ADVANCED THERMODYNAMICS

Handout III – Behavior of Gases, Solution Thermodynamics and the Single-Component Phase Diagram

(Gaskell Chapters 7, 8 & 9)

BACKGROUND

This Handout is primarily concerned with the behavior of gases, leading to solution thermodynamics of the solid and liquid phases, whose link with gases is through the vapor pressure of components in these condensed phases. It begins with a brief review of ideal versus real gases, then onto ideal and real solutions. Also included is the single-component phase diagram, where regions of stability for all three phases are identified, depending on temperature and pressure. The multi-component phase diagrams (Gaskell Chapters 10 and 15) are left to the subsequent handout.

BEHAVIOR OF GASES

As discussed at length in HI, the modern understanding of a gas – leading to the equation of state – first began with Boyle (1660), who observed, at constant T:

PV = constant

If pressure was held constant, the volume of a gas was found to be a function of temperature alone:

$$V(T) = V_o(1 + \alpha V)$$

Here, T is some arbitrary scale, such as Celcius) so that, by definition at, say, 0 °C, volume is taken to be V_o (Charles, 1787). Gay-Lussac observed α to be a constant for most gases, and in 1802 decided on a value of 1/267 at 0 °C. Regnault (1847) with greater experimental precision settled on 1/273, so:

$$PV = \text{constant}' \left(1 + \frac{T}{273} \right)$$
$$= \text{constant}''(T + 272)$$

$$=$$
 constant $(T + 2/3)$

Clearly, the quantity (T + 273), found to not be a function of anything else for constant P and V, was defined as the Ideal Gas Temperature, which is consistent with the Kelvin scale for temperature coming from the SL.

The constant **constant**" clearly depended on *V* at constant *P*, so for *P* measured in atm, *V* was measured in liters. Later, a more significant refinement was due to Avogadro, who hypothesized that one mole of *any* ideal gas occupies the same volume at 273 °K: 22.414 liters.

So, now:

$$PV = \frac{22.414T}{273.16} = 0.08205T = RT$$

In the above equation, \boldsymbol{R} in equivalent units is:

$$= 82.06 \ cm^3 \frac{atm}{K} \text{mole} = 1.987 \frac{cal}{K} \text{mole}$$

Gases are important in materials – first, it is the simplest of the three phases (the others being liquids and solids) and secondly, most gases at pressures and temperatures normally encountered in materials extraction and processing are close to ideal.

With use of the Ideal Gas Law, the chemical potential of a single-component gas can be expressed as follows:

$$dG = VdP$$

But since PV = nRT:

$$dG = \frac{RT}{P}dP = RTd\ln P$$

For a finite change in state:

$$G_2 - G_1 = \Delta G = RT \ln \frac{P_2}{P_1}$$

Since we have no means to compute an absolute value for the free energy corresponding to a particular state, it is customary to choose a particular state, known as the *standard state*, where the free energy is relative to that state.

For ideal gases, the standard state is chosen as the pure gas at 1 atm at the temperature in question (in Kelvin):

$$G(P,T) = G^{o}(T) + RT lnP$$

We can write, since this is a single-component system:

$$G = \overline{G} = \mu$$

Thus, the chemical potential of a one-component ideal gas becomes:

$$\mu(P,T) = \mu^o(T) + RT \ln P$$

Ideal Gas Mixtures

Dalton stated that each component species of an ideal gas mixture behaves as though it alone occupies the volume containing the mixture. Thus, for *i* species:

$$p_i V = n_i RT$$

In the above equation n_i is the number of molar species *i*, and p_i is the partial pressure of *i*. The total pressure is, of course:

$$P = \sum_{i} p_{i}$$

Since the Ideal Gas Law is valid for a mixture if:

$$n = \sum_{i} n_{i}$$

Then, we have:

$$\frac{RT}{V} = \frac{P}{n} = \frac{p_i}{n_i}$$

The partial pressure of *i* is given as:

$$p_i = \frac{n_i}{n}P = X_i P$$

In the above equation: $X_i \equiv n_i/n$.

If we consider a closed system containing one mole of an ideal gas mixture at constant T, we may write:

$$dG = VdP = \frac{RT}{P}\sum_{i} dp_{i} = \sum_{i} dG_{i}$$

In the above equation:

$$dG_i = \frac{RT}{P}dp_i$$

Thus, we may substitute in for $P = p_i/X_i$:

$$dG_i = X_i \frac{RT}{p_i} dp_i = X_i RT d\ln p_i$$

Finally, we have:

$$\frac{dG_i}{X_i} = RTd\ln p_i$$

The LHS of the above equation is just the variation per mole of the Gibbs Free Energy attributable to component *i*; i.e., the chemical potential of *i*:

$$\mu_{i(2)} - \mu_{i(1)} = RT \ln \left[\frac{p_{i(2)}}{p_{i(1)}} \right]$$

As with the pure-component gas, it is convenient to define a standard state of a gas mixture so as to express the chemical potential of each component relative to that standard state. This is chosen as the pure species i at 1 atm and temperature of the mixture, thus:

$$\mu_i(p_i,T) = \mu_i^{\circ}(T) + RT \ln[p_i]$$

$$\mu_i(p_i, T) = \mu_i^{\circ}(T) + RT \ln[X_i P]$$

From this equation, we may write:

$$\overline{G}_i = G_i^o + RT \ln X_i P$$

This can be rewritten as:

$$\frac{\overline{G}_i}{T} = \frac{G_i^o}{T} + RT \ln X_i P$$

In the above equation \overline{G}_i is the partial molar Gibbs Free Energy of component *i*, and G_i^o is its standard state.

If we differentiate and employ the Gibbs-Helmholtz equation:

$$\frac{\partial \left(\overline{G}_{i} / T \right)}{\partial T} = -\frac{\overline{H}_{i}}{T^{2}}$$

(where \overline{H}_i and H_i^o are the partial molar enthalpy of specie *i* in the mixture and in the standard state, respectively), and since:

$$\frac{\partial \left(\overline{G}_{i} / T \right)}{\partial T} = \frac{\partial \left(\overline{G}_{i}^{o} / T \right)}{\partial T}$$

Then, we have:

$$\bar{H}_i = H_i^o$$

Thus:

$$\sum_{i} \overline{H}_{i} n_{i} = \sum_{i} H_{i}^{o}$$

Here $\sum_i n_i \overline{H}_i$ is the total enthalpy of the gas mixture, whereas $\sum_i H_i^o$ is that for the constituent gas species in their respective standard states (i.e., pure gases).

For the mixing of ideal gases, ΔH is zero; viz.:

$$\Delta H_{mix} = \sum_{i} n_i \overline{H}_i - \sum_{i} n_i H_i^o = \mathbf{0}$$

We can write for the Gibbs Free Energy of the mixture:

$$G(\text{mixture}) = \sum_{i} n_{i} \mu_{i} = \sum_{i} n_{i} \mu_{i}^{o} + RT \sum_{i} n_{i} \ln p_{i}$$

Similarly, for the Gibbs Free Energy of the component gases before mixing:

$$G(\text{pure components}) = \sum_{i} n_{i} \mu_{i}' = \sum_{i} n_{i} \mu_{i}^{o} + RT \sum_{i} n_{i} \ln P_{i}$$

Thus, we may write:

$$\Delta G_{mix} = \sum_{i} n_i \left(\mu_i - \mu_i' \right) = RT \sum_{i} n_i \ln \frac{p_i}{P_i}$$

If the mixing process is conducted at constant volume, then:

$$P_1 = P_2 = P_3 = \cdots P$$

Thus, we have:

$$\Delta G_{mix} = RT \sum_{i} n_i \ln \frac{p_i}{P}$$

This is equivalent to:

$$\Delta G_{mix} = RT \sum_{i} n_{i} \ln X_{i}$$

Or, if per mole for the ideal gas:

$$\Delta G_{mix} = RT \sum X_i \ln X_i$$

Finally, since:

$$\Delta S_{mix} = \frac{\Delta H_{mix}}{T} - \frac{\Delta G_{mix}}{T}$$

We find for constant volume for the ideal gas (where $\Delta H_{mix} = \mathbf{0}$):

$$\Delta S_{mix} = -R \sum X_i \ln X_i$$

Note that for an ideal gas, ΔG_{mix} is a negative quantity; this corresponds with the fact that mixing of gases is generally a spontaneous process.

