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Lecture 12 7/25/14
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A. Free Energy and Changes in Composition: The Chemical Potential

- We have thus far considered free energy changes in single component systems, i.e. free energy changes accompanying a changes in pressure of an ideal gas. But many chemical and biochemical systems are naturally composed of a number of components and the composition of such systems may change as a result of chemical reactions, physical transport, etc. In such cases we must consider how the free energy changes when compositions changes. Consider the reaction $n_A A \rightarrow n_B B$. The free energy change is given by

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_A,n_B} dP - \left(\frac{\partial G}{\partial T}\right)_{P,n_A,n_B} dT + \left(\frac{\partial G}{\partial n_A}\right)_{P,T,n_B} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{P,T,n_A} dn_B \quad (12.1)$$
$$= VdP - SdT + \mu_A dn_A + \mu_B dn_B$$

- In general

$$dG = VdP - SdT + \sum_i \mu_i dn_i \quad (12.2)$$

- The terms...

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j} \quad (12.3)$$

...are called a chemical potentials.

- The chemical potential of a pure substance is simply the molar Gibbs energy. For a pure substance:

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{P,T} = \frac{G}{n} = \overline{G} \quad (12.4)$$

- We can relate partial molar quantities using the same derivative equations that we used for thermodynamic state functions. Again for a pure substance: $\left(\frac{\partial \overline{G}}{\partial P}\right)_T = \left(\frac{\partial \mu}{\partial P}\right)_{T\,i} = \frac{V}{n} = \overline{V}$ and $\left(\frac{\partial \overline{G}}{\partial T}\right)_P = \left(\frac{\partial \mu}{\partial T}\right)_P = -\frac{S}{n} = \overline{S}$
- And the chemical potential is an exact differential so that

$$d\mu = \left(\frac{\partial \mu}{\partial T}\right)_P dT + \left(\frac{\partial \mu}{\partial P}\right)_T dP = -\overline{S}dT + \overline{V}dP \quad (12.5)$$

B. The Criterion for Equilibrium

- Equilibria are divided into three categories: mechanical, thermal, and material. We are primarily concerned with material equilibria.
- Material equilibria in turn are classified as either reaction or phase equilibria. In the former substances (i.e. reactants) are converted into other substances (i.e. products). In phase equilibria, substances are transported from one phase to another.
- Consider a system composed of a single substance partitioned into two phases α and β. The Gibbs free energy expression is

$$dG = -S^{\alpha}dT - S^{\beta}dT + V^{\alpha}dP + V^{\beta}dP + \mu^{\alpha}dn^{\alpha} + \mu^{\beta}dn^{\beta} \qquad (12.6)$$

where the chemical potential $\mu^{\alpha(or\beta)} = \left(\frac{\partial G^{\alpha(or\beta)}}{\partial n^{\alpha(or\beta)}}\right)_{\beta(or\alpha),T,P}$.

- For this closed system to be at equilibrium at constant T and P, P-V work only, we have

$$dG = 0 = \mu^{\alpha}dn^{\alpha} + \mu^{\beta}dn^{\beta} \qquad (12.7)$$

- Therefore the criterion for phase equilibrium is
- $$0 = \mu^{\alpha}dn^{\alpha} + \mu^{\beta}dn^{\beta} \qquad (12.8)$$

(dT=dP=0, closed system, P-V work only).

