

Physical Chemistry I

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1 Thermodynamics

1.1 Thermodynamic Systems and Properties

1.1.1 Systems vs. Surroundings

- **System:** The macroscopic part of the universe under study in thermodynamics
- **Surroundings:** The parts of the universe that can interact with the system
- **Open System:** One where transfer of matter between system and surroundings can occur
- **Closed System:** One where transfer of matter between system and surroundings cannot occur
- **Isolated System:** One in which no interaction in any way with the system can occur

1.1.2 Types of Walls

1. Rigid or nonrigid
2. Permeable or impermeable
3. Adiabatic (does not conduct heat) or nonadiabatic/thermally conductive (conducts heat)

1.1.3 Equilibrium

- An isolated system is in equilibrium when its macroscopic properties remain constant with time
- A nonisolated system is in equilibrium when the the system's macroscopic properties remain constant with time but also need to have no change with removal of the system from contact with its surroundings
 - If removal of the system does change the macroscopic properties, it is in a **steady state**
- **Mechanical Equilibrium:** No unbalanced forces act on or within the system
- **Material Equilibrium:** No net chemical reactions are occurring in the system nor is there any net transfer of matter from one part of the system to another
- **Thermal Equilibrium:** No change in the properties of the system or surroundings when they are separated by a a thermally conductive wall
- **Thermodynamic Equilibrium:** Must be in mechanical, material, and thermal equilibrium

1.1.4 Thermodynamic Properties

- The definition of pressure, P , is as follows and relates to force, F , and area, A :

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

- Pressure is uniform and equal to the surroundings in mechanical equilibrium
- An **extensive** property is equal to the sum of its values for the parts of the system (eg: mass)
- An **intensive** property does not depend on the size of the system (eg: density)
- If the intensive macroscopic properties are constant in the system, it is **homogeneous**; otherwise, it is **heterogeneous**

- A homogeneous part of a system is a **phase**
- The definition of density, ρ , is as follows and relates to mass, m , and volume, V :

$$\rho \equiv \frac{m}{V}$$

- **State Functions:** Values that are functions of the system's state that doesn't depend on the system's past history

1.2 Temperature

- **Temperature** is common for systems in thermal equilibrium and is symbolized by θ
- **Zeroth Law of Thermodynamics:** Two systems that are found to be in thermal equilibrium with a third system will be found to be in thermal equilibrium with each other
- A reference system (**thermometer**), r , is used to create a temperature scale

1.3 The Mole

- The molar mass, M_i , of a substance is as follows and relates to m_i , the mass of a substance i in a sample and where n_i is the number of moles of i in the sample:

$$M_i \equiv \frac{m_i}{n_i}$$

- The number of molecules in species i , N_i , is as follows and relates to Avogadro's Constant, N_A , and n_i :

$$N_i = n_i N_A$$

- The mole fraction, x_i , is defined as follows and relates to n_i and the total moles, n_t :

$$x_i \equiv \frac{n_i}{n_{tot}}$$

1.4 Ideal Gases

1.4.1 Boyle's and Charles' Laws

- Boyle's Law is as follows when θ and m are constant:

$$PV = k$$

- Gases are **ideal** in the zero-density limit
- The SI units for pressure can be expressed as either of the following

$$1 \text{ Pa} \equiv 1 \frac{\text{N}}{\text{m}^2}$$

- Some alternate rearrangements of the pressure equation are as follows:

$$P = \frac{F}{A} = \frac{mg}{A} = \frac{\rho V g}{A} = \rho g h$$

- Charles' Law is as follows when P and m are constant:

$$V = a_1 + a_2 \theta$$

- Alternatively, it can be written as

$$\frac{V}{T} = k$$

- The **absolute ideal-gas temperature** is represented as T

1.4.2 Ideal Gas Equation

- The ideal-gas law is

$$PV = nRT$$

- This can be rearranged to make the following two equations where M is molar mass:

$$PV = \frac{mRT}{M} \rightarrow P = \frac{\rho RT}{M}$$

- The **partial pressure**, P_i , of a gas i in a gas mixture is defined as:

$$P_i \equiv x_i P$$

- For an ideal gas mixture,

$$P_i = \frac{n_i RT}{V}$$

1.5 Equations of State

- The **van der Waals equation** accounts for intermolecular forces, with a and b as constants defined for each gas:

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

- An approximate equation of state for most liquids and solids is¹:

$$V_m = c_1 + c_2 T + c_3 T^2 - c_4 P - c_5 PT$$

- The **thermal expansivity**, α , is defined as²

$$\alpha(T, P) \equiv \frac{1}{V_m} \left(\frac{\partial V_m}{\partial T}\right)_P$$

- The **isothermal compressibility**, κ , is defined as

$$\kappa(T, P) \equiv -\frac{1}{V_m} \left(\frac{\partial V_m}{\partial P}\right)_T$$

- These can be combined as,

$$\left(\frac{\partial P}{\partial T}\right)_{V_m} = \frac{\alpha}{\kappa}$$

2 The First Law of Thermodynamics

2.1 Classical Mechanics

- **Work** is simply a force acting over a distance, which can be mathematically expressed as follows if considering the displacement in the x direction:

$$dw \equiv F_x dx$$

¹All variables that are not listed can be found in Ira N. Levine's *Physical Chemistry*, 6th edition

²Calculus Note: The total differential, dz , for $z(x, y)$ is defined as $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

- If we integrate both sides, we get

$$w = \int_{x_1}^{x_2} F(x) dx$$

- Work is measured in joules, where a joule is equivalent to a $N \cdot m$
- **Power** is simply $\frac{dw}{dt}$ and is usually measured in watts
- The **kinetic energy**, or energy of motion, of a particle is

$$K \equiv \frac{1}{2}mv^2$$

- The **work-energy theorem** states that $w = \Delta K$ as well

2.2 P-V Work

- A **reversible process** is one where the system is always infinitesimally close to equilibrium, and an infinitesimal change in conditions can reverse the process to restore both system and surroundings to their initial states
- **P-V Work** is the work done in a volume change, and it can be expressed as

$$dw_{rev} = -P dv$$

2.3 Heat and The First Law of Thermodynamics

- $\frac{dq}{dt} = UA\Delta T$, where U is conductance and A is area
 - Conductance be defined as $U = \frac{k}{r}$ as well, where k is thermal conductivity and r is thickness of the layer
- $|q| \equiv m_1c_1(T_f - T_i) = m_2c_2(T_f - T_i)$
 - When $q > 0$, heat flows from the surroundings to the system
 - When $w > 0$, work is done on a system by the surroundings
- The equation for heat at constant pressure is $dq_p = mc_p dT$, which is usually seen as

$$q_p = mc_p \Delta T$$

- Total energy, E , is defined as the following (V is potential energy)

$$E = K + V + U$$

The First Law for Closed Systems:

1. $\Delta E = q + w$
2. $\Delta E_{sys} + \Delta E_{surr} = 0$
 - (a) When $K = V = 0$, we have the equation $\Delta U = q + w$
 - i. For an infinitesimal change, $dU = dq + dw$
 - (b) For a cyclic process, $\Delta U = 0$

2.4 Enthalpy and Heat Capacity

- The definition of enthalpy is

$$H \equiv U + PV$$

- Similarly, $\Delta H = \Delta U + P\Delta V$ at constant pressure and $\Delta H = \Delta U + \Delta(PV)$ for any process
- For a process with constant moles, $\Delta H = \Delta U + nR\Delta T$

Now for a little derivation:

$$\Delta U = U_2 - U_1 = q + w = q - \int_{v_1}^{v_2} P dv = q_p - P \int_{v_1}^{v_2} dV = q_p - P(V_2 - V_1) \rightarrow$$

$$q_p = U_2 + PV_2 - U_1 - PV_1 = (U_2 + P_2V_2) - (U_1 + P_1V_1) = H_2 - H_1$$

$$\therefore \Delta H = q_p$$

Also,

$$(dH)_p = dq_p$$

- For a constant volume process, $du = dq + dw$, but $dw = 0$ because $dw = -P dV$. Therefore,

$$(dU)_v = dq_v$$

- Heat capacity is defined as

$$C_{process} \equiv \frac{dq_{process}}{dT}$$

- For constant pressure,

$$C_P \equiv \frac{dq_P}{dT} = \frac{dH_P}{dT_P} = \left(\frac{\partial H}{\partial T} \right)_P$$

- For constant volume,

$$C_V \equiv \frac{dq_V}{dT} = \frac{dU_V}{dT_V} = \left(\frac{\partial U}{\partial T} \right)_V$$

- The difference between C_P and C_V is equivalent to

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P$$

- The term in the brackets has units of pressure and is called the “internal pressure.” It has to do with interaction among the particles of a gas.

