

11/8 Lecture outline

- Last time: P, T diagram of e.g. H_2O , with the solid, liquid, and gas phases. If we plot instead a P, V diagram, we see the phase changes as plateaus, along which V changes but T and P are constant. Because P and T are fixed, the useful quantity is G . The correct phase is the one which minimizes G . Consider phases 1 and 2, e.g. liquid and gas respectively. Convert an amount δn of the material from phase 1 to phase 2, $\delta n_2 = -\delta n_1 = \delta n$. Write $G = n_1 g_1 + n_2 g_2$ (neglecting surface effects). Vary the parameters other than T and P ,

$$\delta G = -(g_1 - g_2)\delta n.$$

So the equilibrium phase boundary is when

$$g_1(T, P) = g_2(T, P).$$

Varying this, and using $s = -(\partial g / \partial T)_V$ and $v = (\partial g / \partial p)_T$, we get

$$-s_1 dT + v_1 dP = -s_2 dT + v_2 dP.$$

Write this as

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\ell}{T\delta v},$$

where ℓ is the (specific) latent heat. This is called the ‘‘Clausius-Clapeyron’’ equation.

- Example: suppose $v_2 \gg v_1$, and $Pv_2 = RT$, then the above equation becomes

$$\frac{dP}{P} = \frac{\ell dT}{RT^2},$$

which integrates to $P = P_0 \exp(-\ell/RT)$. This is the vapor pressure, which rapidly increases with T .

- Suppose

$$S = S(U, V, n_1, \dots, n_m).$$

Define the chemical potentials by

$$\mu_j \equiv -T \left(\frac{\partial S}{\partial n_j} \right)_{U, V, n_{i \neq j}}.$$

Let particle numbers vary, then

$$dU = TdS = PdV + \sum_i \mu_i dn_i.$$

Now we find

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}}, \quad T = \left(\frac{\partial U}{\partial S} \right)_{V, n_i}, \quad P = - \left(\frac{\partial U}{\partial V} \right)_{S, n_i}.$$

We similarly obtain

$$\mu_i = \left(\frac{\partial F}{\partial n_i} \right)_{T, V, n_{j \neq i}} = \left(\frac{\partial G}{\partial n_i} \right)_{P, T, n_{j \neq i}} = \left(\frac{\partial H}{\partial n_i} \right)_{P, S, n_{j \neq i}}.$$

Note that μ is an intensive quantity, since it is the ratio of extensive quantities. Also remark that often $\mu < 0$, because adding a particle, with S held fixed, requires that U be reduced.

- We have $dU = TdS - PdV + \mu_i dn_i$. Now rescale all extensive quantities by a factor of λ , and require the dU equality is preserved for all λ . This requires

$$U = TS - PV + \mu_i n_i.$$

Note that this implies that

$$G(T, P) = \sum_i \mu_i n_i \quad (!)$$

It follows that

$$\mu_i = \mu_i(T, P) = g_i(T, P),$$

so

$$\left(\frac{\partial \mu_i}{\partial T} \right)_P = -S/n \equiv -s, \quad \text{and} \quad \left(\frac{\partial \mu_i}{\partial P} \right)_T = V/n \equiv v.$$

- Consider systems 1 and 2, given by (n_1, T_1, P_1) and (n_2, T_2, P_2) . Put them in contact and remove the wall. Get

$$dS = dS_1 + dS_2 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dn \geq 0.$$

The two systems are in equilibrium with each other iff this vanishes for all variations, i.e. $T_1 = T_2$ and $P_1 = P_2$ and $\mu_1 = \mu_2$. Otherwise, get $dS > 0$. If $dU_1 > 0$, see that $T_2 > T_1$. If $dV_1 > 0$, see that $P_1/T_1 > P_2/T_2$, which for $T_1 = T_2$ gives $P_1 > P_2$. If $dn_1 > 0$, see that $\mu_1/T_1 < \mu_2/T_2$, which for $T_1 = T_2$ gives $\mu_1 < \mu_2$. Particles want to go into region of smaller chemical potential.

- Example: the atmosphere has $\mu(T, P, z) = \mu_0(T, P) + mgz$, which should be a constant for equilibrium.