Imperfect Gases – Van der Waals and Joule-Thomson Effects

Real gases are not ideal, but approximately ideal under most experimental conditions. An important way to model any deviation is to modify the ideal gas equation of state by introducing two empirical parameters. Van der Waals (1823) proposed:

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

These parameters *a* and *b* have been evaluated for a number of gases.

By multiplying through, it is seen that this equation is, in fact, cubic in V, with three roots:

$$PV = RT + bP - \frac{a}{V} + \frac{ab}{V^2}$$

It has been found that these three roots are real under certain conditions of temperature and pressure. This represents liquefaction of the gas (Zone B-C in Figure HIII.1 (a), where two phases (liquid and vapor) co-exist.



Figure HIII.1 – (a) P-V isotherms for a typical gas. (b) Fields of stability for the gas, vapor and liquid phases. The gas below the critical temperature is technically called a vapor, because, on isothermal compression the vapor can be condensed.

At temperatures above the *critical temperature*, all three roots are identical, representing the limit of liquefaction. Corresponding to the critical temperature is a *critical pressure*. It may be shown that:

$$\left(\frac{\partial P}{\partial V}\right)_{T_{critical}} = \frac{\partial^2 P}{\partial V^2} = \mathbf{0}$$

This represents an inflection of the pressure versus volume curve.

At T_{Cr} in terms of the Van deer Waals gas, we have:

$$V_{Cr} = 3b$$
$$T_{Cr} = \frac{8a}{27Rb}$$

$$P_{Cr} = \frac{a}{27b^2}$$

By defining a reduced pressure, volume and temperature, we have:

$$\pi = \frac{P}{P_{Cr}}; \phi = \frac{V}{V_{Cr}} and \theta = \frac{T}{T_{Cr}}$$

Substituting for *P*, *V* and *T* into the Van der Waals equation, we find:

$$\left(\pi+\frac{3}{\phi^2}\right)(3\phi-1)=8\theta$$

This equation is referred to as the *reduced equation of state*. It is noted that this resulting equation, neither involves empirical constant a or b, nor the Universal Gas Constant R; thus, it is independent of the substance to which it refers. This means two different gases, which obey the original Van der Waals equation of equal molar volume have the same reduced pressure and volume, therefore, reduced temperature. Such gases are said to be in *corresponding states*.

It is desirable to characterize the degree of deviation of a real gas from ideal behavior by a single parameter. For this, the compressibility κ is chosen (where V is per mole):

$$\kappa \equiv \frac{PV}{RT}$$

The above parameter is unity for the ideal gas.

In terms of reduced properties, we have:

$$\kappa \equiv \frac{P_{Cr}V_{Cr}\pi\phi}{RT_{Cr}\theta}$$

In the above equation:

$$\frac{P_{Cr}V_{Cr}}{RT_{Cr}}\approx 3/8$$

Thus, we may write:

$$\kappa = c \frac{\pi \phi}{\theta}$$

Another means of characterizing deviation from ideality for gases is called the *Joule-Thomson Effect*, which is based on experiments run between 1852 and 1862. The Joule-Thomson coefficient is defined as the change of temperature with respect to pressure at a constant enthalpy:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_{H}$$

This coefficient refers specifically to the temperature change experienced by the gas as it passes through a porous plug, which reduces its pressure (μ_{JT} not to be confused with the symbol for chemical potential μ).

If this experiment is conducted either rapidly, or the system is insulated, virtually no heat is exchanged between the gas and its surroundings, and q = 0. Here, the work done on the gas in forcing it through the plug is P_1V_1 , so that the net work done is:

$$w = P_2 V_2 - P_1 V_1 = U_2 - U_1$$

On re-arranging, this becomes:

$$U_2 + P_2 V_2 = U_1 + P_1 V_1$$

This is equivalent to:

$$H_{2} = H_{1}$$

Applying calculus, we may re-write μ_{IT} as:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_{H} = \frac{\partial H}{\partial H}_{\partial T_{P}}$$

On a molar basis, this becomes (where *H* is per mole):

$$\mu_{JT} = -\frac{1}{c_P} \left(\frac{\partial H}{\partial P} \right)_T$$

In turn, we have (where *H*, *S* and *V* are all per mole):

$$\partial H = TdS + VdP$$

Thus, we have:

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

Moreover, we have:

$$dH = -SdT + VdP$$

So, we have:

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

Here, we define:

$$\alpha \equiv \frac{\partial V}{\partial T_P} / V$$

This is the (volume) coefficient of thermal expansion.

Finally, we have:

$$\mu_{JT} = \frac{V}{c_P} (\alpha T - 1)$$

This expression reverts to zero for the ideal gas.

Following the simplicity of the chemical potential for the ideal gas, we have:

$$\mu(P,T) = \mu^{o}(T) + RT \ln P$$

Or
$$\mu_{i}(P,T) = \mu^{o}(T) + RT \ln X_{i}P$$

It is consistent to define a new function called the fugacity (which literally means the escaping tendency) of a gas, such that:

$$\mu(P,T) = \mu^o(T) + RT \ln f(P,T)$$

The above equation has the following limit:

$$\lim_{P\to 0}\frac{f}{P}=1$$

For a real gas, we have:

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

This has the accompanying limit:

$$\lim_{P\to 0}\frac{f}{p_i}=1$$

Obviously: $f_i = p_i \Rightarrow f = P$ for the ideal gas.

The relationship between the fugacity of a gas and the compressibility factor κ is:

$$d\mu = RTd\ln f$$

But, we also have (where *V* is molar volume):

$$d\mu = V dP$$

At constant temperature:

$$RTd\ln f = VdP$$

If we subtract *RTd* ln *P* from both sides of the above equation, we get:

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

On re-arranging this equation, we have:

$$d\ln\frac{f}{P} = \left(\frac{V}{RT} - \frac{1}{P}\right)dP$$

This is:

$$d\ln\frac{f}{P} = \left(\frac{\kappa-1}{P}\right)dP$$

Integration of the above equation between the limits of P = 0 (where $\frac{f}{P} = 1$) and P = P' (where $\frac{f}{P} = \frac{f'}{P'}$) we have:

$$\ln f' = \ln P' + \int_0^{P'} \left(\frac{\kappa - 1}{P}\right) dP$$

The above equation is for a real, single-component gas. For a real gas mixture, we have:

$$\ln\left(\frac{f_i}{p_i}\right)_{P=P'} = \int_0^{P'} \left(\frac{V_i}{RT} - \frac{1}{P}\right) dP$$

BEHAVIOR OF SOLUTIONS

Ideal Solutions

KTG (HI) and statistical thermodynamics (HII) allow for a useful, albeit, simplistic visualization of equilibrium, as well as temperature and pressure. In KTG, temperature is seen as a measure of the potential or intensity of heat in a system, and a measure of the tendency for heat to leave a system not in thermal equilibrium; pressure is seen as a measure of the potential for massive movement by expansion or contraction if the system is not in mechanical equilibrium. Finally, the chemical potential of a species i in a phase is a measure of the tendency of it to leave the phase – it is a measure of the *chemical pressure* exerted by i in the phase as seen when the system is not in chemical equilibrium.

Consider a pure liquid or solid phase in equilibrium with its own vapor. The interface between these two phases is seen as a continuous flux of those molecules from the condensed phase that have sufficient kinetic energy to escape into the vapor phase, and those molecules in the vapor phase that collide with the condensed phase and are trapped through a loss of kinetic energy.

- At equilibrium, these two fluxes are equal but opposite in magnitude.
- If the vapor pressure is less than equilibrium, the rate of condensation will become less than the rate of evaporation, creating a net flux into the vapor phase, and vice versa.

If the condensed phase of Species A is diluted with another Species B, to a first approximation, the rate at which A escapes into the vapor phase is reduced in proportion to the degree by which their access to the interface is diminished.

- If Species A and B are inert to each other (i.e., in a *mechanical* mixture) this will be proportional to the relative number of A molecules, or mole fraction of A in the condensed phase X_A .
- From KTG, as the rate of collisions of gas molecules with a surface is proportional to the (partial) pressure of those molecules, the partial pressure of gaseous A in equilibrium with the molecules of B in A must be proportionally reduced:

$$p_A = k_A X_A$$

• In the limit of $X_A \rightarrow 1$ (i.e., no B), the partial pressure is that over the pure substance, which can be written as (where p_A^o is the vapor pressure of the pure substance):

$$p_A = X_A p_A^o$$

Real Solutions – Raoult and Henry's Laws

Raoult defined the concept of the *ideal solution* in terms of the relationship between the partial pressure of a component in a solution relative to the vapor pressure of the pure substance.