2.5 The Joule and Joule-Thomson Experiments

- The Joule expansion states that when a gas expands into a vacuum, the work done is zero
 - Note that the Joule Thomson experiment does have work done

- The goal of the Joule experiment was to find departures from the ideal gas behavior in the $\left(\frac{\partial U}{\partial V} \right)_T$ term by measuring $\left(\frac{\partial T}{\partial V} \right)_U$

- The goal of the Joule-Thomson Experiment was to find $\left(\frac{\partial H}{\partial P}\right)_T$ by measuring $\left(\frac{\partial T}{\partial P}\right)_H$

- The Joule coefficient is defined as

$$\mu_J \equiv \left(\frac{\partial T}{\partial V}\right)_U$$

- The Joule-Thomson coefficient is defined as

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_H$$

- Resultantly, $\left(\frac{\partial H}{\partial P}\right)_T = -C_P \mu_{JT}$

- Also, $\left(\frac{\partial U}{\partial V}\right)_T = -C_V \mu_J$

- $\Delta T = 0$ for a perfect gas in the Joule Experiment because $\mu_J = 0$ for a perfect gas

2.6 The Perfect Gas

- A perfect gas is defined as one that follows $PV = nRT$ and $\left(\frac{\partial U}{\partial V}\right)_T = 0$

- This is to assure that U is dependent only on temperature. Since H is also dependent only on temperature for a perfect gas, $\left(\frac{\partial H}{\partial P}\right)_T = 0 = \left(\frac{\partial U}{\partial V}\right)_T$

- For a perfect gas,

$$C_P - C_V = nR \text{ (perf. gas)}$$

- Additionally³,

$$C_{P,m} - C_{V,m} = R \text{ (perf. gas)}$$

- For a perfect gas,

$$dU = C_V dT \text{ (perf. gas)}$$

- For a perfect gas,

$$dH = C_P dT \text{ (perf. gas)}$$

2.7 How to Find Pressure-Volume Work

2.7.1 Non-Ideal Gas (Van der Waals Gas)

- Rearrange the van der Waals equation to solve for $P = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}$ and substitute this into $w = \int_{V_1}^{V_2} P dV$

2.7.2 Ideal Gas

- Rearrange the ideal-gas equation to solve for $P = \frac{nRT}{V}$ and substitute into the work equation to get

$$w = -nR \int_{V_1}^{V_2} \frac{T}{V} dV \text{ (perf. gas)}$$

- If it's isothermal, temperature is constant, so

$$w = -nRT \ln \left(\frac{V_2}{V_1}\right) \text{ (isothermal)}$$

³ $C \equiv nC_m$

2.7.3 Reversible Adiabatic Process in a Perfect Gas

- Assuming that $C_{V,m}$ does not change much with temperature,

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_{V,m}} \quad (\text{adiabatic})$$

- Alternatively,

$$P_1 V_1^\gamma = P_2 V_2^\gamma \quad (\text{adiabatic})$$

- In the above equation, γ is the heat-capacity ratio and is defined

$$\gamma \equiv \frac{C_P}{C_V}$$

- If you're still not happy, you can use

$$\left(\frac{P_1}{P_2}\right)^R = \left(\frac{T_1}{T_2}\right)^{C_{P,m}} \quad (\text{adiabatic})$$

- Since $dU = C_V dT$, it is safe to use $\Delta U = w = C_V \Delta T$

2.8 Summary of Calculating First Law Quantities

- Always start with writing these three equations down⁴:

1. $w = -\int_{V_1}^{V_2} p dV$
2. $\Delta U = q + w$
3. $\Delta H = \Delta U + \Delta(PV)$

- If it's a perfect gas, write these three down as well:

1. $dU = C_V dT$
2. $dH = C_P dT$
3. $C_P - C_V = nR$

- If the pressure is equal to zero, $w = 0$

- If the volume change is equal to zero, $w = 0$

2.8.1 Constant Pressure (Isobaric) Heating

1. P is constant, so $w = -P\Delta V$
2. $\Delta H = q_P = \int_{T_1}^{T_2} C_P dT$

2.8.2 Constant Volume (Isochoric) Heating

1. $w = 0$
2. $\Delta U = \int_{T_1}^{T_2} C_V dT = q_V$
3. $\Delta H = \Delta U + V\Delta P$

(a) Alternatively, $\Delta H = q_P = \int_{T_1}^{T_2} C_P dT$

⁴Whenever you compute work, make sure the units work out. For instance, at constant pressure and using $w = -P\Delta V$, one might obtain units of $L \cdot atm$. However, this is not a Joule, so a conversion factor needs to be set up.

2.8.3 Reversible Isothermal Process in a Perfect Gas

1. $\Delta U = \Delta H = 0$
2. Rearrange the ideal-gas equation to solve for $P = \frac{nRT}{V}$ and substitute into the work equation to get
$$w = -nRT \ln \left(\frac{V_2}{V_1} \right) = nRT \ln \left(\frac{P_2}{P_1} \right)$$
3. $q = -w$

2.8.4 Reversible Adiabatic Process in a Perfect Gas

1. $q = 0$ and $\Delta U = w$
2. $\Delta U = \int_{T_1}^{T_2} C_V dT$
3. $\Delta H = \int_{T_1}^{T_2} C_P dT$
4. The final state of the gas can be found by $P_1 V_1^\gamma = P_2 V_2^\gamma$

2.8.5 Adiabatic Expansion of a Perfect Gas into a Vacuum

1. $q = w = \Delta U = \Delta H = 0$

2.8.6 Reversible Phase Change at Constant T and P

1. q is the measured latent heat of the phase change
2. $w = -P\Delta V$
 - (a) ΔV can be calculated from the densities of the two phases
 - (b) If one phase is a gas, $PV = nRT$ can be used
3. $\Delta H = q_p$
4. $\Delta U = q + w$

2.9 Molecular Modes of Energy Storage

2.9.1 Degrees of Freedom

- Every free particle has three degrees of freedom manifested in each dimension of space
- Bound particles have some changes with respect to degrees of freedom

2.9.2 Classical Mechanics

1. Translation
 - (a) $E = \frac{1}{2}mv^2$ in each dimension
2. Rotation
 - (a) $E = \frac{1}{2}I\omega^2$

3. Vibration

(a) $E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$

- The degrees of freedom of a molecule must be $3N$, where N is the number of nuclei or atoms in the molecule
- For an N atom linear molecule, there are three translational degrees of freedom, 2 rotational, and $3N - 5$ vibrational
- For an N atom nonlinear molecule, there are 3 translational degrees of freedom, 3 rotational, and $3N - 6$ vibrational
- Equipartition Principle states that each degree of freedom gets $\frac{1}{2}RT$ of energy per quadratic term in its energy expression
 - Translational energy gets $\frac{1}{2}RT$, rotational gets $\frac{1}{2}RT$, and vibrational gets $\frac{2}{2}RT$

2.9.3 Quantum Mechanics

- The classical result for H_2 would be $U_m = \frac{3}{2}RT + \frac{2}{2}RT + \frac{2}{2}RT = \frac{7}{2}RT$
 - This would predict $C_{v,m} = \left(\frac{\partial u}{\partial T}\right)_V = \frac{7}{2}R$
 - * This does not agree with the experimental value of $\frac{5}{2}R$ with weak T dependence. This is because energy is not quantized in classical mechanics, and if spacings are large compared to RT , equipartition will not hold
 - * The translational and vibrational terms are fairly consistent between quantum and classical mechanics (small spacing); however, there is a big discrepancy for vibrational motion where there is large energy spacing
- Both classical and quantum mechanical systems must obey the Boltzmann Distribution Law that states $\frac{n_i}{n_j} = e^{-(E_i - E_j)/kT}$, where E_i and E_j are molecular energies and k is the Boltzmann constant
 - An analogous equation is $\frac{n_i}{n_j} = e^{-(E_{i,m} - E_{j,m})/RT}$ and uses molar energies and the ideal-gas constant
- Contributions to U and H come from two sources:
 - Degrees of freedom of individual molecules (translational, rotational, vibrational, and electronic)
 - Interactions between molecules, of which pairwise interactions are most important in gases, but at smaller spacings, higher-order interactions also become important (clusters of more than 2 molecules)
- $U_{molecular} = \sum_i U_i$, where i is all the degrees of freedom
 - Therefore, $U_{molecular} = U_{trans} + U_{rot} + U_{vib}$
- Translation: $U_{q.m.} \approx U_{cl}$, Rotational: $U_{q.m.} \approx U_{cl}$, Vibrational: $U_{q.m.} \ll U_{cl}$, Electronic: $U_{qm} \approx 0$

2.9.4 Classical Equations

$$U_{trans} = n_{trans} \cdot 1 \cdot \frac{kT}{2} = \frac{3}{2}kT$$

$$U_{rot} = n_{rot} \cdot 1 \cdot \frac{kT}{2} = \frac{2}{2}kT = kT \text{ (linear)}$$

$$U_{rot} = \frac{3}{2}kT \text{ (nonlinear)}$$

$$U_{vib} = n_{vib} \cdot 2 \cdot \frac{kT}{2} = (3N - 5) \frac{2}{2}kT = (3N - 5)kT \text{ (linear)}$$

$$U_{vib} = (3N - 6)kT \text{ (nonlinear)}$$

If scaled up to a mole so that $K \rightarrow R$:

$$U_{m,class.} = \frac{RT}{2} (6N - 5) + U_{int} \text{ (linear)}$$

$$U_{m,class.} = \frac{RT}{2} (6N - 6) + U_{int} \text{ (nonlinear)}$$

$$C_{V,m,class.} = \left(\frac{\partial U_m}{\partial T} \right)_V$$

2.9.5 Determining Number of Atoms in a Molecule Given $C_{v,m,class.}$

For a linear molecule with N atoms,

$$C_{V,m,class.} = \frac{R}{2} (6N - 5)$$

For a nonlinear molecule with N atoms,

$$C_{V,m,class.} = \frac{R}{2} (6N - 6)$$

However, all of these theoretical values do not match experimental results due to the necessary quantum mechanical effects. In reality,

$$U_{q.m.} = \frac{5}{2}RT + \text{small terms (linear molecules)}$$

$$U_{q.m.} = 3RT + \text{small terms (nonlinear molecules)}$$

3 Heat Engines

3.1 The Carnot Engine

- A heat engine converts some of the random molecular energy of heat flow into macroscopic mechanical energy known as work
- The essentials of a heat engine cycle is the absorption of heat, q_H , by the working substance from a hot body, the performance of work, $-w$, by the working substance on the surroundings, and the emission of heat, $-q_C$, by the working substance to a cold body, with the working substance returning to its original state at the end of the cycle
- The efficiency of a heat engine is defined as:

$$e = \frac{\text{work output per cycle}}{\text{energy input per cycle}} = \frac{-w}{q_H} = \frac{|w|}{q_H}$$

