Thermodynamics of Materials

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This section reviews the basic tenets of thermodynamics in application to the phase equilibria. In an open system such as a solid, that is absorbing gas, the chemical potential of the gaseous component must be equal in the gas and the solid. This establishes a critical link between the well-known properties of the gas and the properties (to be computed) of the gaseous component atoms in the solid. The equilibrium constant that relates the composition in the solid to the pressure of the gas is determined by the nature of the standard states that are chosen for two phases. These standard states are discussed at length, as they must be thoroughly understood before one can know how to put thermochemical and computational information together to determine the equilibrium constant.

1 Essential Thermodynamic Equations

It will be beneficial to review thermodynamics so as to provide a single source for the essential equations that are required to analyze the thermodynamics of mixtures. The presentation will be brief and is not meant to be more than a compilation of reference equations. However, the aim is to provide enough descriptive text so that the equations are understandable. The general approach is taken from the monograph of Kirkwood & Oppenheim [1].

The combined statements of the first and second laws of thermodynamics for an open system that can do no work other than the work of expansion, and which is dominated by bulk phases that have negligible surface area is given by

$$dE = TdS - pdV + \sum \mu_i dn_i \tag{1}$$

The symbols have their usual meaning, namely:

T = absolute temperature

S = entropy

P = pressure

V = volume

n_i = number of moles of component i

$\mu_i = \left(\dfrac{\partial E}{\partial n_i} \right)_{S,V,n\setminus n_i}$ is the chemical potential of component i, $n \setminus n_i$ means the set of all n_j, except for n_i

[1] JG Kirkwood and I Oppenheim, Chemical Thermodynamics, (McGraw-Hill, 1961).

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An intensive variable is independent of the mass of the system. These are *T*, *P*, and μ_i. Extensive variables are proportional to the mass of the system - *E, S, V*, and n_i.

Equation can be integrated holding the intensive variables fixed, to get

$$E = TS - PV + \sum \mu_i n_i \tag{2}$$

where the integration constant is seen to be zero because an empty system has no energy, volume, entropy, or mass. Now, Eq. (2) has been derived for a particular temperature, pressure, and set of chemical potentials. However, we are free to consider arbitrary changes in the state of the system once we have this equation, as nothing special was assumed about the values of the intensive variables, *i.e.*, the equation must hold for all values of those variables. Thus

$$dE = TdS - PdV - VdP + \sum \mu_i dn_i + \sum n_i d\mu_i \tag{3}$$

but Eq. (1) still holds, and on substituting it for *dE* and canceling terms, one gets

$$SdT - VdP + \sum n_i d\mu_i = 0 \tag{4}$$

which is sometimes known as Gibbs's equation 97 [2], but is most often called the Gibbs-Duhem equation. This deceptively simple equation is critically important for understanding phase equilibria and mixture thermodynamics.

It is usual to define auxiliary thermodynamic functions for convenience. The enthalpy is *H=E+PV*, the Helmholtz free energy is *A=E-TS*, and the Gibbs free energy *G* is

$$G = E + PV - TS = H - TS = \sum \mu_i n_i \tag{5}$$

where use is made of eq. (2) to provide the right-most member.

From the definition *G=E+pV-TS* one computes the differential

$$dG = dE + PdV + VdP - TdS - SdT \tag{6}$$

and substitution from eq for *dE* gives

$$dG = VdP - SdT + \sum \mu_i dn_i \tag{7}$$

These equations seem to chase their own tails, but they are all slightly different and all true.

