

# More on phase diagram, chemical potential, and mixing

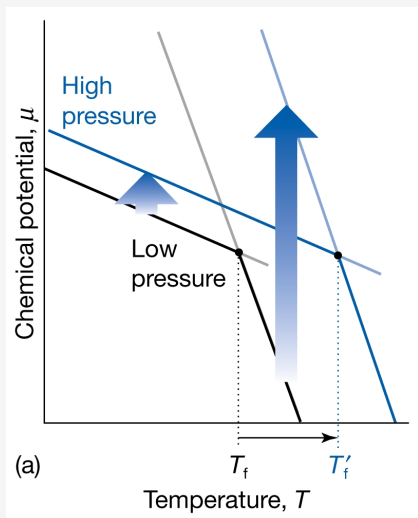
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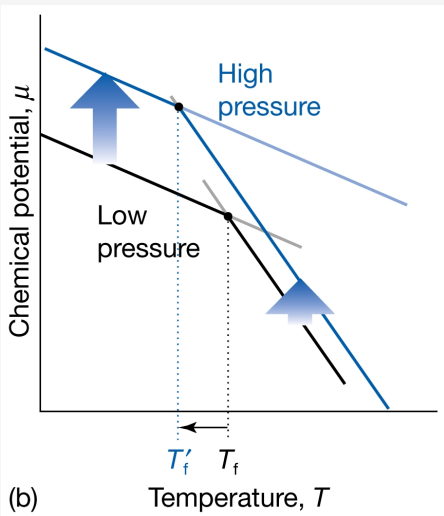
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# Melting point changes with $P$



$$\left( \frac{\partial G_\alpha}{\partial P} \right)_T = V_\alpha$$

$V > 0 \implies G_\alpha \uparrow$  when  $P \uparrow$   
 Intersection point shifts to higher  $T$  because change in  $G_{\text{sol.}}$  is less than change in  $G_{\text{liq.}}$  when  $\rho_{\text{sol.}} > \rho_{\text{liq.}}$ .

Melting point decreases if  $\rho_{\text{sol.}} < \rho_{\text{liq.}}$ .

Intersection point shifts to lower  $T$  because change in  $G_{\text{sol.}}$  is higher than change in  $G_{\text{liq.}}$  when  $\rho_{\text{sol.}} < \rho_{\text{liq.}}$ .

# System of variable composition

Consider a homogeneous phase in which there are  $k$  different substances. Let  $n_1$  be the number of moles of the substance 1 in the phase,  $n_2$  of substance 2, etc. If  $n_1, n_2, \dots, n_k$  are constant, the Gibbs energy depends only on  $S$  and  $V$ . However, for variable composition

$$G = G(T, P, n_1, n_2, \dots, n_k),$$

and thus the total differential of  $G$  is

$$dG = \left( \frac{\partial G}{\partial T} \right)_{P, n_i} dT + \left( \frac{\partial G}{\partial P} \right)_{T, n_i} dP + \sum_{i=1}^k \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_j} dn_i$$

In the first two partials the subscript  $n_i$  implies that the mole numbers of all species are constant. In the last term, the temperature and pressure are constant, **together with all but one of the mole numbers.**

# Definition of Chemical Potential

For constant mole numbers

$$dG = -SdT + VdP$$

is valid, and so we obtain

$$\left(\frac{\partial G}{\partial T}\right)_{P, n_i} = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_{T, n_i} = V$$

Let  $\mu_i$  be defined by

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

Thus we may write

$$dG = VdP - SdT + \sum_{i=1}^k \mu_i dn_i$$

# Significance of the chemical potential

The quantity  $\mu_i$ , called the chemical potential greatly facilitates the discussion of open systems, or closed ones in which there are changes of composition. The chemical potential has an important function like temperature and pressure. A temperature difference determines the tendency of heat to pass from one body to another and a pressure difference determines the tendency towards bodily movement. Similarly, **the chemical potential is the cause for a chemical reaction.**

# Chemical Potential according to Gibbs

Gibbs defined the chemical potential as

*If to any homogeneous mass we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass divided by the quantity of the substance added is the potential for that substance in the mass considered.*

In other words, according to Gibbs

$$\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_j} .$$

Would you be able to show that the Gibbs definition and our definition are the same?