- Alternatively,

$$e = 1 - \frac{T_C}{T_H}$$

- For a cycle, $\Delta U = 0$, so $-w = q_H + q_C$

- Therefore, efficiency is also defined as:

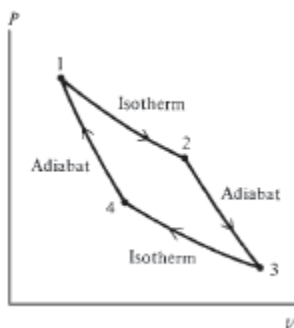
$$e = \frac{-w}{q_H} = 1 + \frac{q_C}{q_H}$$

- Because q_C is negative and q_H is positive, efficiency is always less than 1

- Combining the last two definitions of efficiency, we get

$$\frac{-T_C}{T_H} = \frac{q_C}{q_H}$$

- All reversible heat engines have the same efficiencies if the temperatures are the same
- If two Carnot cycle heat engines operating reversible between the same two temperature can have different efficiencies, then they can be linked together in such a way as to transfer heat from a cold object to a hot object without any work being done from the outside to make the flow occur. This is goes against Clausius' version of the Second Law
- A Carnot cycle can be graphed as follows:



Step 1 to 2:

- This is an isothermal process, so $\Delta U = 0$, $q = nRT_H \ln\left(\frac{V_2}{V_1}\right)$, and $w = -nRT_H \ln\left(\frac{V_2}{V_1}\right)$

Step 2 to 3:

- This is an adiabatic process, so $\Delta U = C_V(T_C - T_H)$, $q = 0$, and $w = C_V(T_C - T_H)$
 - Note: Since T_C is the second temperature state, ΔT is equal to $T_C - T_H$

Step 3 to 4:

- This is an isothermal process, so $\Delta U = 0$, $q = nRT_C \ln\left(\frac{V_4}{V_3}\right)$, and $w = -nRT_C \ln\left(\frac{V_4}{V_3}\right)$
 - Alternatively, $q = -nRT_C \ln\left(\frac{V_2}{V_1}\right)$ and $w = nRT_C \ln\left(\frac{V_2}{V_1}\right)$

Step 4 to 1:

- This is an adiabatic process, so $\Delta U = C_V (T_H - T_C)$, $q = 0$, and $w = C_V (T_H - T_C)$

Overall Cycle:

- This is a cycle, so $\Delta U = 0$, $q = nR(T_H - T_C) \ln\left(\frac{V_2}{V_1}\right)$ and $w = -nR(T_H - T_C) \ln\left(\frac{V_2}{V_1}\right)$
- For a closed system undergoing a Carnot cycle,

$$\oint \frac{dq_{rev}}{T} = \frac{q_C}{T_C} + \frac{q_H}{T_H} = 0$$

3.2 Carnot Refrigerators, Freezers, Air Conditioners, and Heat Pumps

The following equation holds true, where U is conductance and A is area,

$$\frac{dq}{dt} = UA\Delta T$$

$$\eta_{ref,AC} \equiv \text{Coeff. of Performance} = \frac{dq/dt}{dw/dt} = \frac{q_c}{w} = \frac{q_c}{-(q_H + q_c)} = \frac{T_c}{T_H - T_c}$$

$$\eta_{Heat Pump} = \frac{-q_H}{w} = \frac{T_H}{T_H - T_C}$$

3.3 The Otto Engine

1. Step 1 \rightarrow 2 is adiabatic compression
 2. Step 2 \rightarrow 3 is isochoric heating
 3. Step 3 \rightarrow 4 is adiabatic expansion
 4. Step 4 \rightarrow 1 is isochoric cooling
- There are no isotherms

For an Otto engine,

$$e = \frac{-w}{Q_{in}} = 1 - \frac{T_1}{T_3} = 1 - \left(\frac{V_2}{V_1}\right)^{R/C_{V,m}}$$

$$\text{Compression Ratio} \equiv cr \equiv \frac{V_1}{V_2}$$

Efficiency is maximized with an infinite compression ratio, but of course there are practical volume limits

3.4 Historical Perspective

- Knocking or pinging is detonation of a fuel charge that occurs too early
- Straight-chain hydrocarbons knock at low compression ratios and vice versa
- To prevent knocking, antiknock components are added
 - From the 1930s to 1970s, $Pb(Et)_4$ was used, but it caused mental disorders and death due to the lead
 - From the 1970s to the 1990s, $MTBE$ was used, but it was carcinogenic
 - Currently, $EtOH$ is used, which was ironically used before $Pb(Et)_4$

4 The Second Law of Thermodynamics

4.1 Definition of the Second Law of Thermodynamics

- According to the Kelvin-Planck statement of the second law, it is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a heat reservoir and the performance of an equivalent amount of work by the system on the surroundings
- According to the Clausius statement, it is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a cold reservoir and the flow of an equal amount of heat out of the system into a hot reservoir

4.2 Entropy

- The definition of entropy, S , is the following for a closed system going through a reversible process

$$ds \equiv \frac{dq_{rev}}{T}$$

- According to the fundamental theorem of calculus,

$$\Delta S = S_2 - S_1 = \int_{q_1}^{q_2} \frac{dq_{rev}}{T}$$

- The molar entropy of a substance is

$$S_m = \frac{S}{n}$$

4.3 Calculation of Entropy Changes

4.3.1 Cyclic Process

- $\Delta S = 0$ since it is a state function

4.3.2 Reversible Adiabatic Process

- Since $dq_{rev} = 0$, $\Delta S = 0$

4.3.3 Reversible Isothermal Process

$$\Delta S = \frac{q_{rev}}{T} \text{ (isothermal)}$$

4.3.4 Reversible Phase Change at Constant T and P

- At constant temperature, $\Delta S = \frac{q_{rev}}{T}$
- q_{rev} is the latent heat of the transition in this case
- Since P is constant, $q_{rev} = q_P = \Delta H$. Therefore,

$$\Delta S = \frac{\Delta H}{T} \text{ (rev. phase change at const. } T \text{ and } P)$$

4.3.5 Cautionary Note on Units

Question: The melting point of water is 0°C at the interested state. What is ΔS for the melting of two moles of water if heat of fusion is 6 kJ/mol

Answer:⁵

$$\Delta S = \frac{(6\text{ kJ/mol})(2\text{ mol})}{0^\circ\text{C} + 273.15} = 0.044\text{ kJ/K}$$

4.3.6 Constant Pressure Heating with No Phase Change

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT \quad (\text{Const. } P, \text{ no phase change})$$

If C_P is not temperature dependent,

$$\Delta S = C_P \ln\left(\frac{T_2}{T_1}\right) \quad (\text{Const. } P \text{ and } C_P, \text{ no phase change})$$

4.3.7 Change of State of a Perfect Gas

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT + nR \ln\left(\frac{V_2}{V_1}\right) \quad (\text{perf. gas})$$

If C_V is not temperature dependent,

$$\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) \quad (\text{perf. gas})$$

Alternatively,

$$\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{P_1 T_2}{P_2 T_1}\right) \quad (\text{perf. gas})$$

4.3.8 General Change of State Process

Take the example of converting a mole of ice at 0°C and 1 atm to water vapor at 100°C and 0.5atm

- Change the phase at constant pressure and temperature
- Heat the water at constant pressure
- Vaporize the liquid at constant pressure and temperature
- Isothermally expand the vapor (assume it's a perfect gas change of state) to drop the pressure

4.3.9 Irreversible Phase Change

Consider the transformation of 1 mole of supercooled liquid water at -10°C and 1 atm to 1 mole of ice at the same P and T

- We first reversibly warm the supercooled liquid to 0°C and 1 atm
- We then reversibly freeze it at this T and P
- Finally, we cool it reversibly back down to the ice at the original conditions

⁵Note: Be careful of units! To get ΔS , which is *not* on a mole basis, one must multiply the heat of fusion by how many moles are melting

4.3.10 Mixing of Different Inert Perfect Gases at Constant P and T

The general equation can be written as,

$$\Delta S = n_1 R \ln \left(\frac{V_f}{V_1} \right) + n_2 R \ln \left(\frac{V_f}{V_2} \right) + \dots$$

For a perfect gas at constant temperature and pressure,

$$\Delta S_{mix} = -n_1 R \ln(x_1) - n_2 R \ln(x_2) - \dots$$

- The entropy of a perfect gas mixture is equal to the sum of the entropies each pure gas would have if it alone occupied the volume of the mixture at the temperature of the mixture

4.3.11 Joule Expansion

$\Delta S \neq 0$ for a Joule Expansion. Instead, the following is true, where V is the amount of expansion

$$\Delta S = n \int \frac{dq_{rev}}{T} = \frac{n}{T} \int P dV = nR \int \frac{dV}{V} = nR \ln \left(\frac{V_2}{V_1} \right) \text{ (Joule Expansion)}$$

Bringing the system back to its original state will cause $nR \ln \left(\frac{V_2}{V_1} \right)$ to be ΔS_{surr}

4.4 Entropy, Reversibility, and Irreversibility

For a reversible process,

$$dS_{univ} = dS_{syst} + dS_{surr} = 0 \therefore \Delta S_{univ} = 0 \text{ (Rev. Process)}$$

