text{°F}] = \frac{9}{5} T[\text{°C}] + 32$$

1.2.3   PRESSURE

Pressure, P, is also an intensive property. It is defined as the (normal) force, F, per unit area, A:

$$P \equiv \frac{F}{A}$$

Equations of state relate the measured properties T, P, and V. The ideal gas model is a simplified equation to describe the measured properties of a perfect gas:

$$P = \frac{nRT}{V}$$

where R is the ideal gas constant. The ideal gas law is based on the assumption that molecules are infinitesimally small, round spheres that occupy negligible volume and do not experience intermolecular attraction or repulsion.

1.3 EQUILIBRIUM

1.3.1 FUNDAMENTAL DEFINITIONS

Equilibrium refers to a condition in which the state of a system neither changes with time nor has a tendency to spontaneously change (i.e. there are no net driving forces for change). As such, equilibrium can only occur for closed (and isolated) systems. If an open system does not change with time as it undergoes a process, it is said to be in steady-state. With this, we will again define some important conditions:

- **Mechanical equilibrium** – no pressure difference between system and surroundings
- **Thermal equilibrium** – no temperature difference between system and surroundings
- **Chemical equilibrium** – no tendency for a species to change phases or chemical react
- **Thermodynamic equilibrium** – a system that is in mechanical, thermal, and chemical equilibrium
- **Phase equilibrium** – a system with more than one phase present that is in thermal and mechanical equilibrium between the phases such that the phase has no tendency to change
- **Chemical reaction equilibrium** – a system undergoing chemical reactions with no more tendency to react
- **Saturation pressure** – the pressure when the rate of vaporization equals the rate of condensation (for a specific temperature), denoted P^{sat}
- **Saturation temperature** – the temperature when the rate of vaporization equals the rate of condensation (for a specific pressure), denoted T^{sat}
- **Vapor pressure** – a substance's contribution to the total pressure in a mixture at a given temperature
- **State postulate** – for a system containing a pure substance, all intensive thermodynamic properties can be determined from two independent intensive properties while all extensive thermodynamic properties can be determined from three independent intensive properties
- **Triple point** – the value of P and T for which a pure substance has the gas, liquid, and solid phases coexisting in thermodynamic equilibrium
- **Critical temperature** – the temperature at and above which vapor of a substance cannot be liquefied
- **Critical pressure** – the pressure at and above which vapor of a substance cannot be liquefied

1.3.2 INDEPENDENT AND DEPENDENT THERMODYNAMIC PROPERTIES

The Gibbs phase rule states that the degrees of freedom can be given by

$$\Im = m - \pi + 2$$

where m is the number of chemical species in the system and π is the number of phases. The value of $\Im$ is the number of independent, intensive properties needed to constrain the properties in a given phase.

To constrain the state of a system with gas and liquid phases, the fraction that is vapor (called the quality) can be defined:

$$x = \frac{n_v}{n_l + n_v}$$

where n_v and n_l are the number of moles in the liquid and vapor phases, respectively. Any intensive property can be found by proportioning its value in each phase by the fraction of the system that the phase occupies.[1]

1.3.3 PHASES

An example phase diagram is shown in Figure 2, denoting the effects of pressure and temperature for a hypothetical substance.
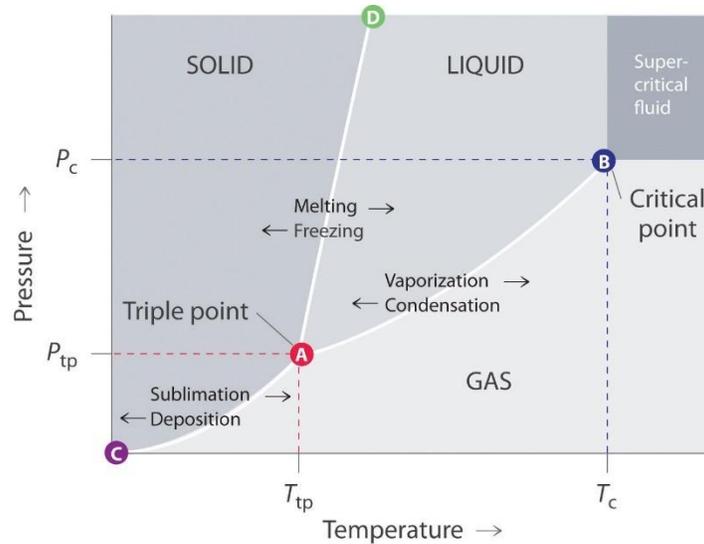
Figure 2. A sample phase diagram. The critical temperature and critical pressure are denoted by T_C and P_C, respectively. The triple point is the point (T_{tp}, P_{tp}).

2 THE FIRST LAW OF THERMODYNAMICS

2.1 DEFINITION OF THE FIRST LAW

The First Law of Thermodynamics states that the total quantity of energy in the universe is constant. Phrased another way,

$$\Delta E_{\text{univ}} = 0$$

or "energy cannot be created or destroyed" although it can change forms. This can also be made to says

$$\Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$$

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[1] For instance, the molar volume of a liquid-vapor system can be found by $v = (1 - x)v_l + xv_v$.

2.2   FUNDAMENTAL DEFINITIONS

- **Kinetic energy** –energy of motion, defined as $E_K = \frac{1}{2}m\vec{V}^2$
- **Potential energy** – energy associated with the bulk position of a system in a potential field, denoted E_P
- **Internal energy** – energy associated with the motion, position, and chemical-bonding configuration of the individual molecules of the substances within a system, denoted U
- **Sensible heat** – a change in internal energy that leads to a change in temperature
- **Latent heat** – a change in internal energy that leads to a phase transformation
- **Heat** – the transfer of energy via a temperature gradient, denoted Q
- **Work** – all forms of energy transfer other than heat, denoted W

2.3   WORK

The work, W, can be described as

$$W = \int F\,dx$$

where F is the external force and dx is the displacement. Work can also be related to the external pressure via

$$W = -\int P\,dV$$

which is typically referred to as PV work and can be computed by taking the area underneath a P vs. V curve for a process (and then negating it). In this context, a positive value of W means that energy is transferred from the surroundings to the system whereas a negative value means that energy is transferred from the system to the surroundings. The same sign-convention is chosen for heat (see below).