- The criterion for equilibrium at constant V and T is also $\mu^{\alpha}dn^{\alpha} + \mu^{\beta}dn^{\beta} = 0$.
- Suppose an amount of the substance leaves phase α and enters phase β. Then $dn^{\alpha} = -dn \text{ and } dn^{\beta} = -dn$. Then

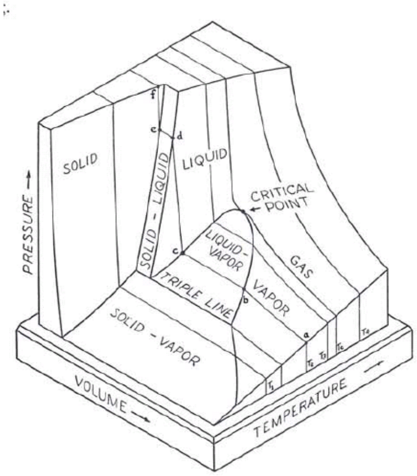
$$\mu^{\alpha}dn^{\alpha} + \mu^{\beta}dn^{\beta} = -\mu^{\alpha}dn + \mu^{\beta}dn = \left(\mu^{\beta} - \mu^{\alpha}\right)dn = 0$$
$$\therefore \mu^{\beta} = \mu^{\alpha} \qquad (12.9)$$

- The criterion for equilibrium is $\mu^{\alpha} = \mu^{\beta}$, closed system, constant P and T, P-V work only.
- If the closed system has not yet reached equilibrium $\left(\mu^{\beta} - \mu^{\alpha}\right)dn < 0$.

  Then it also follows that $\mu^{\alpha} > \mu^{\beta}$.

C. P-V-T Diagrams for One Component Systems

- For a single component system, the gas phase is the most stable phase at high temperatures and low pressures. As the temperature decreases and the pressure increases, liquid and solid phases appear. These facts are visualized in a P-V-T diagram, which displays which phases are most stable at a given P-V-T. At right is a display for a substance which



contracts in volume when it passes from the liquid to the solid state. A common example of such a case is CO_2.

- A second case is represented by a surface where the density of the solid is less than the density of the liquid, so that the volume of the system increases in passing from liquid to solid. Such a case is represented by water, where the density of ice is less than the density of liquid water. See below, right.
- The lines perpendicular to the temperature axis are isotherms. Dark lines represent equilibrium state between the two phases in contact at a particular P and T. The triple line is a condition when three phases are in contact.
- The critical point is a point beyond which gas-liquid equilibrium no longer occurs. Typically occurring at high pressures and temperatures there is a continuous transition from liquid to gas and vice versa.
- Three dimensional phase diagrams are often viewed as projections, where the solid image is collapsed onto the P-T or the P-V plane, as shown below for CO_2 and H_2O. In the P-V projection the gas phase is defined by isotherms that do not intersect a phase equilibrium. At high T and low P the gas phase is the most stable phase. At lower T, a vapor is can condense to a liquid phase or at even lower T and P a vapor can "frost" directly to a solid phase. The opposite of frosting...direct formation of a vapor from a solid... is called sublimation.

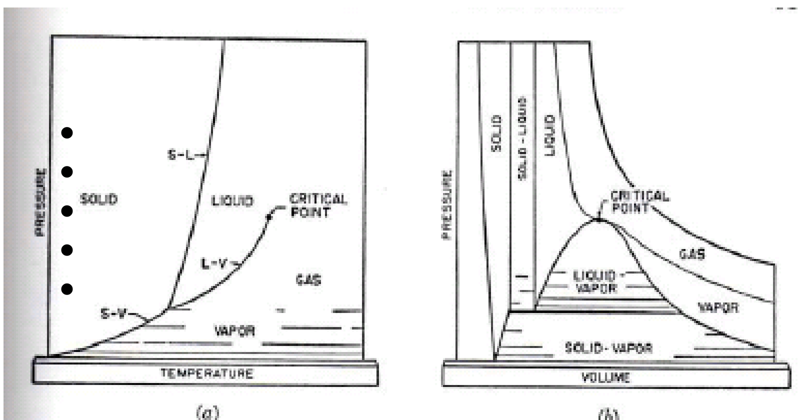


FIG. 6-3. Projections of the surface in Fig. 6-1 on the p-T and p-v planes.