For an irreversible adiabatic process in a closed system, $\Delta S_{syst} > 0$. this is also true for an irreversible process in an isolated system

$$\Delta S_{univ} > 0 \text{ (Irrev. Process)}$$

Removing the constraint of an irreversible process has,

$$\Delta S_{univ} \geq 0$$

- As a result, entropy can be created but not destroyed (there is no conservation of entropy)
- $\Delta S \neq 0$ for a Joule expansion. $\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$ for a Joule Expansion
- $S = k \ln \Omega$, where Ω is the number of microstates
- For an isolated system, thermodynamic equilibrium is reached when the system's entropy is maximized

5 Material Equilibrium

5.1 Entropy and Equilibrium

- Material equilibrium means that in each phase of a closed system the number of moles of each substance present remains constant
- Thermodynamic equilibrium in an isolated system is reached when the system's entropy is maximized
- The condition for material equilibrium in a system is the maximization of the total entropy of the system plus its surroundings
- For the surroundings, $dS_{surr} = \frac{dq_{surr}}{T}$. Also, $dq_{surr} = -dq_{syst}$
 - For the system, $dS_{syst} > \frac{dq_{syst}}{T}$
- At material equilibrium, $dS = \frac{dq_{rev}}{T}$
- For a material change in a closed system in mechanical and thermal equilibrium, $dS \geq \frac{dq}{T}$, where the equality only holds when the system is in material equilibrium
- For an irreversible chemical reaction in thermal and mechanical equilibrium, $dS > dq_{irrev}/T$
- For a closed system of material change in mechanical and thermal equilibrium, $dU \leq T dS + dw$, where the equality only holds at material equilibrium

5.2 The Gibbs and Helmholtz Energies

5.2.1 Derivation of A

1. If we rearrange dU , we can get $dU \leq T dS + S dT - S dT + dw$, where the first summed terms are $d(TS)$
2. $d(U - TS) \leq -S dT + dw$
 - (a) This is a new state function, where A is Helmholtz Free Energy

$$A \equiv U - TS$$

3. Substituting yields, $dA \leq -S dT + dw$
4. If only PV work is done at constant temperature and volume,

$$dA = 0 \text{ (eq., const. } T, V)$$

A is a kind of potential where the system is in equilibrium when A is a minimum

For a reversible process at constant temperature, $dA = dw$. For an irreversible process, $\Delta A < w_{irrev}$

5.2.2 Derivation of G

1. If we consider material equilibrium for constant T and P , we can substitute $dw = -P dV$

$$(a) \quad dU \leq T dS + SdT - S dT - P dV + V dP - V dP$$

2. Grouping gets $dU \leq d(TS) - S dT - d(PV) + V dP$

3. Algebra yields $d(U + PV - TS) \leq -S dT + V dP$

(a) This is a new state function, where G is Gibbs' Free Energy

$$G \equiv PV - TS = H - TS$$

4. Substituting yields, $dG \leq -S dT + V dP$

5. If temperature and pressure are constant, $dG = 0$

G is a kind of potential where the system is in equilibrium when G is a minimum

For a reversible process at constant temperature and pressure, $dG = dW_{non-PV}$. For an irreversible process, $\Delta G < w_{non-PV}$

5.2.3 Connection with Entropy

In a closed system capable of doing only PV work, the constant T and V material equilibrium condition is the minimization of A , and the constant T and P material equilibrium condition is the minimization of G

Since $-\frac{\Delta H_{sys}}{T} = \Delta S_{surr}$ at constant T and P ,

$$\Delta S_{univ} = \frac{-\Delta G_{syst}}{T}$$

Due to the Second Law, entropy of the universe must increase for an irreversible process, so ΔG_{syst} must decrease

5.3 Thermodynamic Relations for a System in Equilibrium

5.3.1 Basic Thermodynamic Quantities

The basic thermodynamic relationships are:

$$H \equiv U + PV$$

$$A \equiv U - TS$$

$$G = H - TS$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

Additionally, for a closed system in equilibrium,

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad (\text{Closed, Eq.})$$

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P \quad (\text{Closed, Eq.})$$

5.3.2 The Gibbs Equations

$$dU = T dS - P dV$$

$$dH = T dS + V dP$$

$$dA = -P dV - S dT$$

$$dG = V dP - S dT$$

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

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

Furthermore,

$$\alpha(T, P) \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \text{ and } \kappa(T, P) \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

Procedure:

1. Write out the corresponding Gibbs Equation
2. Set the designated variable as constant
3. Solving for the desired relation

5.3.3 The Maxwell Relations

The Maxwell Relations can be derived by applying the basic Euler's Reciprocity to the derivative forms of the equations of state. The Euler Reciprocity is⁶,

$$\frac{d^2 z}{dx dy} = \frac{d^2 z}{dy dx}$$

For instance,

$$\frac{\partial^2 G}{\partial T \partial P} = \left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P} \right)_T \right)_P = \left(\frac{\partial}{\partial T} V \right)_P = \left(\frac{\partial V}{\partial T} \right)_P$$

This must equal $\frac{\partial^2 G}{\partial P \partial T} = - \left(\frac{\partial S}{\partial P} \right)_T$ via the Euler Reciprocity

⁶It is important to note that the operator in the denominator of the derivative is performed right to left

Some relationships are shown below:

$$\frac{\partial^2 U}{\partial S \partial V} : \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad \text{and} \quad \frac{\partial^2 H}{\partial S \partial P} : \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

$$\frac{\partial^2 A}{\partial T \partial V} : \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad \text{and} \quad \frac{\partial^2 G}{\partial T \partial P} : \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$$

5.3.4 Dependence of State Functions on T, P, and V

1. Start with the Gibbs equation for dU , dH , dA , or dG
2. Impose the conditions of constant T , V , or P
3. Divide by dP_T , dV_T , dT_V , or dT_P
4. Use a Maxwell relation or heat-capacity equation to eliminate any terms with entropy change in the numerator

Here are a few examples:

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P = \frac{\alpha T}{\kappa} - P$$

$$\left(\frac{\partial H}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P + V = -TV\alpha + V$$

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

5.3.5 Remaining Quantities

$$\mu_{JT} = \left(\frac{V}{C_P} \right) (\alpha T - 1)$$

$$\mu_J = \frac{(P - \alpha T \kappa^{-1})}{C_V}$$

$$C_P - C_V = \frac{TV\alpha^2}{\kappa}$$

Be careful with molar quantities and these equations. To use molar quantities for the second equation, for instance, it'd be $C_{P,m} - C_{V,m} = \frac{TV_m\alpha^2}{\kappa}$

Using the following relationship may also be useful,

$$V_M = \frac{M}{\rho}$$

5.4 Calculation of Changes in State Functions

5.4.1 Calculation of ΔS

The differential equation for entropy is given as,

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = \frac{C_P}{T} dT - \alpha V dP$$

This equation is equivalent to the following when integrated,

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT - \int_{P_1}^{P_2} \alpha V dP$$

Since it's easy to break a process into individual paths:

1. We can analyze a change from T_1 to T_2 at constant P

$$\Delta S_a = \int_{T_1}^{T_2} \frac{C_P}{T} dT (\text{Const. } P)$$

2. Next, P_1 goes to P_2 at constant T

$$\Delta S_b = - \int_{P_1}^{P_2} \alpha V dP = - \int_{P_1}^{P_2} \alpha V_m n dP (\text{Const. } T)$$

3. The total entropy change for a P and T change is $\Delta S = \Delta S_a + \Delta S_b$

5.4.2 Calculation of ΔH and ΔU

$$\Delta H = \int_{T_1}^{T_2} C_P dT + \int_{P_1}^{P_2} (V - TV\alpha) dP$$

Since it's easy to break a process into individual paths:

1. We can analyze a change from T_1 to T_2 at constant P

$$\Delta H_a = \int_{T_1}^{T_2} C_P dT (\text{Const. } P)$$

2. Next, P_1 goes to P_2 at constant T

$$\Delta H_b = \int_{P_1}^{P_2} (V - TV\alpha) dP (\text{Const. } T)$$

3. The total enthalpy change for a P and T change is $\Delta H = \Delta H_a + \Delta H_b$

(a) ΔH values for phase changes must be added if a phase change occurs

4. ΔU can be calculated from ΔH using $\Delta U = \Delta H - \Delta(PV)$

5. Important Note: If you're looking for ΔH_m , for instance, you should make it $C_{P,m}$ and V_m

5.4.3 Calculation of ΔG and ΔA

To calculate ΔG directly, we can use the following formula for isothermal conditions

$$\Delta G = \Delta H - T\Delta S \text{ (Const. } T\text{)}$$

Alternatively, here are three ways to calculate ΔG :

$$\Delta G = \int_{P_1}^{P_2} V dP = \int_{P_1}^{P_2} \frac{m}{\rho} dP = \int_{P_1}^{P_2} nV_m dP \text{ (Const. } T, V\text{)}$$

At constant T and P ,

$$\Delta G = 0 \text{ (rev. proc. at const. } T \text{ and } P\text{)}$$

To calculate ΔA directly, we can use the following formula for isothermal conditions

$$\Delta A = \Delta U - T\Delta S \text{ (Const. } T\text{)}$$

Alternatively,

$$\Delta A = - \int_{V_1}^{V_2} P dV \text{ (Const. } T, P\text{)}$$

If the phase change goes from solid to liquid, ΔA can be calculated by using densities to find ΔV . If the phase change goes from liquid to gas, one can assume $\Delta V \approx V_{gas}$