2.4   HYPOTHETICAL PATHS

It is important to note that hypothetical paths can be used to find the value of a state function. Consider the processes in Figure 3. The actual path is not easy to use for calculations, as both T and v are changing. However, one can proposed alternative hypothetical paths to get from State 1 to State 2 that take advantage of the fact that the path does not matter when computing a state function. All three paths (the real one as well as the two hypothetical ones) will produce the same answer for Δu.
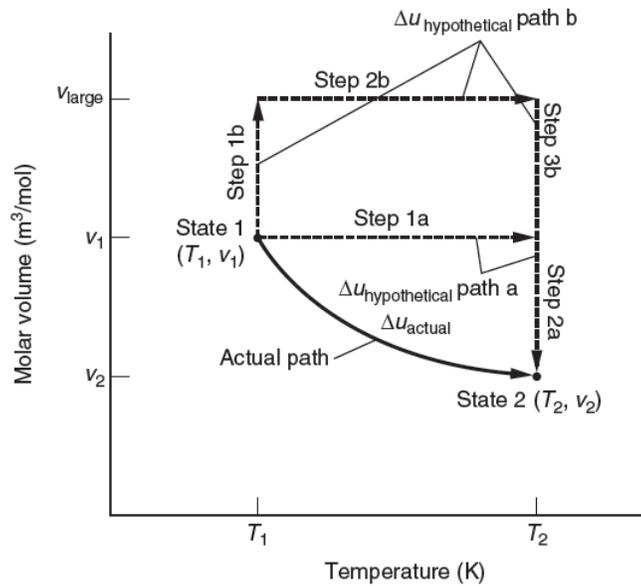
Figure 3. Plot of a process that takes a system from State 1 to State 2. Three alternative paths are shown: the real path as well as two convenient hypothetical paths.

2.5   REVERSIBLE AND IRREVERSIBLE PROCESSES

A process is reversible if, after the process occurs, the system can be returned to its original state without any net effect on the surroundings. This result occurs only when the driving force is infinitesimally small. Otherwise, the process is said to be irreversible. All real processes are irreversible; however, reversible processes are essential for approximating reality.

The efficiency of expansion is typically given by

$$\eta_{\text{exp}=} = \frac{w_{\text{irrev}}}{w_{\text{rev}}}$$

and the efficiency of compressions is typically given by

$$\eta_{\text{comp}} = \frac{w_{\text{rev}}}{w_{\text{irrev}}}$$

2.6   CLOSED SYSTEMS

2.6.1   INTEGRAL BALANCE

The first law of thermodynamics can be written as

$$\Delta U + \Delta E_K + \Delta E_P = Q + W$$

However, the kinetic and potential macroscopic energies can often be neglected such that

$$\Delta U = Q + W$$

Since the mass of a closed system stays constant, one can divide by the total number of moles if no chemical reactions take place to yield the intensive form:

$$\Delta u = q + w$$

2.6.2 DIFFERENTIAL BALANCE

Oftentimes in chemical engineering thermodynamics we must consider how various properties change as a function of time. In this case, differential balances are necessary. The first law can be written similarly as

$$dU + dE_K + dE_P = \delta Q + \delta W$$

or

$$dU = \delta Q + \delta W$$

if we ignore kinetic and potential energy contributions.[2] Of course, for a closed system we can write the equivalent intensive form of the equation as well.

With this differential balance, we can differentiate with respect to time to yield:

$$\frac{dU}{dt} = \dot{Q} + \dot{W}$$

2.7 ISOLATED SYSTEMS

Since isolated systems do not allow for energy transfer, $\Delta U = 0$ for this case. As such, $Q + W = 0$.

2.8 OPEN SYSTEMS

In open systems, mass can flow into and out of the system. This can be expressed via a mole balance as

$$\frac{dn}{dt} = \sum_{\text{in}} \dot{n}_{\text{in}} - \sum_{\text{out}} \dot{n}_{\text{out}}$$

assuming no chemical reactions. For a stream flowing through a cross-sectional area A with a velocity $\vec{V}$, the molar flow rate can be written as

$$\dot{n} = \frac{A\vec{V}}{v}$$

A system at steady-state has all differentials with respect to time being zero, so for steady-state:

$$\sum_{\text{in}} \dot{n}_{\text{in}} = \sum_{\text{out}} \dot{n}_{\text{out}}$$

In addition to this balance, we also must write an energy balance. The energy balance is

$$\frac{dU}{dt} + \frac{dE_K}{dt} + \frac{dE_P}{dt}$$
$$= \sum_{\text{in}} \dot{n}_{\text{in}} \left(u + e_K + e_P\right)_{\text{in}} - \sum_{\text{out}} \dot{n}_{\text{out}} \left(u + e_K + e_P\right)_{\text{out}} + \dot{Q}$$
$$+ \left[\dot{W}_s + \sum_{\text{in}} \dot{n}_{\text{in}} \left(Pv\right)_{\text{in}} + \sum_{\text{out}} \dot{n}_{\text{out}} \left(-Pv\right)_{\text{out}}\right]$$

In steady-state, this reads

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[2] The d differential operator is used for state functions whereas the δ differential operator is used for path functions.

$$0 = \sum_{\text{in}} \dot{n}_{\text{in}} \left(u + e_K + e_P \right)_{\text{in}} - \sum_{\text{out}} \dot{n}_{\text{out}} \left(u + e_K + e_P \right)_{\text{out}} + \dot{Q}$$

$$+ \left[\dot{W}_s + \sum_{\text{in}} \dot{n}_{\text{in}} \left(Pv \right)_{\text{in}} + \sum_{\text{out}} \dot{n}_{\text{out}} \left(-Pv \right)_{\text{out}} \right]$$

The left two terms refer to the energy flowing into and out of the system whereas the last two terms refer to the flow work from the inlet and outlet streams. The $\dot{W}_s$ term refers to the shaft work, or the useful work that is obtained from the system.