Each of these differentials is understood to provide relations between derivatives of the functions on the left by the variables on the right. From Eq. (7) for example, one sees that $G = G(p, T, n_1, n_2, ...) = G(P, T, n)$, meaning that the Gibbs free energy is most naturally considered to be a function of the indicated variables. When viewed this way, it follows that

$$\mu = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n \setminus n_i} \qquad V = \left(\frac{\partial G}{\partial P} \right)_{T,n} \qquad S = -\left(\frac{\partial G}{\partial T} \right)_{P,n} \tag{8}$$

since for any function $F(x, y, ...)$ the differential is $dF = \left(\frac{\partial F}{\partial x} \right) dx + \left(\frac{\partial F}{\partial y} \right) dy + ...$

Furthermore, the second derivatives of a function of several variables are independent of the order of differentiation, which establishes the Euler-Maxwell relations

$$\left(\frac{\partial \mu_i}{\partial P} \right)_{T,n} = \left(\frac{\partial V}{\partial n_i} \right)_{P,T,n \setminus n_i} = \overline{V_i} \tag{9}$$

$$-\left(\frac{\partial \mu_i}{\partial T} \right)_{P,n} = \left(\frac{\partial S}{\partial n_i} \right)_{P,T,n \setminus n_i} = \overline{S_i} \tag{10}$$

that are of great use in treating mixtures. The derivatives on the right, those concerning the number of moles of substance, define the partial molar volume and partial molar entropy, denoted by the over-bar. The chemical potential in Eq. (8) is seen to be the partial molar Gibbs free energy. For a pure substance, X=n X,

[2] JW Gibbs, *The Collected Works of J. Willard Gibbs*, (Yale University Press, 1957).

where *X* is an extensive variable, so that the partial molar X for a pure substance is identically the same as the molar *X*.

2 Thermodynamics of Non-ideal Gases

The equation of state for an ideal gas is

$$V = \frac{Nk_BT}{P} \tag{11}$$

in molecular units. For a pure non-ideal gas, it is customary to add terms in powers of pressure to the hand side, so that

$$\overline{V} = \frac{RT}{P} + B_2(T)P + B_3(T)P^2 + \dots \tag{12}$$

where we've switched to molar units. Eq. (7) for constant *T* and n is just

$$d\overline{G} = d\mu = \overline{V}dP \tag{13}$$

per mole of pure gas. Add and subtract $RTdP/P$ on the right-hand side of Eq. (13) to get

$$d\mu = \left(\overline{V} - \frac{RT}{P}\right)dP + RTd\ln P \tag{14}$$

and integrate between two states, the lower labeled by * and the upper arbitrary, to get

$$\mu(P) - \mu(P^*) = \int_{P^*}^{P} \left(\overline{V} - \frac{RT}{P}\right)dP + RT\ln\frac{P}{P^*} \tag{15}$$

Note: Since *P* always appears as a ratio under the logarithm, the units are immaterial. However, in the next step, the log of the ratio is pulled apart, seemingly creating dimensions. This is only apparent, and one must keep in mind* Eq. (15) *with its ratio of pressures.*

We are now positioned to define the standard state for the gas. In asserting Eq. (12) all gases become ideal when sufficiently dilute. Rearrange the equation and take the limit as p^* goes to zero to first obtain

$$\mu(T,P) = [\mu(T,P^*) - RT\ln P^*] + RT\ln P + \int_{P}^{P^*}\overline{V} - \frac{RT}{P}dP \tag{16}$$

and then

$$\mu(T,P) = \mu^0(T) + RT\ln P + \int_{0}^{P}\left(\overline{V} - \frac{RT}{P}\right)dP \tag{17}$$

in the limit, where now

$$\mu^0(T) = \lim_{P^*\to 0}\left(\mu(T,P^*) - RT\ln P^*\right) \tag{18}$$

The temperature dependence of the chemical potential, previously omitted from consideration on suppression of the *SdT* term, is reinstated in the definition of chemical potential as a reminder that this quantity is a function of temperature in general.

Note: Note that the standard state chemical potential of the gas is a function of T alone, and is not a real state but is instead a measure of the intrinsic chemical properties of the gas apart from the equation of state properties. However, a gas at very low pressure (such as 1 Pa), is a good approximation of this standard state in most cases The standard state chemical potential of the gas, $\mu^0(T)$, is precisely what one calculates in the usual isolated molecule (gas phase) quantum statistics calculation of the free energy.