5.5 Chemical Potentials and Material Equilibrium

The Gibbs Equations previously defined are not useful for a system with interchanging of matter with the surroundings or an irreversible chemical reaction

The chemical potential (an intensive state function) of a substance is defined as

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} \text{ (one-phase)}$$

Alternatively,

$$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_{j \neq i}} \text{ (one-phase)}$$

Gibbs' Free Energy can now be defined as,

$$dG = -S dT + V dP + \sum_i \mu dn_i \text{ (one-phase, Thermal/Mech. Eq.)}$$

Substituting this equation for dG into dU yields,

$$dU = T dS - P dV + \sum_i \mu_i dn_i$$

We can now write two more extensions to the Gibbs Equations:

$$dH = T dS + V dP + \sum_i \mu_i dn_i$$

$$dA = -S dT - P dV + \sum_i \mu_i dn_i$$

For a multiple-phase system, let α denote one of the phase of the system. Therefore,

$$\mu_i^\alpha \equiv \left(\frac{\partial G^\alpha}{\partial n_i^\alpha} \right)_{T, P, n_j^\alpha \neq i}$$

$$dG = -S dT + V dP + \sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha$$

At material equilibrium,

$$dG = \sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha = 0 \text{ (mat. eq., const. } T/P)$$

$$dA = \sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha = 0 \text{ (mat. eq., const. } T/V)$$

For a pure substance, μ_i is the molar Gibbs free energy

$$\mu = G_m \equiv \frac{G}{n} \text{ (One-phase pure substance)}$$

5.6 Reaction Equilibrium

- An equilibrium will shift to go from a location of higher chemical potential to a lower one
- Let ν_i be the unitless stoichiometric number, which are negative for reactants and positive for products
- The extent of reaction is given by the symbol ξ

$$\xi = \frac{\Delta n_i}{\nu_i}$$

- For a chemical-reaction in equilibrium in a closed system,

$$\sum_i \nu_i \mu_i = 0$$

- Gibbs' Free Energy can be expressed as the following, which is zero at equilibrium,

$$\frac{dG}{d\xi} = \sum_i \nu_i \mu_i \text{ (const. } T/P)$$

6 Standard Thermodynamic Functions of Reaction

6.1 Standard Enthalpy of Reaction

- The standard state of a pure substance is defined at pressure of 1 bar ($P^\circ \equiv 1 \text{ bar}$)
 - Gases are assumed to have ideal behavior and partial pressures of 1 bar
- The standard enthalpy of formation, $\Delta_f H_T^\circ$, is the change of enthalpy for the process in which one mole of the substance in its standard state is formed from the corresponding separated elements, each element being in its reference form
- For an element in its reference form, the enthalpy of formation is zero

6.2 Hess' Law

- One can oxidize the reactants completely to CO_2 and H_2O and then make products by the reverse of oxidation
- One can also convert all reactants to elements in their standard states and then make products from elements in these standard states
- However, the most efficient and accepted method is to use the previously defined heat of formation
- The standard enthalpy change is given as the following for the reaction $aA + bB \rightarrow cC + dD$

$$\Delta H^\circ = \sum_i \nu_i \Delta_f H_{T,i}^\circ$$

6.3 The Six-Step Program for Finding ΔH_f°

1. If any of the elements involved are gases at T and 1 bar, we calculate ΔH for the hypothetical transformation of each gaseous element from an ideal gas to a real gas under the same conditions
2. We measure ΔH for mixing the pure elements at these conditions
3. We utilize $\Delta H = \int_{T_1}^{T_2} C_P dT + \int_{P_1}^{P_2} (V - TV\alpha) dP$ to find ΔH for bringing the mixture from the original T and 1 bar to the conditions used to carry out the experiment
4. A calorimeter is used to measure ΔH of the reaction
5. ΔH is found for bringing the compound from the step in which it is formed back to T and 1 bar
6. If there is a compound that is a gas, we calculate ΔH for the hypothetical transformation from a real gas back to an ideal gas

6.4 Calorimetry

- If there are conditions of constant volume, ΔU can be measured. If there are conditions of constant pressure, ΔH can be measured

$$\Delta_r U_{298} = -C_{avg} \Delta T$$

- We know $\Delta H = \Delta U + \Delta(PV)$, and the following assumption can be used by ignoring volume changes of liquids and solids

$$\Delta(PV) \approx \Delta n_{gas} \cdot RT$$

- Therefore,

$$\Delta H_T^\circ = \Delta U_T^\circ + \Delta n_g RT$$

- For the above equation, be careful of what you're solving for. Look at the example below as cautionary measure

6.4.1 Cautionary Calorimetry Calculation

Question: If the standard enthalpy of combustion at $25^\circ C$ of liquid $(CH_3)_2CO$ to CO_2 gas and H_2O liquid is -1790 kJ/mol , find $\Delta_f H_{298}^\circ$ and $\Delta_f U_{298}^\circ$ of $(CH_3)_2CO$ liquid

Solution:

1. Write out the reaction with correct stoichiometry: $(CH_3)_2CO(l) + 4O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$

2. Use tabulated values to solve $-1790 \text{ kJ/mol} = 3\Delta_f H_{298, \text{CO}_2(\text{g})}^\circ + 3\Delta_f H_{298, \text{H}_2\text{O}(\text{l})}^\circ - \Delta_f H_{298, (\text{CH}_3)_2\text{CO}(\text{l})}^\circ - 4\Delta_f H_{298, \text{O}_2(\text{g})}^\circ$ for the desired heat of formation

(a) $\Delta_f H_{298, (\text{CH}_3)_2\text{CO}(\text{l})}^\circ = -248 \text{ kJ/mol}$ via this calculation

3. Since we want $\Delta_f U_{298}^\circ$, we *must* write out the formation reaction. We *cannot* use the stoichiometry of the combustion reaction

(a) This is $3\text{C}(\text{graphite}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow (\text{CH}_3)_2\text{CO}(\text{l})$

4. Find $\Delta n_g/\text{mol}$. Here it is -3.5

5. Use $\Delta_f H_{298, (\text{CH}_3)_2\text{CO}(\text{l})}^\circ = \Delta_f U_{298, (\text{CH}_3)_2\text{CO}(\text{l})}^\circ + \Delta n_g RT$ and solve for ΔU_f°

(a) $\Delta_f U_{298, (\text{CH}_3)_2\text{CO}(\text{l})}^\circ = -239 \text{ kJ/mol}$ via this calculation

6.5 Calculation of $H_{ideal} - H_{real}$

1. First, convert the real gas at P° to a real gas at 0 bar

2. Then convert this gas to an ideal gas at 0 bar

3. Then convert this ideal gas to one at P°

- To perform Step 1 and 3, there is a pressure change under isothermal conditions
- For the overall process, the equation is,

$$\Delta H = H_{id}(T, P^\circ) - H_{re}(T, P^\circ) = \Delta H_1 + \Delta H_2 + \Delta H_3$$

- The enthalpy change for Step 1 is calculated as follows,

$$\Delta H_1 = \int_{P^\circ}^0 (V - TV\alpha) dP$$

- The enthalpy change for Step 2 is $\Delta H_2 = 0$

- The reason for this is because $\Delta(PV)$ is zero and ΔU is just $U_{intermolec}$, which is zero as pressure goes to zero

- The enthalpy change for Step 3 is $\Delta H_3 = 0$

- The reason for this is because H of an ideal gas is independent of pressure

- The enthalpy change for the entire process is calculated as follows,

$$\Delta H = H_{id} - H_{re} = \int_0^{P^\circ} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] dP (\text{Const. } T)$$

- As previously mentioned, $\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$

6.6 Temperature Dependence of Reaction Heats

- The standard heat-capacity change is defined as,

$$\Delta C_P^\circ \equiv \sum_i \nu_i C_{P,m,i}^\circ = \frac{d\Delta H^\circ}{dT}$$

- Alternatively,

$$\Delta H_{T_2}^\circ - \Delta H_{T_1}^\circ = \int_{T_1}^{T_2} \Delta C_P^\circ dT$$

- The standard-state molar heat capacity is typically expressed as,

$$C_{P,m}^\circ = a + bT + cT^2 + dT^3$$

- The Debye approximation states $C_{P,m}^\circ \approx C_{V,m}^\circ = aT^3$ since a solid has only vibrational motion and contributes very little until kT gets larger

6.7 Conventional Entropies and the Third Law

- The entropy for all pure, perfectly crystalline (ordered) substances is zero at absolute zero temperature
 - This does not hold for substances that are not in internal equilibrium
 - For instance, in a crystal of $C \equiv O$, there can be random interactions of the individual molecular dipoles
 - * This is called residual entropy due to the slight amount of disorder
- The following equation can be used to find the standard entropy change of a reaction

$$\Delta S_T^\circ = \sum_i \nu_i S_{m,T,i}^\circ$$

- Alternatively,

$$\Delta S_{T_2}^\circ - \Delta S_{T_1}^\circ = \int_{T_1}^{T_2} \frac{\Delta C_P^\circ}{T} dT$$

- A general equation for molar entropy can be written as,

$$S_{m,T}^\circ = \int_0^{T_{fus}} \frac{C_{p,m}^\circ(s)}{T} dT + \frac{\Delta_{fus}H_m^\circ}{T_{fus}} + \int_{T_{fus}}^{T_v} \frac{C_{p,m}^\circ(l)}{T} dT + \frac{\Delta_{vap}H_m^\circ}{T_{vap}} + \int_{T_{vap}}^T \frac{C_{p,m}^\circ(g)}{T} dT + (S_{m,ideal} - S_{m,real})$$