The above expression can be algebraically rearranged to read

$$0 = \sum_{\text{in}} \dot{n}_{\text{in}} \left[\left(u + Pv \right) + e_K + e_P \right]_{\text{in}} - \sum_{\text{out}} \dot{n}_{\text{out}} \left[\left(u + Pv \right) + e_K + e_P \right]_{\text{out}} + \dot{Q} + \dot{W}_s$$

This form is especially enlightening, as there is a frequent $u + Pv$ term. This is enthalpy:

$$H \equiv U + PV$$

or

$$h \equiv u + Pv$$

This then means the energy balance can be written as

$$0 = \sum_{\text{in}} \dot{n}_{\text{in}} \left[h + e_K + e_P \right]_{\text{in}} - \sum_{\text{out}} \dot{n}_{\text{out}} \left[h + e_K + e_P \right]_{\text{out}} + \dot{Q} + \dot{W}_s$$

Neglecting kinetic and potential energy contributions yields

$$0 = \sum_{\text{in}} \dot{n}_{\text{in}} \, h_{\text{in}} - \sum_{\text{out}} \dot{n}_{\text{out}} \, h_{\text{out}} + \dot{Q} + \dot{W}_s$$

2.9   OPEN-SYSTEM ENERGY BALANCE ON PROCESS EQUIPMENT

2.9.1   INTRODUCTION

For these problems, it is best to start with a general energy balance, such as the one shown in the previous section:

$$\frac{dU}{dt} + \frac{dE_K}{dt} + \frac{dE_P}{dt}$$

$$= \sum_{\text{in}} \dot{n}_{\text{in}} \left(u + e_K + e_P \right)_{\text{in}} - \sum_{\text{out}} \dot{n}_{\text{out}} \left(u + e_K + e_P \right)_{\text{out}} + \dot{Q}$$

$$+ \left[\dot{W}_s + \sum_{\text{in}} \dot{n}_{\text{in}} \left(Pv \right)_{\text{in}} + \sum_{\text{out}} \dot{n}_{\text{out}} \left(-Pv \right)_{\text{out}} \right]$$

From here, approximations and assumptions can be made to simplify the problem further. Generally speaking, it is best to write out the general mass and energy balances at the start of any chemical engineering problem. The mass balances for open-system process equipment is typically just

$$\dot{m}_{\text{in}} = \dot{m}_{\text{out}}$$

2.9.2 NOZZLES AND DIFFUSERS

These devices convert between internal energy and kinetic energy by changing the cross-sectional area through which a fluid flows to change the bulk flow velocity. A nozzle constricts the cross-sectional area to increase the flow whereas a diffuser increases the cross-sectional area to decrease the flow. Note that the cross-sectional area and velocity can be related by

$$A_{in}\vec{V}_{in} = A_{out}\vec{V}_{out}$$

Assuming steady-state (i.e. $\Delta\dot{n} = 0$ if no chemical reactions are occurring, all time-derivative terms are zero), no shaft-work (i.e. $\dot{W}_s = 0$), no heat flow (i.e. $\dot{Q} = 0$), the general energy balance becomes

$$(h + e_K)_{in} = (h + e_K)_{out}$$

2.9.3 TURBINES AND PUMPS

These processes involve the transfer of energy via shaft work. Turbines put out useful work whereas pumps put useful work into the system. Assuming steady-state and that the heat flow is zero (i.e. $\dot{Q} = 0$) then

$$\frac{\dot{W}_s}{\dot{n}} = \Delta(h + e_K + e_P)$$

2.9.4 HEAT EXCHANGERS

Heat exchangers heat up or cool down a fluid through thermal contact with another fluid at a different temperature, so it is converting between enthalpy and heat. Assuming steady-state, no shaft-work (i.e. $\dot{W}_s = 0$), and no change in kinetic or potential energies (i.e. $\Delta e_K = \Delta e_P = 0$) then

$$\frac{\dot{Q}}{\dot{n}} = \Delta h$$

2.9.5 THROTTLING DEVICES

Throttling devices reduce the pressure of flowing streams, typically via a partially opened valve or porous plug. This is most often done to liquefy a gas. These devices have negligible heat loss (i.e. $\dot{Q} = 0$) due to the small amount of time the fluid is in the device. Assuming steady-state and no shaft-work then

$$\Delta h = 0$$

2.10 THERMODYNAMIC DATA FOR U AND H

2.10.1 HEAT CAPACITY

The heat capacity at constant volume, c_v, can be defined as

$$c_v \equiv \left(\frac{\partial u}{\partial T}\right)_v$$

From this, it is clear that

$$\Delta u = \int c_v \, dT$$

The heat capacity at constant pressure, c_P, can be defined as

$$c_P \equiv \left(\frac{\partial h}{\partial T}\right)_P$$

From this, it is clear that

$$\Delta h = \int c_p \, dT$$

For liquids and solids,

$$c_P \approx c_v \text{ [liquids and solids]}$$

For ideal gases,

$$c_P - c_v = R \text{ [ideal gas]}$$

2.10.2 LATENT HEAT

When a substance changes phases, there is a substantial change in internal energy due to the latent heat of transformation. These are typically reported as enthalpies (e.g. enthalpy of vaporization) at 1 bar, which is the normal boiling point, T_b. Therefore, the enthalpy of heating water originally at T_1 to steam at a temperature T_2 where $T_1 < T_b < T_2$, for example, would be

$$\Delta h = \int_{T_1}^{T_b} c_p^l \, dT + \Delta h_{\text{vap},T_b} + \int_{T_b}^{T_2} c_P^v \, dT$$

If it is desired to know the enthalpy of a phase transformation at a pressure other than 1 bar, one can construct a hypothetical path like that shown in Figure 4. The sum of the enthalpy changes from Step 1, Step 2, and Step 3 is equal to that of the actual path.
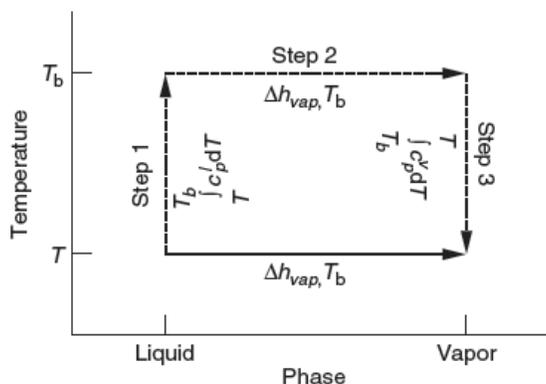

Figure 4. Hypothetical path to calculate Δh_{vap} at a temperature T from data available at T_b and heat capacity data.