# Temperature dependence of $\mu$

We are interested in

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} = \left(\frac{\partial^2 G}{\partial T \partial n_i}\right)_{P,n}$$

Because  $G$  is a state function

$$\left(\frac{\partial^2 G}{\partial T \partial n_i}\right)_{P,n} = \left(\frac{\partial^2 G}{\partial n_i \partial T}\right)_{P,n_j}$$

and as a result

$$\left(\frac{\partial^2 G}{\partial n_i \partial T}\right)_{P,n_j} = \left(\frac{\partial}{\partial n_i} \frac{\partial G}{\partial T}\right)_{T,P,n_j} = \left(\frac{\partial}{\partial n_i}(-S)\right)_{T,P,n_j} = -\bar{S}_i$$



# Pressure dependence of $\mu$

By a similar analysis as with  $T$  we can show (can you?) that

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} = \bar{V}_i$$

The temperature coefficient of  $\mu$  is the partial molar entropy,  $-\bar{S}$ , and the pressure coefficient is the partial molar volume,  $\bar{V}$ , where the partial molar properties are defined as

$$\bar{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_j}$$

# Pressure dependence of $\mu$ for ideal gas

$$d\mu = \bar{V}dP = \frac{RT}{P}dP. \quad T \text{ const.}$$

Integration from a standard state, indicated by a superscript “ $\circ$ ”, yields

$$\mu(T) = \mu^\circ(T) + RT \ln \frac{P}{P^\circ}$$

By analogy the chemical potential of a species in a mixture of ideal gases is

$$\mu_i = \mu_i^\circ + RT \ln \frac{p_i}{p_i^\circ},$$

where  $p_i$  is the partial pressure of the  $i^{\text{th}}$  species.

Note that the standard state is different at different temperatures.

# Integration of the basic equation

Enlarge the size of the system with its  $T$ ,  $P$ , and the relative proportions of components remaining unchanged. The  $\mu_i$ , which are intensive variables like  $T$  and  $P$ , remain unchanged. Integration of

$$dG = VdP - SdT + \sum_{i=1}^k \mu_i dn_i$$

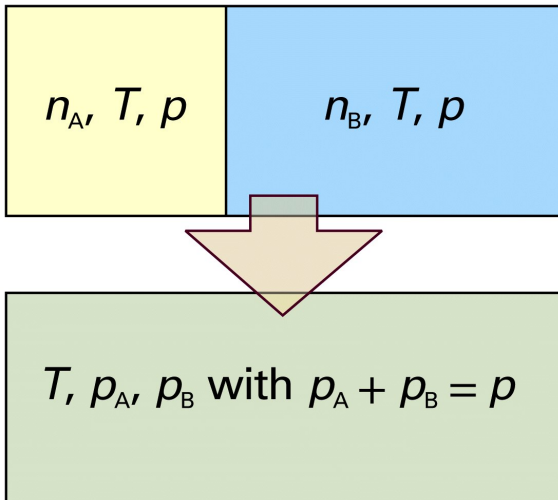
then gives

$$G = \sum_{i=1}^k \mu_i n_i.$$

This derivation depends on the “physical knowledge” that the intensive variables are not affected by the size of the system, whereas the extensive properties are directly proportional to its size.

# Mixing of gases

Consider the mixing of  $n_A$  moles  $A$  with  $n_B$  moles of  $B$ ; both at temperature  $T$  and  $P$ .

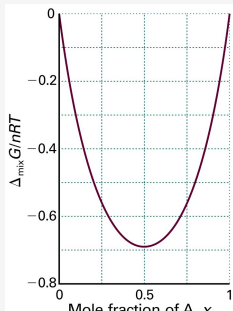


# $G$ decreases when gases are mixed

$$\Delta G_{\text{mix}} = G_f - G_i$$

$$G_f = n_A \mu_A^f + n_B \mu_B^f = n_A \mu_A^\circ + n_B \mu_B^\circ + n_A RT \ln \frac{p_A}{p^\circ} + n_B RT \ln \frac{p_B}{p^\circ}$$

$$G_i = n_A \mu_A^i + n_B \mu_B^i = n_A \mu_A^\circ + n_B \mu_B^\circ + n_A RT \ln \frac{p}{p^\circ} + n_B RT \ln \frac{p}{p^\circ}$$



$$\Delta G_{\text{mix}} = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

$$\Delta G_{\text{mix}} = n_A RT (x_A \ln x_A + x_B \ln x_B)$$