10/28 Lecture outline

• Draw picture of g_1 and g_2 for fixed P as function of T.

• Open and/or multi-species systems: $S(U, V, n_i)$. Invert to write $U(S, V, n_i)$. Define μ_i from

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

This gives $T = (\partial U/\partial S)_{V,n_i}$, $P = -(\partial U/\partial V)_{S,n_i}$, and

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

which is equivalently the definition of μ_i.

• Discuss sign and interpretation of μ_i.

• Discuss H, F, and G in connection with μ_i, e.g. $\mu_i = (\partial G/\partial n_i)_{P,T,n_{k\neq i}}$.

• Use intensive property to show $E = TS - PV + \sum_i \mu_i n_i$. This implies $G(T, P, n_i) = \sum_i n_i \mu_i$. Also show $\sum_i n_i d\mu_i = VdP - SdT$. Implies $\mu_i = \mu_i(T, P) = g_i(T, P)$, and

$$\left(\frac{\partial \mu_i}{\partial T}\right)_P = -s, \qquad \left(\frac{\partial \mu_i}{\partial P}\right)_T = v.$$

• Phase equilibrium and entropy maximization: fix $U_1 + U_2$ and $V_1 + V_2$ and $n_1 + n_2$. Maximize $S = S_1(U_1, V_1, n_1) + S_2(U_2, V_2, n_2)$. So

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dn_1 \geq 0.$$

Therefore, equilibrium when $T_1 = T_2$ and $P_1 = P_2$ and $\mu_1 = \mu_2$. In approach to equilibrium, use $dS > 0$ to see which way energy, or volume, or particle numbers change, e.g. for $dU_1 = dV_1 = 0$, at $T_1 = T_2$, get $dn_1 > 0$ if $\mu_1 < \mu_2$: particles want to go to region of smaller chemical potential.