2.10.3 ENTHALPY OF REACTION

Typically, the standard[3] enthalpies of formation, Δh_f°, of individual species are tabulated. The enthalpy of formation is defined as the enthalpy difference between a given molecule and its reference state, which is typically chosen as the pure elemental constituents as found in nature. As a result, the enthalpy of formation of a pure element is always zero.

The standard enthalpy of a reaction can be computed as

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[3] "Standard" refers to a particular reference state, usually 298.15 K and 1 bar. It is indicated by the ∘ symbol.

$$\Delta h^{\circ}_{\text{rxn}} = \sum v_i \Delta h^{\circ}_f$$

Here, v_i is the stoichiometric coefficient. For a balanced reaction $a\text{A} \rightarrow b\text{B}$, the stoichiometric coefficient of A would be $v_A = -a$ and the stoichiometric coefficient of B would be $v_B = b$. A reaction that releases heat is called exothermic and has a negative enthalpy of reaction, whereas a reaction that absorbs heat is called endothermic and has a positive enthalpy of reaction. An example of using hypothetical paths to calculate the enthalpy of reaction at a temperature other than the reference temperature is shown in Figure 5.
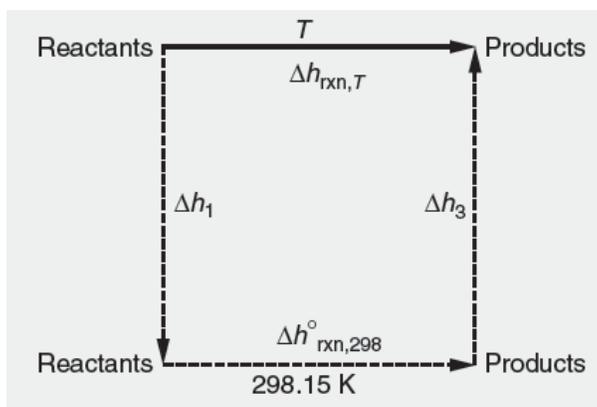
Figure 5. Hypothetical path to calculate Δh_{rxn} at an arbitrary temperature T.

2.11 CALCULATING FIRST-LAW QUANTITIES IN CLOSED SYSTEMS

2.11.1 STARTING POINT

When calculating first-law quantities in closed systems for reversible processes, it is best to always start with the following three equations, which are always true:

$$W = -\int P \, dV$$

$$\Delta U = Q + W$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta U = \int C_V \, dT$$

$$\Delta H = \int C_P \, dT$$

If ideal gas conditions can be assumed then,

$$C_P - C_V = nR$$

$$\Delta H = \Delta H(T)$$

$$\Delta U = \Delta U(T)$$

2.11.2 REVERSIBLE, ISOBARIC PROCESS

Since pressure is constant:[4]

$$W = -P\Delta V$$

We then have the following relationships for enthalpy:

$$Q_P = \Delta H$$

$$\Delta H = \int C_P \, dT$$

$$\Delta H = \Delta U + P\Delta V$$

2.11.3 REVERSIBLE, ISOCHORIC PROCESS

Since volume is constant:

$$W = 0$$

We then have the following relationships for the internal energy:

$$Q_V = \Delta U$$

$$\Delta U = \int C_V \, dT$$

$$\Delta H = \Delta U + V\Delta P$$

2.11.4 REVERSIBLE, ISOTHERMAL PROCESS

If one is dealing with an ideal gas, ΔU and ΔH are only functions of temperature, so

$$\Delta U = \Delta H = 0$$

Due to the fact that $\Delta U = Q + W$,

$$Q = -W$$

For an ideal gas, integrate the ideal gas law with respect to V to get

$$W = -nRT \ln\left(\frac{V_2}{V_1}\right) = nRT \ln\left(\frac{P_2}{P_1}\right)$$

2.11.5 REVERSIBLE, ADIABATIC PROCESS

By definition the heat exchange is zero, so:

$$Q = 0$$

Due to the fact that $\Delta U = Q + W$,

$$W = \Delta U$$

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[4] When dealing with thermodynamic quantities, it is important to keep track of units. For instance, computing $W = -P\Delta V$ will get units of [Pressure][Volume]. To convert this to a unit of [Energy], one must use a conversion factor, such as (8.3145 J/mol K)/(0.08206 L atm/mol K) = 101.32 J/L*atm.

The following relationships can also be derived for a system with constant heat capacity:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$

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

$$P_1 V_1^{C_P/C_V} = P_2 V_2^{C_P/C_V}$$

This means that[5]

$$W = \Delta U = \frac{\Delta(PV)}{C_P/C_V - 1} = \frac{nR\Delta T}{C_P/C_V - 1}$$

2.11.6 IRREVERSIBLE, ADIABATIC EXPANSION INTO A VACUUM

For this case,

$$Q = W = \Delta U = \Delta H = 0$$

2.12 THERMODYNAMIC CYCLES AND THE CARNOT CYCLE

A thermodynamic cycle always returns to the same state it was in initially, meaning all state functions are zero for the net cycle. For a Carnot cycle, there are four stages, as outlined in Figure 6. Since all state functions are zero for the net cycle, we know that

$$\Delta U_{\text{cycle}} = \Delta H_{\text{cycle}} = 0$$

Due to the First Law of Thermodynamics,

$$-W_{\text{net}} = Q_{\text{net}}$$

The net work and the neat heat can be computed by summing up the individual work and heat from each of the four processes. For a Carnot cycle, there is a negative net work.