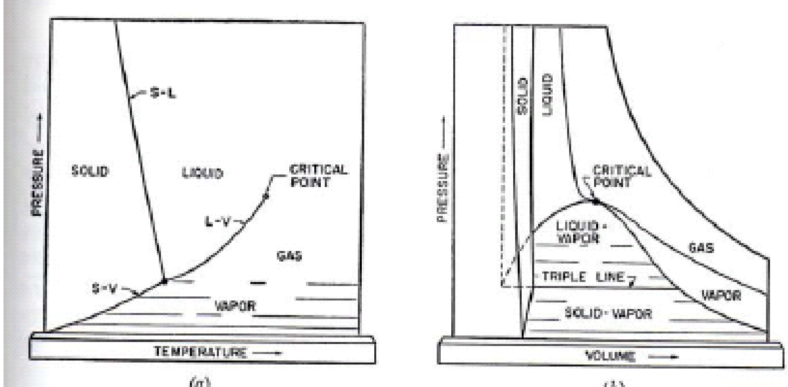


FIG. 6-4. Projections of the surface in Fig. 6-2 on the p-T and p-v planes.

- In a P-V diagram as we move along a vapor isotherm we eventually intersect a vapor-liquid equilibrium line. As the volume is further decreased into a region where vapor and liquid coexist, the isotherms become straight lines parallel to the V-T plane because the pressure has ceased to change. Within the liquid-vapor region , as the volume decreases, vapor is converted to liquid so the pressure does not change. There isotherm/isobars are called tie lines. These tie lines represent the isothermal expansions/compressions experienced by the working fluids of heat engines and refrigerators.
- Once encountering the liquid phase, even small decreases in volume require very large pressure increases, so the isotherms rise steeply. From the P-T diagrams, if the density of the solid is greater than the density of the liquid, increasing the pressure of the liquid will eventually form the solid. This is the case with CO_2. If the density of the liquid is greater than the density of the solid, increasing the pressure on the liquid will not form the solid. This is the case with water.

D. Quantifying the Equilibrium Between Two Phases

- In P-T projections, lines represent equilibria between phases. From the slopes of these lines we can obtain expression for transition enthapies and entropies.
- The slopes of these lines are quantified by the Clausius-Clapeyron equation. Recall for equilibrium between two phases α and β at a given P and T…
- $$\mu^{\alpha}\left(=\bar{G}^{\alpha}\right)=\mu^{\beta}\left(=\bar{G}^{\beta}\right) \qquad (12.10)$$

  Now if P and T are changed by a small amount, changing the chemical potentials slightly but otherwise maintaining the equilibrium we have

  $$\mu^{\alpha}+d\mu^{\alpha}=\mu^{\beta}+d\mu^{\beta} \qquad (12.11)$$
- Combining 12.10 and 12.11 we get

  $$\therefore d\mu^{\alpha}=d\mu^{\beta} \qquad (12.12).$$
- Now $d\bar{G}^{\alpha,\beta}=d\mu^{\alpha,\beta}=-\bar{S}^{\alpha,\beta}dT+\bar{V}^{\alpha,\beta}dP$ so

  $$-\bar{S}^{\alpha}dT+\bar{V}^{\alpha}dP=-\bar{S}^{\beta}dT+\bar{V}^{\beta}dP$$

  $$\therefore\frac{dP}{dT}=\frac{\bar{S}^{\alpha}-\bar{S}^{\beta}}{\bar{V}^{\alpha}-\bar{V}^{\beta}}=\frac{\Delta\bar{S}}{\Delta\bar{V}} \qquad (12.13)$$
- The process of transporting a substances between phases at equilibrium is reversible so

  $$\Delta S=\frac{\Delta H}{T}\ and\ \therefore\frac{dP}{dT}=\frac{\Delta\bar{S}}{\Delta\bar{V}}=\frac{\Delta\bar{H}}{T\Delta\bar{V}} \qquad (12.14)$$
- Equation 12.14 is called the Clausius-Clapeyron equation.

Example 1: Use the Clausius-Clapeyron equation to measures the melting temperature of water ice at P=400 atm.