In the ideal solution, we have:

$$p_A = X_A p_A^o$$

The ratio of these partial pressures is called the *activity of Specie i*:

$$a_i \equiv rac{p_i}{p_i^o} = (X_i)_{ideal \ solution}$$

(It is to be noted that, more rigorously, if the gas is non-ideal, the ratio of partial pressures is replaced by the corresponding ratio of fugacities: f_i/f_i^o .)

It is intuitive to say see that as: $X_i \to 1 \Rightarrow p_i \to p_i^o$, since at $X_i = 1$, the substance is pure.

On the other extreme, such as a solution that is dilute in *i* in a solvent, experiments reveal:

$$\boldsymbol{p}_i = \boldsymbol{k}'(\boldsymbol{X}_i)_{\boldsymbol{X}_i \to \boldsymbol{0}}$$

The above equation is a statement of Henry's Law of dilute solutions.

These two very important laws in materials thermodynamics are illustrated schematically in Figure HIII.2



Figure HIII.2 – Illustration of Raoult's and Henry's Laws in terms of behavior of vapor pressure of a component in a condensed solution versus mole fraction of the component. (a) Showing positive deviation from ideal behavior; and (b) Showing negative deviation from ideal behavior.

Analysis of Figure HIII.2 reveals three possible cases.

Case I – The ideal (Raoultian) solution, where the actual vapor pressure traces the ideal line from $X_A = 0$; $X_B = 1$ to $X_B = 0$; $X_A = 1$.

Case II – The actual vapor pressure deviates positively from the line of ideality, towards a greater, positive slope.

Case III – The actual vapor pressure deviated negatively from the line of ideality, towards a lower, positive slope.

• For Case I – The ideal solution, the attraction or repulsion of A and B atoms is no greater than between like atoms. In terms on bond energies, we have for the *attractive* force between atoms:

$$A \leftrightarrow B = 1/2(A \leftrightarrow A) + 1/2(B \leftrightarrow B)$$

• For Case II – Positive departure from ideality, the attraction of A and B atoms is less than between like atoms. In terms on bond energies, we have for the *attractive* force between atoms:

$$A \leftrightarrow B < 1/2(A \leftrightarrow A) + 1/2(B \leftrightarrow B)$$

Here, the mixture of B and A acts as if the concentration of B in A is greater that it actually is, giving a greater than expected vapor pressure of B from the solution than an equivalent concentration in an ideal solution. This can be interpreted as a tendency towards repulsion. In a sense, dissimilar atoms – not so attractive to each other – show a tendency to escaping.

In the extreme – towards total repulsion of B to A - there is complete separation of A and B into separate phases (as in a mechanical mixture of pure A and pure B) at equilibrium, with complete immiscibility!

• For Case III – Negative departure from ideality, the *effective* concentration is less than that of an ideal solution at an equivalent concentration. In terms on bond energies, we have for the *attractive* force between atoms:

$$A \leftrightarrow B > 1/2(A \leftrightarrow A) + 1/2(B \leftrightarrow B)$$

This case represents a tendency toward mutual solubility, leading, in the extreme, to *compound formation*, the complete opposite to Case II.

The Thermodynamic Activity

If the vapor pressure is approximately ideal (as is typically the case in most materials applications) we have:

$$a_i \cong \frac{p_i}{p_i^o}$$

If the solution is also ideal:

$$\frac{p_i}{p_i^o} = (X_i)_{ideal \ solution}$$

Thus, we have for the ideal solution:

$$a_i = (X_i)_{ideal \ solution}$$

For a *real* solutions (including ideal solutions), at high concentrations of *i*:

$$\left[\frac{a_i}{X_i}\to 1\right]_{as\,X_i\to 1}$$

For real solutions *at extreme dilution of solute i in a solvent*, the activity of *i* is proportional to the concentration of *i*:

$$\left[\frac{a_i}{X_i} \to k\right]_{as X_i \to 0}$$

Unlike the earlier plots, we replace vapor pressure with the activity to show departure from ideality, as shown in Figure HIII.3 below.



Figure HIII.3 – Plot of the activity of component i in solution as a function of concentration, showing a positive deviation, no deviation and negative deviation from ideality. (Note that in all cases, slope k is positive, equaling unity if the solution is ideal.)

Partial Molar Quantities and The Gibbs-Duhem Equation (GDE)

The total free energy of a multi-component solution, consisting of *i* components is:

$$G' = f(P, T, n_A, n_B, \dots n_i)$$

Note that in the above equation, the prime refers to the *extensive* quantity.

When a tiny quantity δn_i of component *i* is added to the system (holding *P* and *T* constant) the total free energy changes by the amount $\delta G'$. As $\delta n_i \to 0$ in the limit, we have:

$$\lim_{\delta n_i \to 0} \left(\frac{\delta G'}{\delta n_i} \right)_{P,T,n_j} = \left(\frac{\partial G'}{\partial n_i} \right)_{P,T,n_j} = \overline{G}_i = \mu_i$$

More formally, the variation of G' with a variation of each component *i* in the solution is:

$$dG' = \left(\frac{\partial G'}{\partial n_i}\right) dn_i_{T,P,n_i \neq n_j} + \left(\frac{\partial G'}{\partial n_j}\right) dn_j_{T,P,n_i,n_k \neq n_j} + \cdots$$

The above equation is equivalent to:

$$dG' = \overline{G}_i dn_i + \overline{G}_j dn_j + \cdots$$

Thus, if \overline{G}_i is the value of G per mole of i as it occurs in solution, the value of G' for a solution of $n_i + n_j + \cdots components$ is:

$$G' = n_i \overline{G}_i + n_j \overline{G}_j + \cdots$$

Now, the complete differential of G' is:

$$dG' = n_i d\overline{G}_i + n_j d\overline{G}_j + \cdots dn_i \overline{G}_i + dn_j \overline{G}_j + \cdots$$

It is now apparent (and this applies to *any* extensive state property Q = G, V, S ...) that:

$$n_i d\overline{G}_i + n_j d\overline{G}_j = 0$$

More generally, we can state:

$$\sum_{i} n_i d\overline{G}_i = 0$$

If we divide through by $n_{tot} = \sum n_i$, we get the famous *Gibbs-Duhem Equation*:

$$\sum_{i} X_{i} d\overline{G}_{i} = 0$$
$$X_{i} = \frac{n_{i}}{n_{tot}}$$

The Gibbs-Duhem Equation (GDE) is of immense importance in determining the behavior of one component from the measurements of the behavior of the other (s) in non-ideal systems.

Relation between the Integral Moalr Free and the Partial Molar Free Energies

We already know how to express the extensive free energy of a solution in terms of the (intensive) partial molar free energies:

$$G' = n_i \overline{G}_i + n_j \overline{G}_j + \cdots$$

For a system of two components A and B, we have $n_{tot} = n_A + n_B =$ **fixed**, so we have the intensive statement of the free energy of the system as:

$$G = X_A \overline{G}_A + X_B \overline{G}_B$$

Where

$$X_A = \frac{n_A}{n_{tot}}$$
 and $X_B = 1 - X_A$

The complete differential of the above equation is:

From the GDE, we have:

$$X_A d\overline{G}_A + X_B d\overline{G}_B = 0$$

Thus:

$$dG = \overline{G}_A dX_A + \overline{G}_B dX_B$$

It is noted that that $dX_A = -dX_B$:

So, we have:

$$\frac{dG}{dX_A} = \overline{G}_A - \overline{G}_B$$

If the above equation is multiplied through by X_B , this gives:

$$X_B \frac{dG}{dX_A} = X_B \overline{G}_A - X_B \overline{G}_B$$

Now, we add the following equation to both sides:

$$G = X_A \overline{G}_A + X_B \overline{G}_B$$

This gives (noting that $X_A + X_B = 1$):

$$G + X_B \frac{dG}{dX_A} = X_A \overline{G}_A + X_B \overline{G}_A = \overline{G}_A (X_A + X_B) = \overline{G}_A$$

Thus, we get a symmetric pair of equations involving only intensive properties:

$$\overline{G}_{A} = G + X_{B} \frac{dG}{dX_{A}}$$
And
$$\overline{G}_{B} = G + X_{A} \frac{dG}{dX_{B}}$$

In the above equations, it is noted that: $X_A + X_B = 1$; $dG/dX_A = -dG/dX_B$. This relationship –between integral and partial molar free energies – can be readily understood graphically by the use of tangential intercept. This is illustrated in Figure III.4.