- Using the Debye approximation will solve the issue of the previous equation being divided by zero for the first term. The result is,

$$\int_0^{T_{fus}} \frac{C_{p,m}^\circ}{T} dT = \frac{C_{p,m}^\circ(\text{at } T)}{3} + \int_{T_{lowest}}^{T_{fus}} \frac{a + bT + cT^2 + dT^3}{T} dT$$

- The correction for nonideality of entropy is,

$$S_{m,id} - S_{m,re} = \int_0^{1\text{bar}} \left[\left(\frac{\partial V_m}{\partial T} \right)_P - \frac{R}{P} \right] dP$$

6.8 Standard Gibbs Energy of Reaction

- The standard Gibbs energy change can be found as,

$$\Delta G_T^\circ = \sum_i \nu_i G_{m,T,i}^\circ$$

- An easier way to calculate this is,

$$\Delta G_T^\circ = \sum_i \nu_i \Delta_f G_{T,i}^\circ$$

- $\Delta_f G^\circ$ values can be obtained from $\Delta G = \Delta H - T\Delta S$ for an isothermal process

- Using the Gibbs equations, one can state that

$$\left(\frac{d\Delta G_{rxn}}{dT} \right)_P = -\Delta S_{rxn}$$

7 Reaction Equilibrium in Ideal Gas Mixtures

7.1 Chemical Potentials in an Ideal Gas Mixture

$$\Delta\mu = \mu(T, P_2) - \mu(T, P_1) = RT \ln \left(\frac{P_2}{P_1} \right) \text{ (Pure Ideal Gas, Const. } T)$$

- We know that $\left(\frac{\partial G}{\partial P} \right)_T = V$, so $\left(\frac{\partial \mu}{\partial P} \right)_T = V_m = \frac{RT}{P}$ for an ideal gas
- At constant T , we can say that $\int_{P^\circ}^P d\mu = \int_{P^\circ}^P V_m dP$. This yields,

$$\mu = \mu^\circ + RT \ln \left(\frac{P}{P^\circ} \right)$$

- The chemical potential of component i of an ideal gas mixture at T and P equals the chemical potential of pure gas i at T and P_i
 - This is true for U , H , S , G , and C_P for an ideal gas mixture

7.2 Ideal-Gas Reaction Equilibrium

- Assume the following definition of the standard equilibrium constant for the reaction $aA + bB \rightleftharpoons cC + dD$,

$$K_P^\circ \equiv \frac{\left(\frac{P_{C,eq}}{P^\circ} \right)^c \left(\frac{P_{D,eq}}{P^\circ} \right)^d}{\left(\frac{P_{A,eq}}{P^\circ} \right)^a \left(\frac{P_{B,eq}}{P^\circ} \right)^b}$$

- Standard change in Gibbs Free Energy can then be expressed as,

$$\Delta G^\circ = -RT \ln (K_P^\circ)$$

- Assume the following mathematical definition,

$$\prod_{i=1}^n a_i \equiv a_1 a_2 \dots a_n$$

- With this, K_P° can be defined as,

$$K_P^\circ \equiv \prod_i \left(\frac{P_{i,eq}}{P^\circ} \right)^{\nu_i}$$

- Using the rules of logarithms,

$$K_P^\circ = e^{-\frac{\Delta G^\circ}{RT}}$$

- K_P° is only a function of temperature and is independent of all other states
- If $\Delta G^\circ \gg 0$, then K_P is very small. Conversely, if $\Delta G^\circ \ll 0$, then K_P is very large
- It is typically easier to write this without the standard restriction as,

$$K_P \equiv \prod_i (P_{i,eq})^{\nu_i}$$

- The molar concentration, c_i , of a species is,

$$c_i \equiv \frac{n_i}{V}$$

- Therefore,

$$P_i = c_i RT$$

- Assuming $c_i^\circ = 1 \text{ mol/L} = 1M$,

$$K_c^\circ = \prod_i \left(\frac{c_{i,eq}}{c^\circ} \right)^{\nu_i}$$

- Therefore,

$$K_c^\circ = K_P^\circ \left(\frac{P^\circ}{RTc^\circ} \right)^{\Delta n/mol}$$

- A mole fraction equilibrium constant, K_x , is defined as,

$$K_x \equiv \prod_i (x_{i,eq})^{\nu_i}$$

- A helpful relationship is simply,

$$K_P^\circ = K_x \left(\frac{P}{P^\circ} \right)^{\Delta n/mol}$$

- K_x depends on P and on T unless $\Delta n = 0$, so it is not as useful

7.3 Qualitative Discussion of Chemical Equilibrium

- While K_P° is *always* dimensionless, K_P is only dimensionless when $\Delta n_{gas} = 0$ and typically has units of Pressure ^{Δn_{gas}}
- For a reaction not necessarily at equilibrium,

$$Q_P \equiv \prod_i (P_i)^{\nu_i}$$

- If $Q_P < K_P$, the reaction will proceed to the right: $\xi > 0$
- If $Q_P = K_P$, the reaction is already at equilibrium: $\xi = 0$

- If $Q_P > K_P$, the reaction must go in the reverse: $\xi < 0$
- If ΔG° is large and negative, K_P° is very large and little reactant is left at equilibrium
- If ΔG° is large and positive, K_P° is very small and there is little product present at equilibrium
- Typically, values of e^{-12} are considered very small and e^{12} are considered very large. With this approximation, reactions at 298K with $\Delta G^\circ < -30 \text{ kJ/mol}$ go to completion, and reactions at 298K with $\Delta G^\circ > 30 \text{ kJ/mol}$ don't proceed at all
- Remember, at the molecular level kT is used for energy comparison, and RT is used at the molecular level
- At low temperature $\Delta G^\circ \approx \Delta H^\circ$, and at high temperature, $\Delta G^\circ \approx -T\Delta S^\circ$

7.4 Temperature Dependence of the Equilibrium Constant

- Differentiation of the equation for K_P° will yield,

$$\frac{d \ln(K_P^\circ)}{dT} = \frac{\Delta G^\circ}{RT^2} - \frac{1}{RT} \frac{d(\Delta G^\circ)}{dT}$$

- Using various mathematical equalities that I will not write out, one yields the van't Hoff equation

$$\frac{d \ln(K_P^\circ)}{dT} = \frac{\Delta H^\circ}{RT^2}$$

- This can be rearranged to

$$\frac{d \ln(K_P^\circ)}{d(1/T)} = -\frac{\Delta H^\circ}{R}$$

- Therefore, for a plot of $\ln(K_P^\circ)$ against $1/T$, the slope is $-\frac{\Delta H^\circ}{R}$, and if ΔH° is approximately temperature independent, the plot produces a straight line
- Using the equation for C_P in **6.6** yields,

$$\Delta H_T^\circ = A + BT + CT^2 + DT^3 + ET^4$$

- Consequently, if $\Delta H^\circ \neq \text{constant}$, then

$$\Delta H^\circ = \Delta H^\circ(T_1) + \Delta a(T - T_1) + \frac{\Delta b}{2}(T^2 - T_1^2) + \frac{\Delta c}{3}(T^3 - T_1^3)$$

- Integrating the van't Hoff equation yields,

$$\ln \left(\frac{K_P^\circ(T_2)}{K_P^\circ(T_1)} \right) = \int_{T_1}^{T_2} \frac{\Delta H_T^\circ}{RT^2} dT$$

- An easier to calculate quantity is the following where ΔH° is assumed to be independent of temperature,

$$\ln \left(\frac{K_P^\circ(T_2)}{K_P^\circ(T_1)} \right) \approx \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

- If the K_P° at some arbitrary temperature is needed, one can easily find $K_{P,298}^\circ$ with corresponding $T = 298.15 \text{ K}$ and ΔH° from tabulated values with Hess' Law
- If ΔH° cannot be assumed to be independent of temperature but C_P° can, one can use the equation in **6.6** to find ΔH_T° by finding ΔH_{298}° and ΔC_P° from tabulated values with Hess' Law

7.5 Ideal-Gas Equilibrium Calculations

1. Calculate $\Delta_r G^\circ$ from tabulated data
2. Calculate K_P° using $\Delta_r G^\circ = -RT \ln(K_P^\circ)$
3. Use the stoichiometry of the reaction to express mole numbers in terms of initial mole number and equilibrium extent of reaction
 - (a) This is simply the creation of an I.C.E. table
4. Analyze reaction conditions

(a) If the reaction is at fixed temperature and pressure, use $P_i = x_i P = \frac{n_i}{n_{tot}} P$

- i. A simplified equation under constant temperature and pressure for an ideal system is the following, where all moles and mole fractions are amounts at equilibrium:

$$K_P^\circ = \frac{(x_C)^c (x_D)^d}{(x_A)^a (x_B)^b} \cdot \left(\frac{P}{P^\circ}\right)^{\nu_i} = \frac{(n_C)^c (n_D)^d}{(n_A)^a (n_B)^b} \cdot \left(\frac{P}{n_{Total} \cdot P^\circ}\right)^{\nu_i} \quad (\text{Derived by me})$$

A. Note: If $\nu_i = 0$, you don't even need the pressure!

(b) If the reaction is at fixed temperature and volume, use $P_i = \frac{n_i RT}{V}$

- i. A simplified equation under constant temperature and volume for an ideal system is, where all moles are amounts at equilibrium:

$$K_P^\circ = \frac{(n_C)^c (n_D)^d}{(n_A)^a (n_B)^b} \cdot \left(\frac{RT}{P^\circ V}\right)^{\nu_i} \quad (\text{Derived by me})$$