The following relationships apply to the Carnot cycle:

$$\frac{P_2}{P_1} = \frac{P_3}{P_4}$$

and

$$\frac{Q_H}{Q_C} = -\frac{T_H}{T_C}$$

The efficiency of the Carnot cycle is defined as

$$\eta \equiv \frac{\text{net work}}{\text{wasted heat}} = \frac{|W_{\text{net}}|}{Q_H} = 1 - \frac{T_C}{T_H}$$

The efficiency of the Carnot cycle run in reverse (i.e. a Carnot refrigerator) is characterized by the coefficient of performance, given by

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[5] The term $\Delta(PV) \equiv P_2 V_2 - P_1 V_1$.

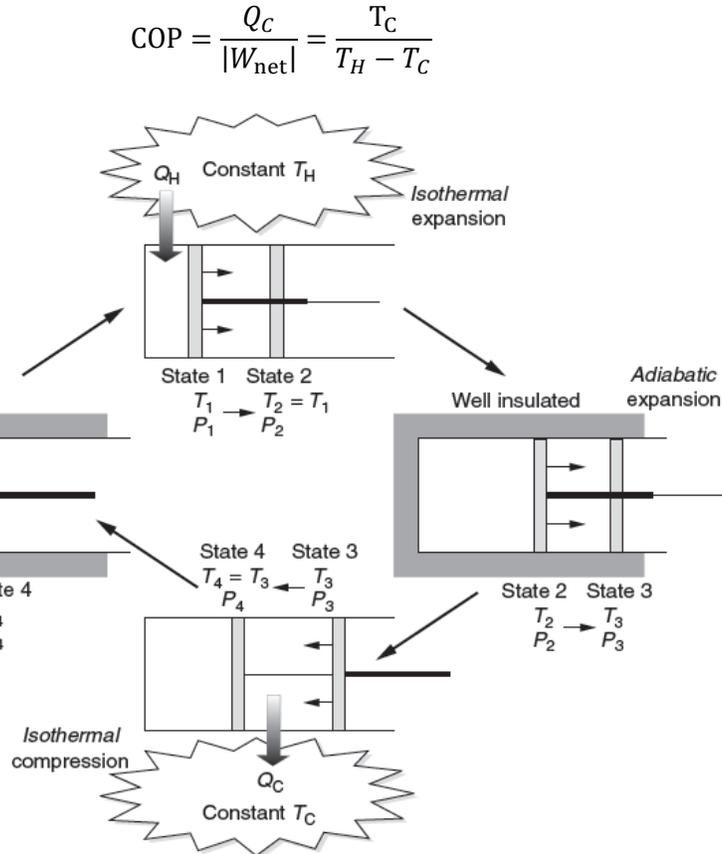$$\text{COP} = \frac{Q_C}{|W_{\text{net}}|} = \frac{\text{T}_\text{C}}{T_H - T_C}$$

Figure 6. An ideal gas undergoing a Carnot cycle.

3   ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

3.1   DEFINITION OF ENTROPY AND THE SECOND LAW

Irreversible processes are distinct and show directionality whereas **reversible** processes do not show directionality and are simply an idealization. Entropy

Entropy is defined in terms of the heat absorbed during a hypothetical reversible process:

$$ds \equiv \frac{\delta q_{\text{rev}}}{T}$$

which means that

$$\Delta s = \int \frac{1}{T} \delta q_{\text{rev}}$$

Entropy quantitatively describes the directionality of a process. **The Second Law of Thermodynamics** says that the entropy of the universe increases for all real, irreversible processes (and does not change for reversible processes). By stating

$$\Delta s_{\text{univ}} = \Delta s_{\text{sys}} + \Delta s_{\text{surr}}$$

the Second Law would read

$$\Delta s_{\text{univ}} \geq 0$$

3.2   THE SECOND LAW OF THERMODYNAMICS FOR CLOSED SYSTEMS

3.2.1   REVERSIBLE, ADIABATIC PROCESSES

Since the process is reversible and there is no heat transfer[6],

$$\Delta s = 0, \quad \Delta s_{surr} = 0, \quad \Delta s_{univ} = 0$$

3.2.2   REVERSIBLE, ISOTHERMAL PROCESSES

Since temperature is constant,

$$\Delta s = \frac{q_{rev}}{T}$$

If the ideal gas assumption can be made, then $\Delta u = 0$ such that $q_{rev} = w_{rev} = -\int P \; dV$. Plug in the ideal gas law to get

$$\Delta s = -R \ln\left(\frac{P_2}{P_1}\right)$$

Since all reversible processes have no change in the entropy of the universe (i.e. $\Delta s_{univ} = 0$), we can say that $\Delta s_{surr} = -\Delta s$.

3.2.3   REVERSIBLE, ISOBARIC PROCESSES

Since $\delta q_P = dh = c_P \; dT$ for isobaric processes,

$$\Delta s = \int \frac{c_P}{T} dT$$

Since all reversible processes have no change in the entropy of the universe (i.e. $\Delta s_{univ} = 0$), we can say that $\Delta s_{surr} = -\Delta s$.

3.2.4   REVERSIBLE, ISOCHORIC PROCESSES

Since $\delta q_V = du = c_V \; dT$ for isochoric processes,

$$\Delta s = \int \frac{c_V}{T} dT$$

Since all reversible processes have no change in the entropy of the universe (i.e. $\Delta s_{univ} = 0$), we can say that $\Delta s_{surr} = -\Delta s$.

3.2.5   REVERSIBLE PHASE CHANGE AT CONSTANT T AND P

In this case, q_{rev} is the latent heat of the phase transition. As such,

$$\Delta s = \frac{q_P}{T} = \frac{\Delta h_{transition}}{T}$$

Since all reversible processes have no change in the entropy of the universe (i.e. $\Delta s_{univ} = 0$), we can say that $\Delta s_{surr} = -\Delta s$.

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[6] It will be tacitly assumed any quantity without a subscript refers to that the system.

3.2.6 IRREVERSIBLE PROCESSES FOR IDEAL GASES

A general expression can be written to describe the entropy change of an ideal gas. Two equivalent expressions are:

$$\Delta s = \int \frac{c_V}{T} dT + R \ln \left(\frac{V_2}{V_1} \right)$$

and

$$\Delta s = \int \frac{c_P}{T} dT - R \ln \left(\frac{P_2}{P_1} \right)$$

In order to find the entropy change of the universe, one must think about the conditions of the problem statement. If the real process is adiabatic, then $q_{surr} = 0$ and then $\Delta s_{surr} = 0$ such that $\Delta s_{univ} = \Delta s$. If the real process is isothermal, note that $q = w$ from the First Law of Thermodynamics (i.e. $\Delta u = 0$) amd that due to conservation of energy $q_{surr} = -q$. Once q_{surr} is known, simply use $\Delta s_{surr} = \frac{q_{surr}}{T}$. The entropy change in the universe is then $\Delta s_{univ} = \Delta s + \Delta s_{surr}$.