Figure III.4 – Illustration of the relationship between the integral and partial free energies by the use of the tangent and its intercepts in a binary system.

Why is this so important? Because – as we will see in the following handout – the equilibrium composition of two or more phases is located at the minimum positions of the integral molar free energy by a common tangent (a line in the binary system) thus expressing the equilibrium condition of equal partial molar free energies (or, chemical potentials) of all of the phases participating in the equilibrium.

For a ternary system A-B-C, where $X_A + X_B + X_C = 1$, composition is represented by an equilateral triangle. The intercept of a *tangential plane* to the integral molar free energy *surface* with the pure component axes of the compositional triangle gives the three partial molar free energies of the three components. This is illustrated in figure HII.5.



Figure HIII.5– Illustration of the relationship between the integral and partial free energies by the use of the tangent and its intercepts in a ternary system.

Relationship Between Partial Molar Free Energy and Activity

First, we need to review the free energy change due to a change in pressure:

$$dG = (VdP)_{T,fixed \ comp}$$

For an ideal gas, where *V* is molar:

$$PV = RT$$

Thus, we have:

$$dG = \frac{RT}{P}dP = RTd\ln P$$

Then, we have, on integration:

$$G(P_2, T) - G(P_1, T) = RT \ln \frac{P_2}{P_1}$$

The above equation applies in the case of vapor pressure – exerted by a component in a condensed mixture p_i compared to that exerted by the pure condensed substance p_i^o – all at constant temperature:

$$\Delta G_i = G_i(p,T) - G_i(p_i^o,T) = RT \ln \frac{p_i}{p_i^o}$$

But, we also know that:

$$\overline{G}_i - G_i^o = RT \ln \frac{p_i}{p_i^o}$$

Since, we already defined the activity in terms of the ratio of these partial pressures; viz.:

$$a_i = \frac{p_i}{p_i^o}$$

Hence, we arrive at the following important equation:

$$\overline{G}_i - G_i^o = RT \ln a_i \equiv \Delta \overline{G}_i^M$$

Or, in terms of the chemical potential
$$\mu_i - \mu_i^o = RT \ln a_i = \Delta \mu_i$$

The following notation is now introduced:

The partial molar free energy of *mixing* (M) relative to a standard state:

$$\Delta \overline{G}_i^M = \overline{G}_i - G_i^o$$

The chemical potential relative to a standard state:

$$\Delta \mu_i = \mu_i - \mu_i^o = \Delta \overline{G}_i^M$$

The chemical potential can also be referred to as the relative partial molar free energy.

Partial Molar Free Energy of the Ideal Solution

The ideal (or Raoultian) solution obeys a simple relationship with composition:

$$a_i = X_i$$

Also, we have:

$\Delta G^M = RTX_A \ln a_A + RTX_B \ln a_B$

The above equation becomes on substation in for the activity:

$$\Delta G^M = RTX_A \ln X_A + RTX_B \ln X_B$$

It is noted that the above equation is always a negative number for $X_i < 1$ because of the logarithm of a number less than unity is negative. Employing the notation of *M* for mixing, we have for the ideal solution:

$$\Delta \overline{G}_A^M = RT \ln X_A$$
And
$$\Delta \overline{G}_B^M = RT \ln X_B$$

From this equation, we can deduce the molar enthalpy and entropy of mixing for the solution relative to the pure components. Recall earlier the Gibbs-Helmholtz equation:

$$\frac{d\left(\frac{G}{T}\right)}{dT} = -\frac{H}{T^2}$$

This relation also applies to the integral, as well as the partial molar properties; viz.:

$$\frac{d\left(\frac{\Delta G^{M}}{T}\right)}{dT} = -\frac{\Delta H^{M}}{T^{2}}$$

For an ideal solution:

$$\frac{\Delta G^M}{T} = R(X_A \ln X_A + X_B \ln X_B)$$

But, we know:

$$\frac{\partial \left(R(X_A \ln X_A + X_B \ln X_B) \right)}{\partial T} = 0$$

Thus, we conclude for the *ideal solution*:

$$\Delta H^M = \mathbf{0} \text{ and } \overline{H}_i - H_i^o = \mathbf{0}$$

Since: G = H - TS, or $\Delta G = \Delta H - T\Delta S$, then we have for the ideal solution:

$$\Delta S^{M} = -R(X_{A} \ln X_{A} + X_{B} \ln X_{B})$$
With
$$\Delta \overline{S}_{A}^{M} = -R \ln X_{A}$$
And
$$\Delta \overline{S}_{B}^{M} = -R \ln X_{B}$$

The above expressions for ΔS^{M} for the ideal liquid or solid solution is due sole to *configurational entropy* – this is a measure of the increase in the number of configurations which are available to the system as a result of the mixing process (see HII).

This calculation – first encountered in HI - is reviewed below. The configurational entropy can be calculated by examining the number of distinguishing ways in which discrete particles (here, atoms) of a system can be arranged or mixed over a fixed number of positions (here, lattice sites). Consider n_A particles of A and n_B particles of B:

 $A + B(\text{unmixed}) \rightarrow A = B \text{(mixed)}$

$$\Delta S'_{conf} = k \ln \left[\frac{(n_A + n_B)!}{n_A! n_B!} \right]$$

This leads to the following equation for one mole total of atoms (where $N_{A\nu}$ is Avogadro's Number):

$$\Delta S_{conf} = \Delta S^{M}_{ideal} = -kN_{Av}(X_A \ln X_A + X_B \ln X_B)$$

Figure HIII.6 shows schematically the variation of ΔS^{M} with composition, with a maximum at 50% of Component B when the solution is ideal. Figure HIII.7 shows the effect of temperature on ΔG^{M}_{ideal} , due solely to the entropy component when the solution is ideal.



Figure HIII.6 – Plot of ideal entropy in the A-B binary system.





Real (Non-Ideal) Solutions

Departure from ideality was introduced earlier in the discussion of Henry's Law. In general, the departure of the chemical potential from ideality is quantified by the activity coefficient γ :

$$\gamma_i = \frac{a_i}{X_i}$$
where:

$$\gamma \leq 1$$

When γ_i	>1	Positive Departure	$\ln(\gamma > 1)$ is +
When γ_i	= 1	Ideal Solution	$\ln(\gamma = 1)$ is 0
When γ_i	< 1	Negative Dep.	$\ln(\gamma < 1)$ is -

We invoke the same interpretation in term of bond strength as before to understand the activity coefficient. First, we employ the Gibbs-Helmholtz equation:

$$\frac{d\left(\frac{\Delta \overline{G}_{i}^{M}}{T}\right)}{dT} = -\frac{\Delta \overline{H}_{i}^{M}}{T^{2}}$$

Since $\Delta \overline{G}_i^M = RT \ln a_i = RT \ln \gamma_i + RT \ln X_i$, we have:

$$\frac{d\left(\frac{\Delta \overline{G}_{i}^{M}}{T}\right)}{dT} = \frac{\partial (R \ln \gamma_{i})}{\partial T} = -\frac{\Delta \overline{H}_{i}^{M}}{T^{2}}$$

Since $d(1/T) = -dT/T^2$, we have:

$$\Delta \overline{H}_i^M = \frac{\partial (R \ln \gamma_i)}{\partial (1/T)}$$

What does this equation say mathematically? This is answered in Figure HIII.8.



Figure HIII.8 – Logarithm of activity coefficient versus 1/T.

The foregoing can be summarized as:

- A positive slope corresponds to $\gamma_i > 1$. This means that $\Delta \overline{H}_i^M$ is positive;
- A negative slope corresponds to $\gamma_i < 1$. This means that $\Delta \overline{H}_i^M$ is negative;
- No slope corresponds to $\gamma_i = 1$. This means that $\Delta \overline{H}_i^M$ is zero;

We can interpret the sign of $\Delta \overline{H}_i^M$ in terms of the relative bond energies, and the tendency toward repulsion or attraction.