In anticipation of the chapter on chemical equilibrium, it is noted here that chemists like to keep the remaining integral in Eq. (6) under the logarithm. The fugacity, *f*, is therefore defined such that

$$\ln f = \ln P + \int_0^P \left(\frac{\overline{V}}{RT} - \frac{1}{P} \right) dP \tag{19}$$

and

$$\mu(T, P) = \mu^0(T) + RT \ln f \tag{20}$$

for all pressures. The fugacity coefficient φ, defined by $f = \varphi P$, is just

$$\Phi = \exp \left(\int_0^P \frac{\overline{V}}{RT} - \frac{1}{P} dP \right) \tag{21}$$

Substitution of the virial equation, Eq. (12) , into Eq. (21) allows one to write this as a power series in the pressure. However, the virial coefficients, the $B_i(T)$, must be determined by experiment or statistical mechanics; they are not calculable from thermodynamics alone.

It should be apparent that there is a straightforward part of thermodynamics, the *PdV* part and the entwined equation of state, *V*(*P*, *T*), that can be handled explicitly. The other part, the *TdS* term is more difficult. However, there is a piece of the entropy that we can get at this stage. Eq. (10) shows us that $S = - \left(\frac{\partial \mu}{\partial T} \right)_P$ for a pure substance. This is messy if we are going to differentiate equations (20) and (21), but for the ideal gas one gets the simple equation

$$\overline{S}_{ideal}(T, P) = \overline{S}^0(T) - R \ln P \tag{22}$$

showing that the $\ln P$ term is contributed by the entropy, not the enthalpy.

3 Thermodynamics of Ideal Solutions

A discussion of solutions, including phase equilibria, begins with Gibbs's equation [our Eq. (4)]. For a multi-component mixture at constant *T* and *P*, one has simply

$$\sum n_i d\mu_i = 0 \tag{23}$$

Divide this equation by the total number of moles of substances that comprise the mixture, $n = \sum n_i$ and define the mole fraction of component i as x_i, so that $1 = \sum \frac{n_i}{n} = \sum x_i$, and therefore

$$0 = \sum dx_i \tag{24}$$

Now Eq. (23) can be written

$$\sum_i x_i d\mu_i = 0 \tag{25}$$

What is the simplest assumption that one can make for $d\mu_i$ such that this equation is satisfied? The answer is provided by Eq. (24); simply put $d\mu_i = A \left(\frac{dx_i}{x_i} \right)$, where *A* is any constant. It follows that the simplest solution to the Gibbs-Duhem equation is provided by chemical potentials of the form

$$\mu_i = \mu_i^+ + A \ln x_i \tag{26}$$

This equation must be true for gases as well as for liquids and solids. That is sufficient to establish that $A = RT$.

Note: This quick heuristic derivation of the form of the chemical potential for a component in an ideal mixture is not intended to be rigorous. The μ_i^+ term is an integration constant, which must be allowed to be a function of any variables not explicitly integrated. For a gas mixture, the pressure is implicit in this term. To expose this dependence one asserts Dalton's law of partial pressure, $p_i = x_i p$, so that Eq. (26) becomes

$\mu_i = \mu_i^0 + RT \ln (x_i p)$. This is perfectly consistent with Eq. (18) for a pure ideal gas, i.e., $x_i = 1$, and is also consistent with Eq (26). This establishes the value of the constant A for gases, and in anticipation of equating chemical potentials for substances at equilibrium in different phases, the constant is RT for all phases.

This simple law is to mixtures what the ideal gas law is to gases, and it defines an "ideal mixture" as one with

$$\mu_i^{ideal} = \mu_i^0 + RT \ln x_i \tag{27}$$

When this equation is inserted into the right-hand side of equation we get, after a little rearrangement,

$$\Delta G_M^{ideal} = \sum n_i \left(\mu_i - \mu_i^0 \right) = RT \sum n_i \ln x_i \tag{28}$$

which is the change in Gibbs free energy on forming an ideal mixture from the specified number of moles of pure components. Since the right-hand side is directly proportional to *T*, it follows that the free energy change is entirely entropic. There is no heat of mixing for an ideal solution, nor is there a volume change (since the right-hand side of Eq. (28) is independent of pressure). To include these effects, one needs to study non-ideal mixtures.