If the ideal gas approximation cannot be made, try splitting up the irreversible process into hypothetical, reversible pathways that may be easier to calculate.

3.2.7 ENTROPY CHANGE OF MIXING

If we assume that we are mixing different inert, ideal gases then the entropy of mixing is

$$\Delta S_{mix} = R \sum n_i \ln \left(\frac{V_f}{V_i} \right)$$

For an ideal gas at constant T and P then

$$\Delta S_{mix} = -R \sum n_i \ln \left(\frac{P_i}{P_{tot}} \right) = -R \sum n_i \ln(y_i)$$

where P_i is the partial pressure of species i and y_i is the mole fraction of species i.

3.3 THE SECOND LAW OF THERMODYNAMICS FOR OPEN SYSTEMS

Since mass can flow into and out of an open system, the Second Law must be written with respect to time:

$$\left(\frac{dS}{dt} \right)_{univ} = \left(\frac{dS}{dt} \right)_{sys} + \left(\frac{dS}{dt} \right)_{surr} \geq 0$$

At steady-state,

$$\left(\frac{dS}{dt} \right)_{sys} = 0$$

If there is a constant surrounding temperature, then

$$\left(\frac{dS}{dt} \right)_{surr} = \sum \dot{n}_{out} s_{out} - \sum \dot{n}_{in} s_{in} - \frac{\dot{Q}}{T_{surr}}$$

3.4   THE MECHANICAL ENERGY BALANCE

For steady-state, reversible processes with one stream in and one stream out, the mechanical energy balance is

$$\frac{\dot{W}_s}{\dot{n}} = \int v \, dP + \Delta e_K + \Delta e_P$$

which can frequently be written as

$$\frac{\dot{W}_s}{\dot{n}} = \int v \, dP + \text{MW}\left[\frac{\Delta(\vec{V}^2)}{2}\right] + \text{MW}g\Delta z$$

Where MW refers to the molecular weight of the fluid. The latter equation is referred to as the Bernoulli Equation.

3.5   VAPOR-COMPRESSION POWER AND REFRIGERATION CYCLES

3.5.1   RANKINE CYCLE

The ideal Rankine cycle can be used to convert fuel into electrical power and is shown in Figure 7. The efficiency of a Rankine cycle can be given by

$$\eta_{\text{Rankine}} = \frac{|\dot{W}_s| - \dot{W}_C}{\dot{Q}_H} = \frac{|\hat{h}_2 - \hat{h}_1| - (\hat{h}_4 - \hat{h}_3)}{\hat{h}_1 - \hat{h}_4}$$
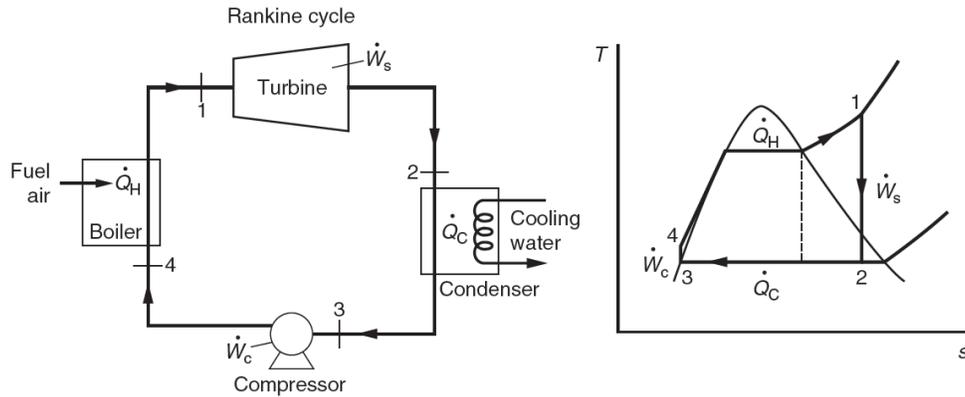

Figure 7. The ideal Rankine cycle and its corresponding Ts diagram.

3.5.2   THE VAPOR-COMPRESSION REFRIGERATION CYCLE

The ideal vapor-compression refrigeration cycle is shown in Figure 8. The efficiency can be described by the coefficient of performance as

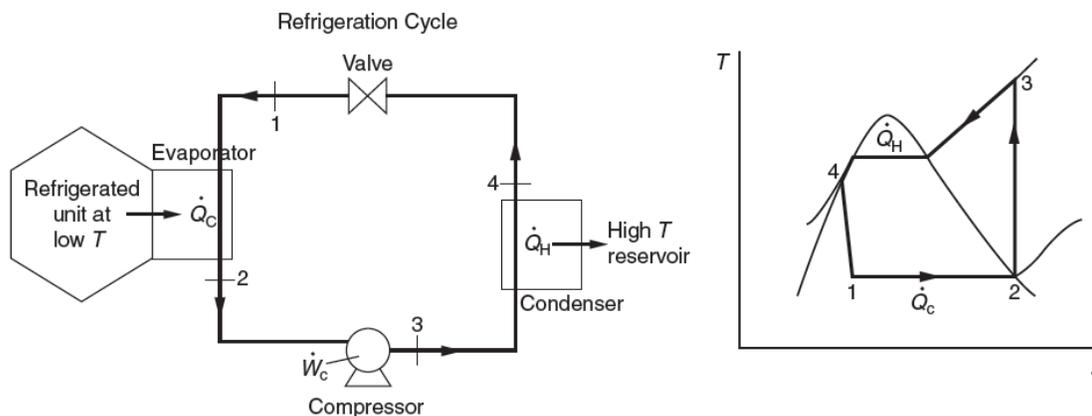$$\text{COP} = \frac{\dot{Q}_C}{\dot{W}_C} = \frac{h_2 - h_1}{h_3 - h_2}$$

Figure 8. The ideal vapor-compression refrigeration cycle and its corresponding Ts diagram.