Generally, bond energies are *negative* numbers. What determines *repulsion* or *attraction* is the relative difference on forming a solution, where, now, the difference can be positive, negative or none at all.

Case for $\gamma_i > 1$:

This is the case corresponding to a positive departure, so that both $\Delta \overline{H}_i^M$ and ΔH^M are positive:

$$A \leftrightarrow B < \frac{1}{2}(A \leftrightarrow A) + \frac{1}{2}(B \leftrightarrow B)$$

$$|H_{AB}| < \left|\frac{1}{2}(H_{AA} + H_{BB})\right|$$

$$\Delta H^{M} = H_{AB} - \frac{1}{2}(H_{AA} + H_{BB}) > 0 \Rightarrow$$

Tendency toward repulsion.

The attractive force is the absolute value of the bond energy |H|. Here, the A-A and B-B bonds 's attractive forces are a larger (negative) number than the A-B attractive force. As a result, the change is a positive number.

Case for $\gamma_i < 1$:

This is the case corresponding to a negative departure, so that both $\Delta \overline{H}_i^M$ and ΔH^M are negative:

$$A \leftrightarrow B > \frac{1}{2}(A \leftrightarrow A) + \frac{1}{2}(B \leftrightarrow B)$$
$$|H_{AB}| > \left|\frac{1}{2}(H_{AA} + H_{BB})\right|$$
$$\Delta H^{M} = H_{AB} - \frac{1}{2}(H_{AA} + H_{BB}) < 0 \Rightarrow$$

Tendency toward attraction.

The attractive force is the absolute value of the bond energy |H|. Here, the A-A and B-B bonds 's attractive forces are a smaller (negative) number than the A-B attractive force. As a result, the change is a negative number.

We have examined what determines ΔH^M , but the equilibrium lattice configuration will also depend on ΔS^M . We will now see that ΔH^M reflects a tendency toward or away from ordering, whereas ΔS reflects a tendency towards or away from random mixing.

In an absence currently of a mathematical model to describe the behavior of the solution (to be developed soon) the Gibbs-Duhem Equation (GDE) allows for determining γ for one component, based on a measures value of another (others). In this case, a mathematical model is not needed. On the other hand, with a model that describes mathematically the solution behavior, all values for γ can be calculated. Thus, a mathematical model is more powerful in that it can be used to interpolate/extrapolate among data points, once it is confirmed to adequately represent the data.

As just discussed, no assumptions are needed for application of the GDE, short of activity data for the remaining components. This involves a graphical method that employs the data directly.

In recent years much effort has been focused on developing solution models to represent the data. These can be totally empirical, semi-empirical or fundamentally based, the latter derived from statistical mechanics, but with still some *adjustable parameters*. In this handout, we will here develop an important, but simple fundamental model *the Quasi-chemical Model* (QCM).

First, however, we introduce the empirical Regular Solution Model.

The Regular Solution Model

This is technically a classification of a specific type of behavior. Its roots are empirical; it is a one-parameter model, but it is consistent with the more sophisticated QCM, and ascribes meaning to the one parameter of the model. Margules (1835) decided to express $\ln \gamma$ as a function of composition employing a power-series expansion (here for binary system A-B, where $X_A + X_B = 1$:

$$\ln \gamma_{A} = \alpha_{1}X_{B} + \frac{1}{2}\alpha_{2}X_{B}^{2} + \frac{1}{3}\alpha_{3}X_{B}^{3} + \cdots$$
$$\ln \gamma_{B} = \beta_{1}X_{A} + \frac{1}{2}\beta_{2}X_{A}^{2} + \frac{1}{3}\beta_{3}X_{A}^{3} + \cdots$$

He showed by application of the GDE:

$$X_A d \ln X_A = -X_B d \ln X_B$$

that $\alpha_1 = \beta_1 = 0$. This is an example of the power of the GDE, which imposes an internal thermodynamic consistency on the model, because the GDE it itself thermodynamic.

On limiting the power series to the first two terms (with little loss of accuracy) he found $\alpha_2 = \beta_2$. Then, Hildebrand (1929) assigned the term *regular solution* to one which obeys the simple quadratic form:

$$RT \ln \gamma_A = \alpha X_B^2$$
$$RT \ln \gamma_B = \alpha X_A^2$$

Unlike the ideal solution, $\Delta H^M \neq 0$. In the so-called *strictly* regular solution, the entropy of mixing remains ideal:

$$\Delta S^{M} = \Delta S^{M}_{ideal} = -R \sum X_{i} \ln X_{i}$$

That is, the departure from ideality in the model occurs only in the enthalpy, not the entropy of the solution.

This analytical treatment, though simple, is applicable across many systems, particular over limited composition domains within a given system. This is because in many materials systems, there is little departure in the entropy of mixing from ideality. In the absence of a validated mathematical model or data, choosing the behavior of a phase to be regular is a much better choice than choosing ideality. (Of course, at least one data point is needed to determine the value for α , or *some* knowledge of how a given system has similar characteristics to other systems for which this is known or, if the phase diagram within which the phase is stable is known, then if other critical parameters are known, α may be back-calculated from details of the equilibria in the phase diagram.)

The properties of the strictly regular solution model are best examined by removing the ideal (entropy) contribution to the (molar) free energy of mixing for analysis:

$$\Delta \boldsymbol{G} = \Delta \boldsymbol{G}^{ideal} + \Delta \boldsymbol{G}^{Excess}$$

On re-arrangement, this becomes:

$$\Delta G^{Ex} = \Delta G - \Delta G^{Id}$$

Because $\Delta H^{id} = 0$, $\Delta G^{id} = -T \Delta S^{id}$, then:

$$\Delta G^{Ex} = \Delta H^M = RT(X_A \ln \gamma_A + X_B \ln \gamma_B)$$

On substituting in for gamma, we have for the regular solution:

$$\Delta G^{Ex} = RT\alpha X_A X_B$$

It is noted that the regular solution is symmetrical in composition in its free energy. As a result, a plot of the activity curve in composition for one component is the mirror image of that for the other component in the binary system, as shown in Figure HIII.9.



Figure HIII.9 – Plot of the activity curves for the strictly regular solution.

In case of a *strictly* regular solution, $\Delta G^{Ex} = \Delta H^{Ex}$ is not a function of temperature (note that the temperature dependence for ΔG_{Reg} for a strictly regular solution is from the (ideal) entropy portion). This means:

$$RT\alpha = \alpha' \neq f(T)$$

Note that $\alpha = \alpha'/RT$.

Finally, we have:

$$\Delta \overline{G}_i^{Ex} = RT_1 \ln \gamma_1(T_1) = RT_2 \ln \gamma_2(T_2) = \alpha'(1-X_i)^2$$

Thus:

$$\left[\frac{\ln \gamma_{i,T_2}}{\ln \gamma_{i,T_1}}\right]_{Reg} = \frac{T_1}{T_2}$$

The Quasi-Chemical (QC) Model

This is the simplest fundamental model in which important atomistic factors are taken into account. As a result, the parameters of the model have meaning.

Here, the individual atom to atom bond energies are summed as a distinct parameter. This model not only predicts regular solution behavior under certain conditions, but the model also anticipates both the tendency of real solutions towards ideality as $X_i \rightarrow 1$, as well as Henrian behavior as $X_i \rightarrow 0$.

The energy of the solution is calculated by summing the short-range atom to atom bonding energies. Consider one mole of A & B atoms in a crystal (noting $X_B = 1 - X_A$):

$$X_A = \frac{n_A}{n_A + n_B} = \frac{n_A}{N_{A\nu}}$$

There are three types of bonds:

- A-A bonds, each of energy E_{AA} ;
- B-B bonds, each of energy E_{BB} ;
- A-B bonds, each of energy E_{AB} .

Energies E_{AA} , E_{BB} and E_{AB} are all negative quantities, which only approach zero when atoms are separated by an infinite distance.

Let z be the co-ordination number, so that each atom has z nearest neighbors.

In our crystal, there are:

- *P*_{AA} number of A-A bonds;
- P_{AB} number of B-B bonds;
- *P*_{*BB*} number of A-B bonds.

