

Chem-131C-Lec19

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May 2017

Lecture 19 ; 5/19/17

If we want to characterize a phase transition we could look at the sharp spikes in heat capacity that occur during the transition (the temperature does not change so our heat capacity becomes ∞ during the process). When you look at a phase diagram, the lines refer to two phases in equilibrium. This equilibrium is characterized by their chemical potentials being equal ($\mu_\alpha = \mu_\beta$). If you are not in equilibrium, whatever phase dominates has the lower chemical potential. If $\mu_\alpha < \mu_\beta$ then β will spontaneously become α .

If we are working with transitions between only two phases then the change of phase 1 must become phase 2, they are linked. In this scenario it is useful to define molar quantities where we divide by n (if there are more than 2 phases it is not clear what you would divide by).

$$\begin{aligned}d\mu_\alpha &= d\mu_\beta \\d\mu &= -SdT + VdP \xrightarrow{\text{equilibrium}} \\ \mu_\alpha = \mu_\beta &\implies -S_\alpha dT + \bar{V}_\alpha dP = -S_\beta dT + \bar{V}_\beta dP \implies \\ \frac{dP}{dT} &= \frac{\Delta \bar{S}}{\Delta \bar{V}}\end{aligned}\tag{1}$$

This last equation is the slope of a line on a P, T phase diagram (along this line your chemical potentials are equal).

Chapter 24; Mixtures

We want to start considering c-component chemical systems. Our thermodynamic potentials will need to account for all of these chemical species now.

$$\begin{aligned}U(S, V, n_1, n_2, \dots, n_c) \\ A(S, V, n_1, n_2, \dots, n_c) \\ G(S, V, n_1, n_2, \dots, n_c) \\ \dots\end{aligned}\tag{2}$$

A chemical reaction is at equilibrium when the total Gibbs Energy is at a minimum wrt n_i .

Extensive Quantities

A **Homogeneous Equation** can be written mathematically as a function that obeys

$$U(\lambda S, \lambda V, \lambda n_1, \dots, \lambda n_c) = \lambda U(S, V, n_1, \dots, n_c)\tag{3}$$

In fact this is a degree = 1 Homogeneous Equation. All of our functions are factorable wrt λ . Some explicit examples of Homogeneous Equations would be $f(x,y) = ax + by$: degree 1. $f(x,y) = ax^2 + bxy + cy^2$; degree 2 (the total order of variables defines the degree in this context). Consider a derivative of our homogeneous equation (I am being lazy,

all other variables are held constant during the partial derivatives).

$$\begin{aligned}
\frac{d}{d\lambda} U(\lambda S, \lambda V, \lambda n_1, \dots, \lambda n_c) &= \frac{d}{d\lambda} \lambda U(S, V, n_1, \dots, n_c) \\
\frac{\partial U}{\partial \lambda S} \frac{\partial \lambda S}{\partial \lambda} + \frac{\partial U}{\partial \lambda V} \frac{\partial \lambda V}{\partial \lambda} + \sum_{i=1}^c \frac{\partial U}{\partial \lambda n_i} \frac{\partial \lambda n_i}{\partial \lambda} &= U(S, V, n_1, \dots, n_c) \\
S \frac{\partial U}{\partial \lambda S} + V \frac{\partial U}{\partial \lambda V} + n_i \sum_{i=1}^c \frac{\partial U}{\partial \lambda n_i} &= U(S, V, n_1, \dots, n_c) \xrightarrow{\lambda \equiv 1} \\
S \frac{\partial U}{\partial S} + V \frac{\partial U}{\partial V} + n_i \sum_{i=1}^c \frac{\partial U}{\partial n_i} &= U(S, V, n_1, \dots, n_c) \\
S(T) + V(-P) + \sum_{i=1}^c (n_i) \mu_i &= U \\
U = TS - PV + \sum_i \mu_i n_i
\end{aligned} \tag{4}$$

This last line is a very famous equation known as the **Euler Equation**. We also know that $G = U + PV - TS$, from our Fundamental Equations. To be consistent it must be true that

$$G = \sum_{i=1}^c \mu_i n_i \tag{5}$$

Consider

$$dU = TdS + SdT - PdV - VdP + \sum_i (n_i d\mu_i + \mu_i dn_i) \tag{6}$$

Before we found the fundamental equation for U to be

$$dU = TdS - PdV + \sum_i \mu_i dn_i \tag{7}$$

Thermodynamics must be consistent, therefore

$$0 = SdT - VdP + \sum_{i=1}^c n_i d\mu_i \tag{8}$$

And this realization is known as the **Gibbs Duhem Equation**.

The Gibbs Duhem Equation tells us for a constant T,P process $\sum n_i d\mu_i = 0$. If we had a 2-component system we can use this equation as a constraint.

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \tag{9}$$

Pressure Dependence

If we are interested in the pressure dependence of G and μ .

$$\begin{aligned}
dG &= -SdT + VdP \\
dG(P) &= VdP \xrightarrow{I.G.} \\
dG &= \frac{nRT}{P} dP \\
G &= G_0 + nRT \ln \left(\frac{P}{P_0} \right) \\
\mu &= \mu_0 + RT \ln \left(\frac{P}{P_0} \right)
\end{aligned} \tag{10}$$

The last line follows if we assume a 1-component system; the Euler Equation would read ($G=n\mu$).

Free Expansion; Again

If we consider a free expansion into vacuum (double the volume) for an ideal gas we know there is no Temperature change. If we have a 1 component system (n=1) then

$$\begin{aligned}\mu_i &= \mu_0 + RT \ln \frac{P_i}{P_0} \\ \mu_f &= \mu_0 + RT \ln \frac{P_f}{P_0} \\ P_f(2V_0) &= RT_0 \implies P_f = \frac{1}{2}P_i \\ \Delta\mu &= -RT \ln(2)\end{aligned}\tag{11}$$

We could also get this same result from a Fundamental Equation, we know the entropy change for this process is $R \ln(2)$.

$$\begin{aligned}\Delta\mu &= \Delta H - T\Delta S \\ \Delta\mu &= -R \ln(2)\end{aligned}\tag{12}$$