4 Thermodynamics of Non-ideal Solutions

If a mixture of interest is non-ideal (which can only be decided by experiment or a statistical mechanical calculation), a modification of Eq. (27) that adheres to the "preservation of logarithmic function" principle asserts that the mole fraction be transformed to "activity," so that

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{29}$$

where the activity of component *i*, a_i, is a function of composition as well as *T* and *p*, in general. In applying Eq. (29) to condensed phases, both liquids, and solids, one needs a convention for the standard state. For mixtures that might span the entire range of compositions, it is convenient to choose the pure substances as standard states, so that

$$\lim_{x_i \to 1} \frac{a_i}{x_i} = 1 \quad \text{and} \quad \mu_i^0 = \lim_{x_i \to 1} \mu_i \tag{30}$$

On the other hand, if the mixtures are always relatively dilute in at least one component, the kth, the standard state for this component is most conveniently chosen to be the infinitely dilute state, so that

$$\lim_{x_k \to 0} \frac{a_k}{x_k} = 1 \quad \text{and} \quad \mu_k^0 = \lim_{x_k \to 0} [\mu_k - RT \ln x_k] \tag{31}$$

It is unfortunate that the same symbol is used for these two different standard states, as it is a trap for the unwary when consulting tabulated thermochemical data. In any event, Eq. (29) is the standard state that one wants to use to describe the solubility of a sparingly soluble gas in a metal, as will be shown in Section *Equation of Chemical Equilibrium*.

For a non-ideal mixture, one may write the analog of Eq. (29) here as

$$\Delta G_M = \sum n_i (\mu_i - \mu_i^0) = RT \sum n_i \ln a_i \tag{32}$$

This form is preferred if there is only experimental and no theoretical knowledge about the system. However, if the departures from the ideality are relatively small, it is common to retain the ideal entropy of mixing and simply add in corrections for the enthalpy of mixing and possibly also an "excess" entropy of mixing. To keep the mathematics simple, restrict attention to a binary mixture. A first approximation to non-ideality may be written

$$\Delta G_M = RT \left[n_1 \ln x_1 + n_2 \ln x_2 + B n_1 x_2 \right] \tag{33}$$

which supposes that the mixture thermodynamics is symmetric, since $n_1 x_2 = \dfrac{n_1 n_2}{n_1 + n_2}$.

Here *B* might be taken to be a (dimensionless) constant; alternatively, it may be expressed as a power series in the composition with coefficients that depend on *T* and *p*, in the same spirit as the non-ideal gas. Assuming

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the former behavior to keep this discussion simple, the chemical potential that is derived from Eq. (32) by differentiation is

$$\mu_1 - \mu_1^0 = \left(\frac{\partial \Delta G_M}{\partial n_1}\right)_{T,P,n_2} = RT\left[\ln x_1 + Bx_2^2\right] \tag{34}$$

Eq. (4) can be used to show that departure from ideality can only enter as the square or higher power of the concentration, *when pure components are the standard states*. The result in Eq. (34) is thus quite general when the Bx_2^2 term is seen as the first term in a power series for the chemical potential. Note that it is a power series in the mole fraction of the other component; it has to be this way so that the added terms go to zero as the mole fraction of the other components vanishes and component 1 becomes pure.

The behavior of the chemical potential when the dilute limit is chosen for the standard state can be much more complicated. Now one wants to write departures from ideality for the dilute solute, component 2 for this discussion, as

$$\mu_2 = \mu_2^0 + RT\ln x_2 + Cx_2^a + ... \tag{35}$$

where *a* is any positive power. This choice is made because we want the non-ideal terms to go to zero as the mole fraction of this component goes to zero. For this choice of standard state, it is not difficult to see that Eq. (4) is almost powerless in constraining the form of the departures from ideality. A case in point is provided by Debye-Huckel theory of electrolytes, for which $a = 1/2$. The flexibility in the functional form of departures from ideality for this choice of standard state has great consequences for gas solubility, as we will see.