3.6 MOLECULAR VIEW OF ENTROPY

From a molecular viewpoint, entropy can be written as

$$S \equiv k \ln \Omega$$

where k is Boltzmann's constant and Ω is the number of microstates (roughly the number of configurations of a given system). This is typically why entropy is associated with molecular-scale "disorder".

4 EQUATIONS OF STATE AND INTERMOLECULAR FORCES

4.1 REVIEW OF THE IDEAL GAS LAW

Recall that the ideal gas equation states

$$PV = RT$$

and assumes that the gas consists of molecules that are infinitesimally small, hard round spheres that occupy negligible volume and do not have intermolecular forces (i.e. only exert forces through collisions). As pressure decreases and temperature increases, all real gases approach the ideal gas limit.

4.2 EQUATIONS OF STATE

4.2.1 CHOOSING AN EQUATION OF STATE

Choosing a proper thermodynamic model and equation of state is not clear-cut. Figure 9 is a good roadmap for figuring out what model might be a good starting point. There are too many equations of state to include here, so only the most fundamental are shown.
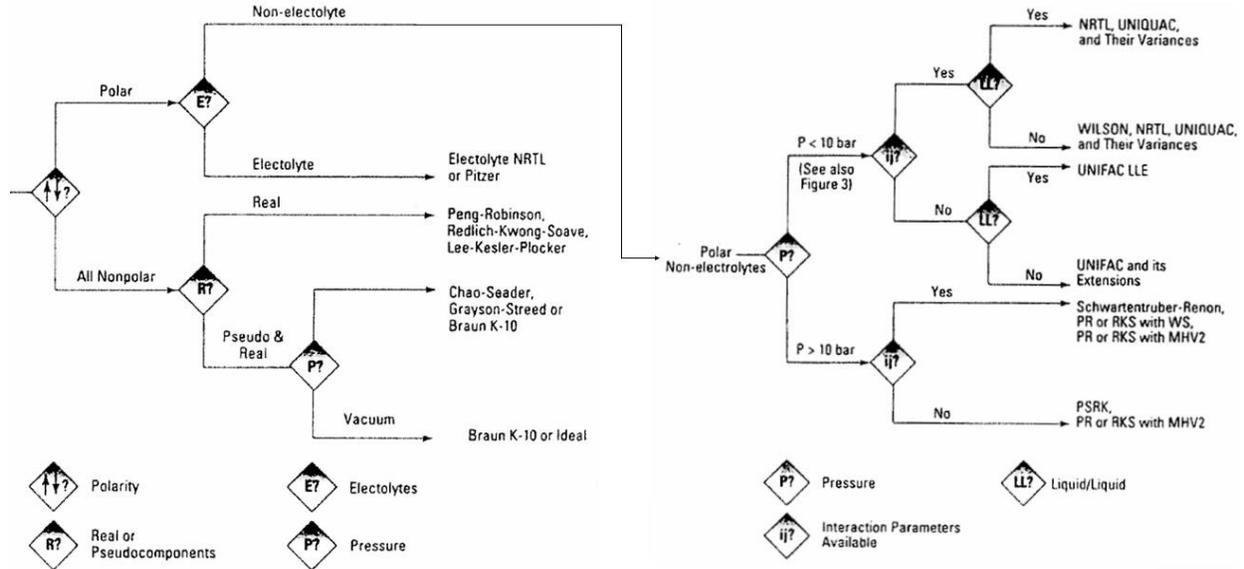
Figure 9. A flowchart for choosing an equation of state/thermodynamic model for process simulations.

4.2.2 COMPRESSIBILITY EQUATION

The ideal gas equation can be improved by using a dimensionless compressibility factor, z:

$$z = \frac{Pv}{RT}$$

4.2.3 VAN DER WAALS EQUATION

The van der Waals equation of state is

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

This is the most accurate equation of state for a gas that one can get from theory alone. It assumes that gases have a finite volume (in the b term) and intermolecular forces (in the a term). The a and b parameters are empirical and found from data. They are most typically approximated as

$$a = \frac{27}{64} \frac{(RT_c)^2}{P_c} \quad b = \frac{RT_c}{8P_c}$$

where T_C and P_C are the critical temperature and pressure, respectively.

5 THE THERMODYNAMIC WEB

5.1 MATHEMATICAL RELATIONS

The change in any intensive thermodynamic property of interest, z, can be written in terms of partial derivatives of the two independent intensive properties, x and y:[7]

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

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[7] For instance, consider $u(T, v)$. This can be expressed as $du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$.

The following relationship is also true:

$$\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial z}{\partial y}\right)_x = -1$$

5.2 DERIVED THERMODYNAMIC QUANTITIES

The measured properties of a system are P, v, T and composition. The fundamental thermodynamic properties are u and s, as previously discussed. There are also derived thermodynamic properties. One of which is h. There are also two other convenient derived properties: a, which is Helmholtz free energy, and g, which is Gibbs free energy. The derived thermodynamic properties have the following relationships:

$$h \equiv u + Pv \quad a \equiv u - Ts \quad g \equiv h - Ts$$

Also recall the heat capacity definitions discussed earlier:

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v \quad c_p = \left(\frac{\partial h}{\partial T}\right)_P$$

5.3 FUNDAMENTAL PROPERTY RELATIONS

The First Law of Thermodynamics states

$$du = \delta q_{\text{rev}} + \delta w_{\text{rev}}$$

Now consider enthalpy:

$$dh = du + d(Pv)$$

Similarly, consider Helmholtz free energy:

$$da = du - d(Ts)$$

Finally, consider Gibbs free energy:

$$dg = dh - d(Ts)$$

Recall that $\delta q_{\text{rev}} = T\,ds$ from the Second Law and $\delta w_{\text{rev}} = -Pdv$. With this, we can write a new expression for du and therefore new expressions for dh, da, and dg as well. These are called the fundamental property relations:

$$du = T\,ds - P\,dv$$

$$dh = T\,ds + v\,dP$$

$$da = -P\,dv - s\,dT$$

$$dg = v\,dP - s\,dT$$

With these expressions, one can write a number of unique relationships by holding certain values constant. By doings so, one yields:

$$\left(\frac{\partial u}{\partial s}\right)_v = T \quad \left(\frac{\partial u}{\partial v}\right)_s = -P$$