Thus, the crystal the total energy (per mole) is:

$E = P_{AA}E_{AA} + P_{BB}E_{BB} + P_{AB}E_{AB}$

The number of bonds P is evaluated as follows. Consider A atoms. The total number of bonds is the number of A atoms times the number of bonds containing the A atom:

Total number bonds = number of A - B bonds + 2 \cdot number of A - A bonds

Thus, we have:

$$n_A Z = P_{AB} + 2P_{AA}$$
 = number of nearest atoms between A or B

Re-arranging the above equation, we get:

$$P_{AA} = \frac{n_A Z}{2} - \frac{P_{AB}}{2}$$

Similarly, for the B atoms:

$n_B Z = P_{AB} + 2P_{BB}$ = number of nearest atoms between A or B

Or:

$$P_{BB}=\frac{n_BZ}{2}-\frac{P_{AB}}{2}$$

We now substitute for P_{AA} and P_{BB} in terms of n_A , Z and P_{AB} in our total energy:

$$E = \left(\frac{n_{A}Z}{2} - \frac{P_{AB}}{2}\right)E_{AA} + \left(\frac{n_{B}Z}{2} - \frac{P_{AB}}{2}\right)E_{BB} + P_{AB}E_{AB}$$
$$= \left\{\frac{1}{2}Zn_{A}E_{AA} + \frac{1}{2}Zn_{B}E_{BB} + P_{AB}\right\}\left\{E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})\right\}$$

It is clear that if A & B were un-mixed, then:

$$P_{AA}=\frac{1}{2}n_A Z$$

And

$$P_{BB}=\frac{1}{2}n_B$$

Thus, we have:

$$\Delta E^{M} = E_{mix} - E_{pure} = P_{AB} \left\{ E_{AB} - \frac{1}{2} \left[E_{AA} + E_{BB} \right] \right\}$$

In this model, it is assumed that volume remains constant on mixing, thus:

$$\Delta H^M = \Delta E^M - P dV \approx \Delta E^M$$

Finally, we have for the QC model:

$$\Delta H^{M} = P_{AB} \left\{ E_{AB} - \frac{1}{2} (E_{AA} + E_{BB}) \right\}$$

Obviously, the case where $\Delta H^M = 0$ corresponds to the ideal solution, where:

$$E_{AB} = \frac{E_{AA} + E_{BB}}{2}$$

Departure from ideality is summarized below:

$ E_{AB} > \frac{ E_{AA} + E_{BB} }{2}$	ΔH^M is negative	$\gamma_i < 1$
$ E_{AB} < \frac{ E_{AA} + E_{BB} }{2}$	ΔH^M is positive	$\gamma_i > 1$

Now, we want to calculate P_{AB} as a function of composition. The model assumes the same random distribution of atoms as in an ideal solution.

Consider two neighboring lattice sites, labeled 1 and 2 in our model of the A-B crystal.

The probability that Site 1 is occupied by an atom of A is:

 $\frac{\text{number of A atoms}}{\text{number of lattice sites}} = \frac{n_A}{N_{Av}} = X_A$

Similarly, the probability that Site 1 is occupied by a B atom is X_B .

The probability that Site 1 is occupied by A when Site 2 is occupied by B is also $X_A X_B$.

The reverse – the probability that Site B is occupied by B when Site 2 is occupied by A is also $X_A X_B$, thus the probability a neighboring pair of sites contain an A-B pair is $2X_A X_B$.

In a similar fashion, that two neighboring sites contain an A-A pair is X_A^2 , or contain a B-B pair is X_B^2 .

In total, there are $\frac{1}{2}Z N_{A\nu}$ pairs of sites. Thus, the total number of A-B pairs is:

number of pairs times probability of A - B pair

Or

$$P_{AB} = \frac{1}{2}Z(N_{Av})2X_A X_B = Z(N_{Av})X_A X_B$$

Similarly, we have:

And

$$P_{BB} = \frac{1}{2} Z(N_{Av}) X_B^2$$

Finally, we have ΔH^M as a function of both bond energy differences and composition:

$$\Delta H^{M} = Z(N_{Av})X_{A}X_{B}\left[E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})\right]$$

If we define:

$$\Omega = Z(N_{A\nu}) \left[E_{AB} - \frac{1}{2} (E_{AA} + E_{BB}) \right]$$

Then, we have:

$$\Delta H^{M} = \Omega X_{A} X_{B}$$
Where
$$\Omega = \alpha RT = \alpha'$$

We see that Ω from the QC model is exactly the empirical regular solution parameter αRT , but, now, we have insight into its meaning and the compositional dependency of $\Delta H^M = \alpha X_A X_B$.

We immediately see that the parabolic compositional term $X_A X_B$ arises from the probability of nearest neighboring sites being an A-B bond.

Now that we have confidence in the QC model, we want to express the partial thermodynamic properties in terms of Ω . We already know the relationship between molar and partial properties For enthalpy, we have (dropping notation *M* for molar):

$$\Delta \overline{H}_A = \Delta H + X_B \frac{d\Delta H}{dX_A}$$

And

$$\Delta \overline{H}_B = \Delta H + X_A \frac{d\Delta H}{dX_B}$$

Given the QC model, we now have:

$$\frac{\partial \Delta H}{\partial X_A} = \Omega(X_B - X_A)$$

Thus, we have:

$$\Delta \overline{H}_A = \Omega X_A X_B + X_B \Omega (X_B - X_A) = \Omega X_B^2$$

Similarly, we have:

$$\Delta \overline{H}_B = \Omega X_A^2$$

Finally, we have:

$$\Delta \overline{G}_A = \Delta \overline{H}_A - T \Delta \overline{S}_A = \Omega X_B^2 + RT \ln X_A$$

And
$$\Delta \overline{G}_B = \Delta \overline{H}_B - T \Delta \overline{S}_B = \Omega X_A^2 + RT \ln X_B$$

Also, we have:

$$\ln \gamma_A = \frac{\Delta \overline{H}_A}{RT} = \frac{\Omega}{RT} X_B^2 = \frac{\Omega}{RT} (1 - X_A)^2$$
And
$$\ln \gamma_B = \frac{\Delta \overline{H}_B}{RT} = \frac{\Omega}{RT} X_A^2 = \frac{\Omega}{RT} (1 - X_B)^2$$

Consider both Raoult's Law and Henry's Law for each component in solution AB in terms of the QC model:

For component B, Raoult's Law is satisfied by this model, since:

$$(\ln \gamma_B)_{X_B \to 1} \to 0 \Rightarrow \gamma_B \to 1$$

Henry's Law is also satisfied as follows:

$$(\ln \gamma_B)_{X_B \to 0} \to \frac{\Omega}{RT} \Rightarrow \text{a constant}$$

Generally, the equilibrium configuration of a solution is, at constant T and P, that which minimizes ΔG , where $\Delta G = \Delta H - T\Delta S$ is a measure of the effect of mixing relative to unmixed components.

It is a compromise between ΔH and ΔS . If the latter is ideal, minimization of the term $T\Delta S = T\Delta S^{ideal}$ always occurs at a 50-50 mixture, and increases to more negative values with increasing temperature.

Enthalpy ΔH opposes this entropy effect if positive, and adds to it if negative, further lowering free energy. This is illustrated in the following figures (HIII.10 (a) and (b)).



Figure HIII.10 (a) Enthalpy, entropy (multiplied by *T*) and Gibbs Free Energy changes with composition, here for ΔH being positive. (b) Same as (a), but for ΔH being negative. Note for both cases the symmetry about the 50-50 mixture.

For *real* solutions, ΔH varies in sign and magnitude, depending on the components. The entropy change is close to ideal (within experimental verification) for many alloy systems (for example, Sn-Ti) but departure can be rather significant in other systems, such as oxide systems).

In the cases where there is significant departure, it is seen as a skewing of s plot of ΔS To the right, or to the left of the 50-50 composition. *If skewed by a small amount* (especially if within the experimental error), the QC model can be used to represent the solution behavior, but, obviously, this becomes a limitation of this particular model.

In the QC model, A and B are assumed to mix randomly, yet ΔH is allowed to accommodate a tendency to cluster, or to order. This appears to be somewhat

contradictory, but it is really a question of the degree of departure of ΔS from ideality! This is discussed in greater detail below.

The critical parameters in the QC model are Ω and T, where $|\Omega|$ refers to the *bond* energy differences on mixing relative to un-mixing:

$$|E_{AB}| \leqq \frac{1}{2} |E_{AA} + E_{BB}|$$

But, $|\Omega|$ does not refer to the number of A-B pairs P_{AB} , which is assumed to be random; viz.:

$$P_{AB} = Z(N_{A\nu})X_A X_B = P_{AB}^{random}$$

If $\boldsymbol{\Omega}$ is negative, this is a tendency toward ordering of A and B (ultimately leading to compound formation, such as AB).