5 Equation of Chemical Equilibrium

A very brief recapitulation of the equations of chemical equilibrium is to clarify some issues of units, where to apply non-ideality corrections, and so on. One begins by associating the components of a mixture with a chemical reaction

$$aA + bB \rightleftharpoons cC + dD \tag{36}$$

This can be written formally in a manner that is more suitable for thermodynamic analysis as

$$\sum \nu_k A_k = 0 \tag{37}$$

where the stoichiometric coefficients, ν_k, are positive for products and negative for reactants. The Gibbs free energy of the mixture, regardless of the reaction, is just

$$G = \sum n_k \mu_k \tag{38}$$

Suppose now that the system suffers a virtual displacement resulting from the reaction proceeding (virtually, either to the right or to the left). Since $dG_{T,P} = \sum_k \mu_k dn_k$ at constant *T* and *p* from Eq. (7), and since the change in the amounts of the substances are related by the chemical Eq. (37) as expressed by $dn_k = \nu_k d\lambda$, one can relate the general change in free energy to the reaction. The *progress variable* λ may have either sign, positive for the reaction to the right and negative for the reaction to the left. In any case,

$$dG_{T,P} = \sum \mu_k dn_k = \sum \nu_k \mu_k d\lambda = \Delta G_{rx} d\lambda \tag{39}$$

where the free energy change for the reaction, ΔG_{rx}, is defined by the sum of the chemical potentials with given stoichiometric coefficients, positive for products and negative for reactants. Now, if the system is at equilibrium, any virtual displacement away from equilibrium must increase the free energy (as is established by thermodynamic conditions for stability that are not considered in this report, but which may be found in the references [3]). That is, at equilibrium the free energy is at a minimum with respect to the progress variable, so that

$$\Delta G_{rx} = 0 \tag{40}$$

[3] JG Kirkwood and I Oppenheim, Chemical Thermodynamics, (McGraw-Hill, 1961).JW Gibbs, The Collected Works of J. Willard Gibbs, 1957.

Now we can proceed rapidly. Use equation (29) for the chemical potential of any component, to write

$$\Delta G_{rx} = 0 = \sum \nu_k \mu k = \sum \nu_k \left(\mu_k^0 + RT \ln a_k \right) = \Delta G_{rx}^0 + RT \ln \prod a_k^{\nu_k} \tag{41}$$

or

$$\prod a_k^{\nu_k} = \exp\left(-\frac{\Delta G_{rx}^0}{RT} \right) \tag{42}$$

with

$$\Delta G_{rx}^0 = \sum \nu_k \mu_k^0 = \Delta H_{rx}^0 - T\Delta S_{rx}^0 \tag{43}$$

For gaseous components, replace the corresponding activity by fugacity. This is the extremely important *mass action* principle of chemistry. Note that the equation is dimensionless.

Note: It is possible to define mass action ratios with dimensions, but compensating standard state terms must appear on the right of Eq. (42) to make the units balance. Specific examples should be worked through in detail, paying close attention to the definition of standard states, if there is any dimensional ambiguity.

The thermodynamics is left in this general form at this point, but the equations will be specialized to gas solubility problems later in the report. The equations above apply to any thermodynamic problem that conforms to the restrictions of the second paragraph of Section *Essential Thermodynamic Equations*, that is the only work is the work of expansion against an isotropic pressure.

The last topic for this section is the use of tabulated data to compute δG_{rx}^0. Now that we understand standard states for gases, pure substances, and infinitely dilute solutions, it should be apparent that the data that is tabulated for heats of formation, third law entropies, and free energy functions can be assembled with the use of Eq. (43) to find the free energy at any temperature that is encompassed by the tabulation. Free energies of formation are normally tabulated, for which the substance in its standard state is produced from the elements in their standard states. But for free energies of formation the temperature is referenced to 25 °C, and at this temperature the free energies of formation as well as the heats of formation of the elements in their standard states are zero. However, one will see third law entropies for the elements that are not zero in the standard state, so one must exercise care in combining free energies, enthalpies, and entropies of reactions to be certain that reference states, standard states, and arbitrarily chosen zeros of energy are treated consistently.