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

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

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

5.4 MAXWELL RELATIONS

The Maxwell Relations can be derived by applying Euler's Reciprocity to the derivative of the equation of state. The Euler Reciprocity is

$$\frac{\partial^2 z}{\partial x\, \partial y} = \frac{\partial^2 z}{\partial y\, \partial x}$$

Another useful identity to keep in mind is

$$\frac{\partial^2 z}{\partial x\, \partial y} = \left(\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right)_y$$

These mathematical relationships allow one to derive what are called the Maxwell Relations.[8] These are shown below:

$$\frac{\partial^2 u}{\partial s\, \partial v}: \left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \qquad \frac{\partial^2 h}{\partial s\, \partial P}: \left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

$$\frac{\partial^2 a}{\partial T\partial v}: \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \qquad \frac{\partial^2 g}{\partial T\, \partial P}: \left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

By using the thermodynamic property relations in conjunction with the Maxwell Relations, one can also write heat capacities in terms of T and s:

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v \qquad c_p = T\left(\frac{\partial s}{\partial T}\right)_P$$

5.5 DEPENDENT OF STATE FUNCTIONS ON $T, P,$ AND v

With the previous information, one can find the dependence of any state function on $T, P,$ or v quite easily. The procedure to do so can be broken down as follows:[9]

1) Start with the fundamental property relation for $du, dh, da,$ or dg
2) Impose the conditions of constant $T, P,$ or v
3) Divide by $dP_T, dv_T, dT_v,$ or dT_P as necessary

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[8] For instance, consider $\frac{\partial^2 G}{\partial T\, \partial P}$. This can be rewritten as $\frac{\partial^2 G}{\partial T\, \partial P} = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right)_P$ using Euler's Reciprocity. Using the appropriate fundamental property relation, $\frac{\partial^2 G}{\partial T\, \partial P} = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right)_P = \left(\frac{\partial v}{\partial T}\right)_P$.

[9] For instance, consider trying to find what $\left(\frac{\partial u}{\partial v}\right)_T$ can also be written as. Write out the fundamental property relation: $du = T\, ds - P\, dv$. Then impose constant T and divide by dv_T: $\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - P$. Recognize that $\left(\frac{\partial s}{\partial v}\right)_T = \frac{\beta T}{\kappa}$ from the Maxwell Relations such that $\left(\frac{\partial u}{\partial v}\right)_T = \frac{\beta T}{\kappa} - P$.

4) Use a Maxwell relation or other identity to eliminate any terms with entropy change in the numerator (if desired)

It is useful to know the following identities:

$$\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \qquad \kappa \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

where β and κ are the thermal expansion coefficient and isothermal compressibility, respectively.

5.6 THERMODYNAMIC WEB
A roadmap that outlines the previously discussed relations is shown in Figure 10.
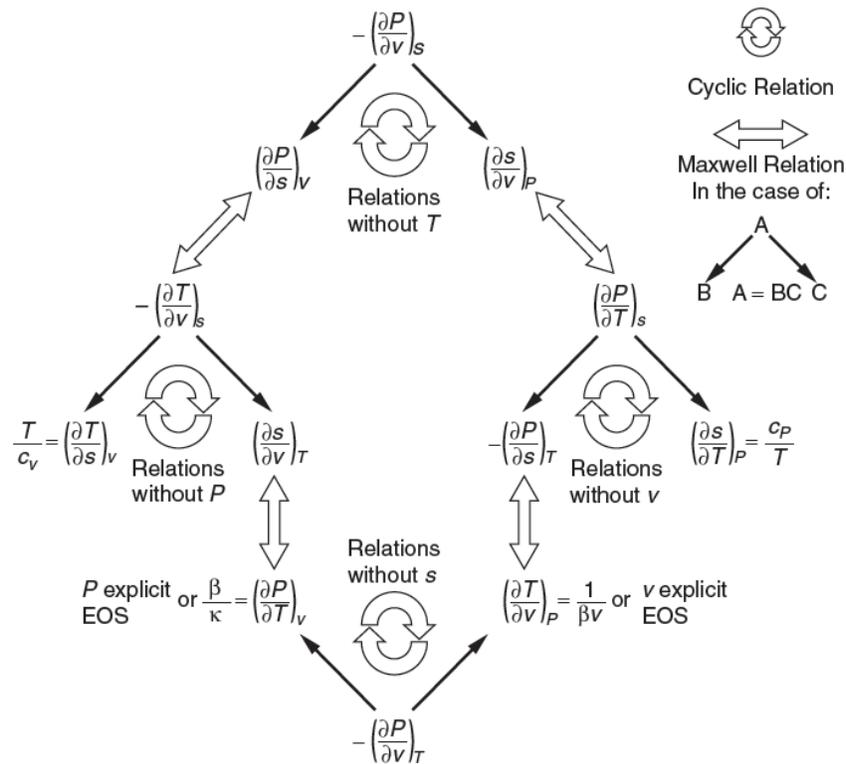

Figure 10. Thermodynamic web relating partial derivatives of $T, P, s,$ and v.

5.7 REFORMULATED THERMODYNAMIC STATE FUNCTIONS
One can write $s(T, v)$ as

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

By using the thermodynamic relations and Maxwell relations and integrating, this yields

$$\Delta s = \int \frac{c_v}{T} dT + \int \left(\frac{\partial P}{\partial T}\right)_v dv$$

Similarly, one can write $s(T, P)$ as

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

By using the thermodynamic relations and Maxwell relations and integrating, this yields

$$\Delta s = \int \frac{c_P}{T} dT - \left(\frac{\partial v}{\partial T}\right)_P dP$$

One can do the same with u. If one writes $u(T, v)$ then

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

After much substitution one can come to find that

$$\Delta u = \int c_v dT + \int \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

If one write $h(T, P)$ as

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

then after much substitution

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