If Ω is a large, negative number, the greater the tendency to ordering means the actual P_{AB} should be larger than P_{AB}^{random} .

Because the actual P_{AB} is larger, the number of ways of arranging the atoms randomly on the lattice is smaller, and ΔS decreases below the random value. Higher temperatures help to maximize $T\Delta S$ to compensate for smaller ΔS values.

If $P_{AB} \gg P_{AB}^{random}$, the model is *not* applicable.

If $\boldsymbol{\Omega}$ is positive – this being a tendency towards clustering of A to A and B to B – or, phase separation. (In the extreme, this leads to complete immiscibility of A in B and B in A.)

If Ω is a large, positive number, this also means the actual P_{AB} is below P_{AB}^{random} , and ΔS , again, decreases because the number of ways to arrange the atoms on the lattice decreases below the random number. To maximize $T\Delta S$, temperature again needs to be increased. If $P_{AB} \ll P_{AB}^{random}$, again, the model is not applicable.

Application of the GDE to Determine Activity

It is very commonly the situation that data is more easily measured for one component than another.

However, a problem often exists when applying the GDE to activities, where it can be asymmetric in the composition variable X_B/X_A . This can be circumvented by working with the activity coefficient rather than the activity:

$X_A d \log \gamma_A + X_B d \log \gamma_B = \mathbf{0} \Rightarrow$

$$(\log \gamma_A)_{X_A = X_A^*} = -\int_{\log \gamma_B}^{\log \gamma_B} at X_A = X_A^* \frac{X_B}{X_A} d\log \gamma_B$$

This technique is illustrated in Figure HIII.11 (a) and (b).





A further aid in application of the GDE to obtain activity coefficient data for one component from another is to introduce the following function:

$$\alpha_i = \frac{\ln \gamma_i}{(1 - X_i)^2} \Rightarrow \ln \gamma_A = \alpha_A X_B^2 \text{ and } \ln \gamma_B = \alpha_B X_A^2$$

This function has the benefit of being finite as $\gamma_i \rightarrow 1$ when $X_i \rightarrow 1$. In this application:

$$\ln \gamma_A = -X_A X_B \alpha_B - \int_{X_A=1}^{X_A=X_A^*} \alpha_B dX_A$$

This function allows for evaluation of $\ln \gamma_A$ and α_A , given $\ln \gamma_B$ and α_B .

Note that *no assumption* has been made as to solution behavior, other than the fact that $\alpha_A X_B^2$ is empirically the second-order term of a power series expansion, where the third and higher-order terms are assumed to be insignificant. (The first-order terms are zero.) If it turns out that $\alpha_A = \alpha_B$, the solution over the composition region investigated may be considered regular!)

The GDE provides an excellent illustration of thermodynamic consistency – of Raoult's and Henry's Laws.; when the former applies for the solvent, the latter also applies for the dilute solution for the solute.

For the Henrian solution composition range for Solute B, we have:

$$a_B = k_B X_B \Rightarrow \log a_B = \log k_B + \log X_B$$

Thus, we have:

$$d\log a_B = d\log X_B$$

The GDE is for the binary system:

$$X_A d \log a_A + X_B d \log a_B = 0$$

So, we have:

$$d\log a_A = -\frac{X_B}{X_A} d\log X_B = -\frac{dX_B}{X_A} = \frac{dX_A}{X_A} = d\log X_A$$

Integration of the above equation gives:

$$\log a_A = \log X_A + \log \operatorname{constant} \therefore a_A = \operatorname{constant} \cdot X_A$$

Since, by definition $a_i = 1$ when $X_i = 1$, the constant must equal unity, regardless of the value of near unity. Thus Raoult's Law is obeyed for Solvent A when Henry's Law is obeyed for Solute B, and vice-versa.

PHASE EQUILIBRIA IN A ONE-COMPONENT SYSTEM

The remainder of this handout is devoted to phase equilibria, in the simplest – the onecomponent - system. Consideration of the one-component diagram that includes pressure stems naturally from the treatment of gases earlier in the present handout, since the equilibria includes the gas phase as a stable phase in equilibrium with condensed phases.

Portrayal of phase equilibria for the one-component system typically employs T and P as co-ordinates. Since there is no composition co-ordinate – the substance being pure – such a depiction is not normally thought of as a phase diagram. This is because the two-dimensional phase diagram normally encountered in materials involves temperature and composition, but not pressure, as variables (pressure being constant at 1 atm for most materials phase diagrams). But, multi-component phase diagram can also include pressure, as is treated in Gaskell's Chapter 14. The subsequent handout (HIV) treats two or more components.

Variation of Gibbs Free Energy With Temperature

Consider Species A undergoing a phase change, such as melting:

 $A(s) \rightarrow A(l) @ T, P$

$$\Delta G = G_{A,l} - G_{A,s} = \mathbf{0} \Rightarrow$$
$$G_{A,l} = G_{A,s}$$

For the system of solid and liquid A (where G' refers to the *extensive* Gibbs Free Energy:

$$G' - n_{A,l}G_{A,l} + n_{A,s}G_{A,s}$$

Earlier, we had:

$$dG' = -SdT + VdP + \sum \mu_i n_i$$

So that, at constant *T*,*P*:

$$G' = \mu_{A,l} n_{A,l} + \mu_{A,s} n_{A,s} \Rightarrow$$

 $G_i = \mu_i$

Above the melting point of A T_A^{mp} :

$$\boldsymbol{G}_{\boldsymbol{A},\boldsymbol{l}} - \boldsymbol{G}_{\boldsymbol{A},\boldsymbol{s}} < 0$$

The above equation indicates the system becomes unstable, and melts, in which case:

$$G_{A,l} < G_{A,s}$$

Why? Because the phase with the *lowest* free energy is the more stable phase (for example, the liquid phase is the more stable phase *above* the melting point).

Below T_A^{mp} :

$$G_{A,l} > G_{A,s}$$

This situation is shown schematically in Figure HIII.12.



Figure HIII.12 – Schematic of molar Gibbs Free Energy of pure solid and liquid with temperature (constant pressure).

Since we have:

$$dG = -SdT + VdP$$

And

$$\frac{\partial G}{\partial T_P} = -S$$

The slope of the line in Figure HIII.12 corresponds to entropy.

Now consider the curvature of the line (i.e., change in slope):

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P} = -\frac{\partial S}{\partial T_P} = -\frac{c_P}{T}$$

If we subtract the two lines from each other, we get $\Delta G_A^{s \to l} = f(T)$. This is depicted in Figure HIII.13.



Figure HIII.13 – Schematic of Gibbs Free Energy of melting of a pure material with temperature (constant pressure).

Figure HIII.13 can be summarized as:

Below T_A^{mp}	$\Delta G_A^{s \to l}$ is positive	Liquid is unstable
At T_A^{mp}	$\Delta G_A^{s \to l}$ is zero	L/S equilibrium
Above T_A^{mp}	$\Delta G_A^{s \to l}$ is negative	Solid is unstable

Since G = H - TS:

$$G_{l} = H_{l} - TS_{l}$$
And
$$G_{s} = H_{s} - TS_{s} \Rightarrow$$

$$\Delta G_{A}^{s \to l} = \Delta H_{A}^{s \to l} - T\Delta S_{A}^{s \to l}$$

To know precisely $\Delta G_A^{s \to l} = f(T)$, we must use enthalpy and entropy (via the Kirchoff Square) to evaluate $\Delta H_A^{s \to l} = f(T)$ and $\Delta S_A^{s \to l} = f(T)$. But, if we assume $c_P^l \approx c_P^s \Rightarrow \Delta c_P \approx 0$, then we have the following useful expressions:

$$\Delta G_A^{s \to l} \approx \Delta H_A^{s \to l} - \frac{T}{T^{mp}} \Delta H_A^{s \to l}$$

Or
$$\Delta G_A^{s \to l} \approx \Delta H_A^{s \to l} \left(1 - \frac{T}{T^{mp}} \right)$$

Variation of Gibbs Free Energy With Pressure

For most materials, molar volume increases on melting; not so for water, where $V^s > V^l$. From the expression dG = VdP - SdT, we have:

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = V$$



We can express this graphically in Figure HIII.14, analogous to Figure HIII.12.