Solution: A practical use of the C.-C. equation is to predict a melting point T_f at a pressure P_f above P_i=1 atm where T_i=273.15K...basically tracing out the solid-liquid equilibrium line in the P-T diagram. To do this we integrate the C.-C. equation:

$$\frac{dP}{dT} = \frac{\Delta \bar{H}}{T\Delta \bar{V}} \Rightarrow \frac{dT}{T} = \frac{\Delta \bar{V}}{\Delta \bar{H}} dP \Rightarrow \ln\left(\frac{T_f}{T_i}\right) = \frac{\Delta \bar{V}}{\Delta \bar{H}}\left(P_f - P_i\right)$$

Now at T=273.15K and P=1 atm, the densities of liquid water and ice are $\rho_{liq} = 0.9998 mL/gm \; and \; \rho_{ice} = 0.9917 mL/gm$. Note $\bar{V} = \frac{M}{\rho}$ where the specific volume is per mole and M is the molecular weight of water= 18gm/mole. The heat of fusion for water is $\Delta \bar{H} = 6010 J/mole$. Then

$$\int_{T_i=273.15K}^{T_f} \frac{dT}{T} = \frac{\Delta \bar{V}_{fusion}}{\Delta \bar{H}_{fusion}} = \frac{M\left(\frac{1}{\rho_{liq}} - \frac{1}{\rho_{ice}}\right)}{\Delta \bar{H}}\left(P_f - P_i\right)$$

$$\ln\left(\frac{T_f}{273.15K}\right) = \frac{\left(18 gm/mole\right)\left(\frac{1}{0.9998 gm/mL} - \frac{1}{0.9917 gm/mL}\right)}{6010 J/mole}\left(400atm - 1atm\right)$$

$$= \frac{\left(18gm\right)\left(-0.0903mL\right)}{6010J}\left(399atm\right)\left(0.101 J/mLatm\right) = -0.0109$$

$$\therefore T_f = \left(273.15K\right)e^{-0.0109} = 270.19K$$

- If one of the phases in equilibrium is a vapor and is treated as ideal, the Clausius-Clapeyron Equation can be simplified. There are two cases. If vapor is in equilibrium with liquid we can a vaporization equilibrium. If vapor is in equilibrium with solid we have a sublimation equilibrium.

$$\frac{dP}{dT} = \frac{\Delta \bar{H}}{T\Delta \bar{V}} = \frac{\Delta \bar{H}}{T_{vap,subl}}\left(\frac{1}{\bar{V}_{vapor} - \bar{V}_{liq,solid}}\right) \approx \frac{\Delta \bar{H}}{T_{vap,subl}\bar{V}_{vapor}}$$

- From the ideal gas law

$$\bar{V} = \frac{V}{n} = \frac{RT}{P} \Rightarrow \frac{dP}{dT} = \frac{\Delta \bar{H}}{T\bar{V}} = \frac{\Delta \bar{H} P}{RT^2}$$

$$\therefore \frac{d \ln P}{\left(-dT/T^2\right)} = \frac{d \ln P}{d\left(1/T\right)} = -\frac{\Delta \bar{H}}{R}$$

- This modification of the Clausius-Clapeyron equation is used to calculate the change in the pressure of a vapor in equilibrium with a liquid or a solid as a function of temperature. The relevant equation is obtained by integrating both sides of the equation

$$d \ln P = -\frac{\Delta \bar{H}}{R} d\left(1/T\right) \Rightarrow \int_{P_i}^{P_f} d \ln P = -\frac{1}{R} \int_{T_i}^{T_f} \Delta \bar{H} d\left(1/T\right)$$

- If the heat of fusion or sublimation is constant over the temperature range we can take it out of the temperature integration

$$\ldots \ln\left(\frac{P_f}{P_i}\right) = -\frac{\Delta \bar{H}}{R}\left(\frac{1}{T_i} - \frac{1}{T_f}\right)$$