5. Substitute the P_i values into the equilibrium-constant expression and solve for ξ_{eq}
6. Calculate the equilibrium mole numbers from ξ_{eq} and the expressions for n_i

7.6 Equilibrium Shifts

1. Increasing pressure at constant volume by adding inert gas will not change the equilibrium composition since partial pressures are the same
2. Adding an inert gas while holding temperature and pressure constant will shift the reaction to the side of greater moles
 - (a) This is analogous to decreasing pressure at constant temperature
3. Adding a reactant or product gas at constant temperature and volume will shift the equilibrium to the side opposite of the addition since other partial pressures don't change
4. Adding a reactant or product gas at constant temperature and pressure changes other partial pressures, so there is no simple rule
 - (a) For example, if we have $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, we can establish equilibrium at constant temperature and pressure. Then, we can add some N_2 at constant total pressure. The partial pressure of N_2 will go up while the other partial pressures go down. Under certain conditions, equilibrium will shift to the left to produce more of the added gas even though this goes against intuition
5. Decreasing volume at constant temperature will be the same as increasing the pressure at constant temperature. It will shift the reaction to the side of lower moles of gas
6. An increase in temperature at constant pressure will shift the equilibrium to the direction in which the system absorbs heat from the surroundings via the van't Hoff equation

8 One-Component Phase Equilibrium and Surfaces

8.1 Qualitative Pressure Dependence of G_m

- Typical values for V_m are 19.65cm^3 for solids, 18cm^3 for liquids, and 22400cm^3 for gases. Also,

$$\left(\frac{\partial G_m}{\partial P}\right)_T = V_m > 0$$

- The gas phase G_m is most sensitive to pressure. Next is liquid and then solid (except for water)

8.2 The Phase Rule

- The number of independent intensive variables (degrees of freedom) is the following, where c is the number of different chemical species, p is the number of phases present, and r is the number of independent chemical reactions,

$$f = c - p + 2 - r$$

- For a additional restrictions on the mole fractions,

$$f = c - p + 2 - r - a$$

- Additionally,

$$c_{ind} \equiv c - r - a \therefore f = c_{ind} - p + 2$$

- There are no degrees of freedom at the triple point; therefore, it has a definite T and P

8.3 One-Component Phase Equilibrium

- The stable phase at any point in a one-component P-T phase diagram is where G_m , also μ , is lowest
- At any temperature above the critical point temperature, liquid and vapor phases cannot coexist in equilibrium
- The Trouton's Rule approximation states that

$$\Delta_{vap}S_{m,,nbp} = \frac{\Delta_{vap}H_{m,nbp}}{T_{nbp}} \approx 10.5R$$

- Trouton's Rule fails for highly polar liquids and temperatures below 150K or above 1000K. The following is a better approximation,

$$\Delta_{vap}S_{m,,nbp} \approx 4.5R + R \ln(T_{nbp})$$

8.4 The Clapeyron Equation

8.4.1 General Clapeyron Equation

- For a pure phase, the Gibbs Equation derived earlier is,

$$dG_m = V_m dP - S_m dT$$

- Using the fact that $dG_m^1 = dG_m^2$ ($\Delta G = 0$) at equilibrium,

$$\Delta V_m dP = \Delta S_m dT$$

- Rearranging this equation yields,

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta S}{\Delta V}$$

- The Clapeyron Equation states that for one component two-phase equilibrium system,

$$\frac{dP}{dT} = \frac{\Delta H_m}{T\Delta V_m} = \frac{\Delta H}{T\Delta V}$$

- For phase transitions from solid to liquid, solid to gas, and liquid to gas, $\Delta V_m > 0$, $\Delta H_m > 0$, and $\left(\frac{dP}{dT}\right) > 0$
 - An exception to this is substances that have $\Delta V_m < 0$, such as water, when going from solid to liquid. This changes it to $\left(\frac{dP}{dT}\right) < 0$
 - Also, if $\Delta V_{s \rightarrow l} = 0$, then $\frac{dP}{dT} = \infty$. This implies that ΔT is very small for large changes in P

8.4.2 Liquid-Vapor and Solid-Vapor Equilibrium

- If the assumption is made that $\Delta V \approx V_{gas}$,

$$\left(\frac{dP}{dT}\right)_{vap\ or\ sub} = \frac{\Delta H_m}{TV_{m,gas}}$$

- Using $V_{gas} \approx \frac{RT}{P}$, the Clausius-Clapeyron Equation is obtained

$$\left(\frac{dP}{dT}\right)_{vap\ or\ sub} = \frac{P\Delta H_m}{RT^2}$$

- Integration the above separable differential equation yields

$$\frac{d \ln P}{dT} \approx \frac{\Delta H_m}{RT^2}$$

- An approximation, albeit a very crude one⁷, is that $\frac{\Delta P}{\Delta T} \approx \frac{dP}{dT} \therefore \Delta T = \frac{\Delta PRT^2}{P\Delta H_m}$
- To obtain a better approximation, begin by substituting $d(1/T) = -(1/T^2)$,

$$\frac{d \ln P}{d(1/T)} \approx \frac{-H_m}{R}$$

- If ΔH_m is independent of temperature, the above equation can be integrated to yield

$$\ln \left(\frac{P_2}{P_1}\right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- In handbooks, A and B constants can be found⁸ to make,

$$\ln P \approx \frac{A}{T} + B$$

⁷It is not recommended to use this approximation

⁸Crude form of the Antoine Equation

8.4.3 Effects of Pressure on Phase Transitions

- Higher altitudes cause boiling point decreases since the pressure is lower
- For small variations in pressure,

$$\Delta T_{bp} = T_{boil} \frac{\Delta V_{vap}}{\Delta H_{vap}} \Delta P$$

- For larger variations in P , the following is true where nbp stands for normal boiling point,

$$\ln \left(\frac{P}{1 \text{ atm}} \right) = \frac{\Delta H}{R} \left(\frac{1}{T_{nbp}} - \frac{1}{T} \right)$$

8.4.4 Solid-Liquid Equilibrium

- Since the solid-liquid transitions doesn't involve a gas phase, $\Delta V \approx V_{gas}$ is unreasonable.
- The applicable equation for solid-liquid equilibrium is⁹,

$$\int_{P_1}^{P_2} dP = \int_{T_1}^{T_2} \frac{\Delta_{fus} S}{\Delta_{fus} V} dT = \int_{T_1}^{T_2} \frac{\Delta_{fus} H}{T \Delta_{fus} V} dT$$

- Using the approximation $\frac{\Delta P}{\Delta T} \approx \frac{dP}{dT}$ for small pressure changes or assuming $\frac{\Delta_{fus} S}{\Delta_{fus} V}$ is constant yields,

$$\Delta P = \frac{\Delta T \Delta_{fus} S}{\Delta_{fus} V} = \frac{\Delta T \Delta_{fus} H}{T_1 \Delta_{fus} V}$$

- For larger changes in P for solid-liquid transitions, assume $\Delta_{fus} H$ and $\Delta_{fus} V$ are constant to make,

$$\Delta P \approx \frac{\Delta_{fus} H}{\Delta_{fus} V} \ln \left(\frac{T_2}{T_1} \right)$$

8.4.5 Effects of Pressure on Vapor Pressure

- For phase equilibrium, $\mu_g = \mu_{cond}$
- At constant temperature, the system will go to a new vapor pressure where the gas has a higher μ and vapor pressure with applied external pressure
- At constant volume and vapor pressure, T would fall with an applied external pressure

9 Solutions

9.1 Solution Composition

- The definition of molarity is,

$$c_i \equiv \frac{n_i}{V}$$

- The definition of mass concentration is,

$$\rho_i \equiv \frac{m_i}{V}$$

- The definition of molality of solute B is the following where solvent mass is w_A and M_A is the solvent molar mass,

$$m_B \equiv \frac{n_B}{w_A} = \frac{n_B}{n_A M_A}$$

⁹Fusion is defined as going from solid to liquid

9.2 Partial Molar Quantities

- From now on, V^* is the total volume of unmixed components, where * denotes a property of pure, unmixed substances. As such,

$$V^* = \sum_i n_i V_{m,i}^*$$

- $\Delta_{mix} V = V - V^* = 0$ for ideal solutions and $\Delta_{mix} V \neq 0$ for real solutions
 - Ideality also implies that, for a solution of B and C, the B-B interactions, B-C interactions, and C-C interactions are all the same
- The total differential can be applied knowing that $V(T, P, n_i, \dots, n_r)$

$$dV = \left(\frac{\partial V}{\partial T} \right)_{P, n_i} dT + \left(\frac{\partial V}{\partial P} \right)_{T, n_i} dP + \sum_i \bar{V}_i dn_i$$

- The partial molar volume is

$$\bar{V}_j \equiv \left(\frac{\partial V}{\partial n_j} \right)_{T, P, n_{i \neq j}}$$

- Additionally,

$$\bar{V}_i = \frac{RT}{P} \text{ (Ideal Gas Mixture)}$$

- The partial molar volume of a pure substance is equal to its molar volume,

$$\bar{V}_j^* = V_{m,j}^*$$

- As a result,

$$V = \sum_i \bar{V}_i n_i = \sum_i x_i \bar{V}_i n_{tot}$$

- Also,

$$\Delta_{mix} V = \sum_i n_i (\bar{V}_i - V_{m,i}^*)$$

- For a multi-component system,

$$n_1 d\bar{V}_1 + n_2 d\bar{V}_2 + \dots = 0 = x_1 d\bar{V}_1 + x_2 d\bar{V}_2 + \dots$$

- Therefore, for a two component system,

$$x_1 d\bar{V}_1 = -x_2 d\bar{V}_2 \quad \text{and} \quad d\bar{V}_1 = \frac{-x_2}{x_1} d\bar{V}_2$$

$$n_1 d\bar{V}_1 = -n_2 d\bar{V}_2 \quad \text{and} \quad d\bar{V}_1 = \frac{-n_2}{n_1} d\bar{V}_2$$

- Moreover¹⁰,

$$\left(\frac{\partial \bar{V}_1}{\partial n_1} \right)_{n_2} = -\frac{n_2}{n_1} \left(\frac{\partial \bar{V}_2}{\partial n_2} \right)_{n_1}$$

¹⁰I do not get this. How can you hold n_2 constant and have it be changing by an infinitesimal amount, ∂n_2 ?