Figure HIII.14 – Schematic of the Gibbs Free Energy of pure liquid and solid with pressure (constant temperature).

For the system of liquid and solid:

$$\left(\frac{\partial \Delta G^{s \to l}}{\partial P}\right)_T = \Delta V^{s \to l}$$

Gibbs Free Energy As a function of Temperature and Pressure

In consideration of Figures HIII.12-14, it is clear that equilibrium between a solid and a liquid of a pure substance could be maintained by simultaneously varying T vs. P, keeping $\Delta G^{s \rightarrow l} = 0$. The precise relationship between T and P at equilibrium can be derived, as follows.

For any infinitesimal (i.e., reversible) change in *T* and *P*:

$$dG_{l} = dG_{s}$$

$$dG_{l} = -S_{l}dT + V_{l}dP = S_{s}dT + V_{s}dP \Rightarrow$$

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{S_{s} - S_{l}}{V_{s} - V_{l}} = \frac{\Delta S^{l \to s}}{\Delta V^{l \to s}}$$

At equilibrium $\Delta H^{l \to s} = T \Delta S^{l \to s}$, thus, we get the Claperyon Equation:

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H^{l \to s}}{T \Delta V^{l \to s}}$$

The Claperyon Equation is not restricted to just to the liquid/solid equilibrium, but equilibrium between any two phases.

For all materials $\Delta H^{l \to s}$ is positive; for most materials on melting $\Delta V^{s \to l}$ is also positive, so dP/dT generally is positive. However, for water $\Delta V^{s \to l}$ is negative. Thus, for most materials, as pressure is increased, the melting point increases; for water, as pressure increases, its melting point decreases. (That is why skating on ice works – the pressure of your body weight melts and lubricates the contact area between the blade and the ice.) Figure HIII.15 shows the melting point range for pure water as a function of T and P(points *m-o*).



Figure HIII.15 – Gibbs Free Energies of pure solid and liquid water as a function of T and P.

Saturated Vapor Pressure

If the molar volume of the condensed phase (l or s) is much smaller than that of the equilibrium vapor pressure, then, without much error, we can state:

$$\Delta V \approx V_{vapor}$$

In addition, if it can be assumed that the vapor phase behaves as an ideal gas (where PV = nRT) then, the Claperyon Equation can be modified into the Clasius-Claperyon Equation:

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T\Delta V} \approx \frac{\Delta H}{TV} = \frac{P\Delta H}{RT^2} \Rightarrow$$

$$\frac{dP}{P} = \frac{\Delta H}{RT^2} dT$$

Or
$$d\ln P = \frac{\Delta H}{RT^2} dT$$

Finally, if $c_p^{vapor} \approx c_p^{condensed phase}$, then $\Delta H \neq f(T)$, so, on integration, we have:

$$\ln P = -\frac{\Delta H}{RT} + \text{constant}$$

The value of P from this equation is the *saturated vapor pressure* exerted by the condensed phase in equilibrium with the vapor phase at temperature T. In this equation, ΔH refers to the heat of evaporation.

The Phase Diagram for the One-Component System and the Gibbs Phase Rule

The effect of T and P on the solid/liquid; solid/vapor and liquid/vapor equilibria of a pure component when displayed in a plot constitutes a phase diagram for the one-component system. This phase diagram for water is shown in Figure HIII.16.



Figure HIII.16 – Log-log schematic plot of the *P-T* phase diagram for H_2O .

For the *l/s* line (i.e., *the line of saturation of the l/s equilibrium*) is calculated from the Claperyon Equation of the form:

$$P = \frac{\Delta H}{\Delta V} \ln T + constant$$

For water, $\Delta H^{l \to s}$ is generally a function of temperature, unless it is assumed that $c_P^l \approx c_P^s$.

It is seen that the intersection of all three lines of saturation occurs at a precise T and P (viz.: 0.006 atm and 0.0075 °C). This is a unique (*invariant*) point called the *triple point* (labeled O in figure HIII.16). Obviously, if only two of the lines of saturation are known/calculated, their intersection identifies the triple point, so that the third line of saturation must begin there.

This figure also illustrates what is known as a guiding principle in the construction and interpretation of phase diagrams: the *Gibbs Phase Rule* (GPR). The lines in this figure are

identified as Lines OA, OB and OC. These divide the phase diagram into three areas, within each of which only one phase is stable. This means that within any one of these domains, temperature and pressure can be varied independently, and the domain for the single phase remains stable. Thus, this particular equilibrium – the single phase domain – has two degrees of freedom, which means that the two variables of P and T can be varied independently. The lines OA, OB and OC delineate the boundaries of the single-phase domain. On any of these three boundary lines, if T or P is varied, the other must follow suit. This means that there is now only one degree of freedom. Finally, at the unique (*invariant*) triple point, there is no single variable (T or P) to be varied; it occurs at a unique value of T and P, corresponding to zero degrees of freedom.

The GPR can be stated as:

$$F = \mathbb{C} - \wp + 2$$

In the above equation, F is the degrees of freedom; \mathbb{C} is the number of components (here, equal to one) and \mathscr{P} is the number of phases participating in the equilibrium.

As an example, for the single phase region in the one-component system, $\mathcal{D} = 1$, thus F = 1 - 1 + 2 = 2; for the boundary lines, F = 1 - 2 + 2 = 1; finally, for the triple point, F = 1 - 3 + 2 = 0.

Solid/Solid Equilibria in the One-Component System

Elements that exhibit one or more crystal structures are called *alloptropic* (for compounds, it is called polymorphic). Figure HIII.17 shows the variation of the vapor pressure of pure iron with temperature, where there are three triple points: α (BCC)/ γ (FCC)/ ν ; γ (FCC)/ δ (BCC)/ ν and δ (BCC)/ l/ν . Note the slope of the α/γ equilibrium line, which is negative. This means that a decrease of V^{γ} compared to V^{α} . Likewise, the line for the γ/δ equilibrium is positive, indicating V^{δ} is greater than V^{γ} .



Figure HIII.17 – The phase diagram for pure iron

In the following figure (HIII.18), the variation of the molar Gibbs Free Energy for the BCC, FCC, liquid and vapor phases of iron are shown as a function of T, P. Here, it is seen that the slope $(\partial G/\partial T)_P = -S$ corresponding to each phase progressively increase with T. This indicates that the entropy of the solid phase at higher temperatures is larger than at lower temperatures.



Figure HIII.18 – Schematic representation of the variation of the molar Gibbs Free Energy of the BCC, FCC, liquid and vapor phases of iron with temperature at constant pressure.

Finally, back to water, the phase diagram at very high pressures and a range of temperatures from -60 to 40 °C is given in Figure HIII.19. Clearly, there are five different crystal structures for ice!



Figure HIII.19 – The *P-T* phase diagram for water, showing five crystal structures for ice.

The P-T-V Phase Diagram for the One-Component System

The phase diagram for *any* one-component system need not be restricted to just P and T as variables, but also may include molar volume V.

Earlier, we illustrated (Figure HIII.1) a version of this, showing the existence of a region of liquefaction for a gas. The *critical temperature* represents the limit of liquefaction in this diagram, and it is actually a phase diagram.

In point of fact, *any* pure substance exhibits such behavior as shown in this phase diagram for a gas, albeit, at, possibly extreme temperatures, extreme pressures, or both! So, Figure HIII.1 is reproduced here as Figure HIII.20 to represent any pure substance on a P-V plot with isotherms.



Figure HIII.20 – Isotherms in a *P-V* phase diagram of a pure substance.

So, the *P*-*T* phase diagrams shown earlier can be expanded to include *V* as a third variable, producing a 3-D phase diagram as *P*-*T*-*V* space.

Figure (HIII.21) shows such a plot (here, schematically) for a substance that contracts on melting (such as water). Also, note that the original *P-T* plot for water (Figure HIII.15) is log-log.



Figure HIII.21 – A schematic *P-V-T* phase diagram for a pure substance that contracts on melting, where θ is temperature.

The final figure (HIII.22) shows the actual 3-D plot for water, with the various differing structural form of ice, and corresponding triple points. Note that the scale here is not log-log, thus Figure HIII.16 does not directly correspond.



Figure HIII.22 – The actual *P-V-T* phase diagram for water.