- The other thermodynamic functions can be defined similarly to \bar{V}_i , for instance \bar{H}_i , by taking the partial derivative of the thermodynamic function and dividing it by ∂n_i while holding $T, P, n_{j \neq i}$ constant. The arbitrary variable Y can then be used to state,

$$\bar{Y}_i \equiv \left(\frac{\partial Y}{\partial n_i} \right)_{T, P, n_{j \neq i}} \quad \text{and} \quad Y = \sum_i n_i \bar{Y}_i$$

- The relationship for Gibbs' Free Energy is notable,

$$\bar{G}_i \equiv \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} \equiv \mu_i$$

9.3 Deviations

9.3.1 Positive Deviations

- This occurs when the dissolution process is not energetically favorable

$$\Delta V_{mix} > 0, \quad \Delta H_{mix} > 0$$

9.3.2 Negative Deviations

- This occurs when the dissolution process is very energetically favorable (A-B interactions is stronger than A-A or B-B)

$$\Delta_{mix} V < 0, \quad \Delta_{mix} H < 0$$

$$P_i < P_{i, ideal}$$

9.4 Finding Partial Molar Volumes

9.4.1 Experimental

- Fix n_A , vary n_B , and measure V_{tot} as n_B increases
- Plotting V_{tot} against n_B will yield a plot with slope of \bar{V}_B at $x_B = \frac{n_B}{n_A + n_B}$

9.4.2 Theoretical

- As already derived,

$$\left(\frac{\partial \mu_i}{\partial T} \right)_{P, n_j} \equiv \left(\frac{\partial \bar{G}_i}{\partial T} \right)_{P, n_j} = -\bar{S}_i \quad \text{and} \quad \left(\frac{\partial \mu_i}{\partial P} \right)_{T, n_j} \equiv \left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T, n_j} = \bar{V}_i$$

9.5 Mixing Quantities

- Here is a moderately useless derivation for you to enjoy,

$$\begin{aligned} \left(\frac{\partial \Delta_{mix} G}{\partial P} \right)_{T, n_j} &= \frac{\partial}{\partial P} \sum_i n_i (\bar{G}_i - G_{m,i}^*) = \sum_i n_i \left[\left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T, n_j} - \left(\frac{\partial G_{m,i}^*}{\partial P} \right)_T \right] = \sum_i n_i (\bar{V}_i - V_{m,i}^*) \\ \therefore \left(\frac{\partial \Delta_{mix} G}{\partial P} \right)_{T, n_j} &= \Delta_{mix} V \end{aligned}$$

- Similarly,

$$\left(\frac{\partial \Delta_{mix} G}{\partial T} \right)_{P, n_j} = -\Delta_{mix} S$$

9.6 Ideal Solutions and Thermodynamic Properties

- An ideal solution is one where the molecules of the various species are so similar to one another that replacing molecules of one species with molecules of another species will not change the spatial structure or the intermolecular interaction energy in the solution
- When substances are mixed,

$$\Delta_{mix} G = RT \sum_i n_i \ln x_i = -T \Delta_{mix} S$$

$$\Delta_{mix} S = -R \sum_i n_i \ln x_i$$

- With respect to chemical potential,

$$\sum_i n_i \mu_i = \sum_i n_i (\mu_i^* + RT \ln x_i)$$

$$\mu_i = \mu_i^* + RT \ln x_i \quad \text{and} \quad \mu_i^\circ \equiv \mu_i^*$$

- Therefore, a solution is ideal if the chemical potential of every component in solution obeys the above equation for all solution compositions and for a range of temperature and pressure
 - As x_i approaches zero, μ_i^* approaches $-\infty$

- Also,

$$\Delta_{mix} V = \Delta_{mix} H = \Delta_{mix} U = 0 \text{ (Ideal soln, Const. T/P)}$$

- In equilibrium,

$$\mu_i^l = \mu_i^v$$

- Raoult's Law states,

$$P_i = x_i^l P_i^*$$

- Alternatively,

$$x_i^v P_{tot} = x_i^l P_i^*$$

9.7 Ideally Dilute Solutions

- In an ideally dilute solution, solute molecules (i) interact essentially only with solvent molecules (A)

$$\mu_i = RT \ln x_i + f_i(T, P)$$

- $f_i(T, P)$ is some function of T and P
- Also,

$$\mu_A = \mu_A^* + RT \ln x_A$$

9.8 Thermodynamic Properties of Ideally Dilute Solutions

- Since $\mu_i^\circ \equiv f_i(T, P)$,

$$\mu_i = RT \ln x_i + \mu_i^\circ$$

- Additionally,

$$\mu_A = \mu_A^\circ + RT \ln x_A$$

$$\mu_A^\circ \equiv \mu_A^*$$

$$\frac{P_i}{x_i^l P^\circ} = \exp\left(\frac{\mu_i^{\circ l} - \mu_i^{\circ v}}{RT}\right)$$

- A new (Henry's) constant can be defined as,

$$K_i \equiv P^\circ \exp\left(\frac{\mu_i^{\circ l} - \mu_i^{\circ v}}{RT}\right)$$

- Finally, Henry's Law can be expressed as,

$$P_i = K_i x_i^l$$

- Furthermore, Raoult's Law applies as,

$$P_A = x_A^l P_A^*$$

- For an ideal solution, the solute obeys Henry's Law, and the solvent obeys Raoult's Law
- For an application of external pressure,

$$P' = P_0 e^{\frac{\bar{v}_P P}{RT}}$$

- For a gas dissolved in liquid,

$$x_i^l = \frac{P_i}{K_i}$$

- Therefore, solids dissolve in liquids better at higher temperatures while gases dissolved in liquids better at lower temperatures
 - Classic example is the dissolution of carbon dioxide in soda - it goes flat at higher temperatures (less CO_2 dissolved)
- Since this is an ideally dilute solution,

$$P_i = K_{i,m} m_i = K_{i,c} c_i$$

- Henry's Law does not apply to strong electrolytes
- If $K_{Henry} > P^*$, then $P_{ideal} > P^*$ and $\mu^\circ = \mu_{ideal} > \mu^*$
- If $K_{Henry} < P^*$, then $\mu^\circ = \mu_{ideal} < \mu^*$

10 Nonideal Solutions

10.1 Activities and Activity Coefficients

- The activity of a substance is defined as,

$$a_i \equiv \exp\left(\frac{\mu_i - \mu_i^\circ}{RT}\right)$$

- Rearranging this to a familiar form yields,

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

- Then, for an ideal or ideally dilute solution, $a_i = x_i$
- The difference between the real and ideal μ_i is,

$$\mu_i - \mu_i^{id} = RT \ln\left(\frac{a_i}{x_i}\right)$$

- The activity coefficient, γ_i , is defined so that,

$$a_i = \gamma_i x_i$$

- The new μ_i equation is now,

$$\mu_i = \mu_i^\circ + RT \ln(\gamma_i x_i)$$

- Substitution of $\mu_i^{ideal} = \mu_i^\circ + RT \ln x_i$ yields,

$$\mu_i^{id} + RT \ln \gamma_i$$

- There are two conventions for the standard state

Convention I The standard state of each solution component i is taken as pure liquid i at the temperature and pressure of the solution such that,

$$\mu_{I,i}^\circ \equiv \mu_i^*(T, P)$$

- Additionally, $\gamma_{I,i} \rightarrow 1$ as $x_i \rightarrow 1$ for each chemical species i
- Use this convention if the mole fractions vary widely and both components are liquids

Convention II This convention treats the solvent differently from the other components. The standard state of the solvent A is pure liquid A at the temperature and pressure of the solution such that,

$$\mu_{II,A}^\circ = \mu_A^*(T, P)$$

- Additionally, $\gamma_{II,i} \rightarrow 1$ as $x_A \rightarrow 1$ for each $i \neq A$
 - Note that this means $x_i \rightarrow 0$
- Choose this convention if solids or gases are in dilute concentrations in a liquid

10.2 Determination of Activities and Activity Coefficients

10.2.1 Convention I

- Raoult's Law is now,

$$P_i = a_{\text{I},i} P_i^*$$

- The following then can be stated,

$$P_i = x_i^v P_{\text{tot}} = \gamma_{\text{I},i} x_i^l P_i^*$$

- If component i has $P_i > P_i^{id}$, then $\gamma_{\text{I},i} > 1$ and vice versa
- If γ_{I} is less than 1, it means that the chemical potentials are less than the ideal chemical potentials. This means that G is lower than G^{id} , and, thus, the solution is more stable

10.2.2 Convention II

- Raoult's Law is now,

$$P_A = a_{\text{II},A} P_A^* = \gamma_{\text{II},A} x_A^l P_A^*$$

- Henry's Law is now,

$$P_i = K_i a_{\text{II},i} = K_i \gamma_{\text{II},i} x_i^l$$

- γ_{I} measures deviations from ideal-solution behavior while γ_{II} measures deviations from ideally dilute solution behavior