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Gibbs-Duhem Equation

From fist law:

$$dU = TdS - PdV + \mu dN$$

From Euler Relation:

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$$

Since $dU = dU$

$$SdT - VdP + Nd\mu = 0$$

Intensive Variables are Not Independent!!!

Gibbs Free Energy:

At constant pressure and temperature, the condition for equilibrium in a system is obtained by minimizing the Gibbs free energy.

$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

$$\left.\frac{\partial G}{\partial T}\right)_P = -S \quad \left.\frac{\partial^2 G}{\partial T^2}\right)_P = -\frac{-C_P}{T}$$

$$\left.\frac{\partial G}{\partial P}\right)_T = +V \quad \left.\frac{\partial^2 G}{\partial P^2}\right)_T = -\kappa_T V$$

At constant pressure and temperature:

$$dG = \sum_i \mu_i dN_i$$

Clausius-Clapeyron Equation

If two phases are at equilibrium,

$$G^\alpha = G^\beta$$

At the coexistence line, any change in the Gibbs energy of α must be matched by a corresponding change in the Gibbs energy of β:

$$dG^\alpha = dG^\beta$$

Therefore,

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

Consequently,

$$\frac{dT}{dP} = \frac{\Delta V^{\alpha \to \beta}}{\Delta S^{\alpha \to \beta}}$$

Gibbs Phase Rule

Let ϑ be the number of degrees of freedom that exist in a system with φ phases and m components. The phases are considered to be at equilibrium.

Let us calculate the number of variables that can be controlled in each phase. For each phase, there are $P, T, m-1$ variables. The total number of variables for a system of φ is given by:

$$\# \text{ var} = \varphi\,(m+1)$$

If we use the equilibrium conditions, we also have the following equations:

$$T^\alpha = T^\beta = \cdots = T^\Phi = (\varphi - 1)$$
$$P^\alpha = P^\beta = \cdots = P^\Phi = (\varphi - 1)$$
$$\mu_i^\alpha = \mu_i^\beta = \cdots = \mu_i^\Phi = (\varphi - 1)\,m$$

The total number of equations in the system is then

$$\#equ = (m+2)\,(\varphi - 1)$$

The number of degrees of freedom of the system is then given by:

$$\vartheta = \# \text{ var} - \#equ = m + 2 - \varphi$$

This is the Gibbs Phase Rule

Open Systems

Open Systems: Variables: S,V, N:

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

where

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

For the Legendre Transforms, we have:

$$H \equiv U + PV \qquad \rightarrow \qquad dH = TdS + VdP + \sum_i \mu_i dn_i$$
$$F \equiv U - TS \qquad \rightarrow \qquad dF = -SdT - PdV + \sum_i \mu_i dn_i$$
$$G \equiv U - TS + PV \qquad \rightarrow \qquad dG = -sdT + VdP + \sum_i \mu_i dn_i$$

$$\mu_i = \left.\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left.\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} = \left.\frac{\partial F}{\partial n_i}\right)_{T,V,n_j} = \left.\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

The chemical potential, μ_i has different definitions, depending on the potential. However, the definitions are equivalent, as can be seen in the previous equation.

Using the Euler Relations:

$$U = TS - PV + \sum_i \mu_i n_i$$
$$H = TS + \sum_i \mu_i n_i$$
$$F = -PV + \sum_i \mu_i n_i$$
$$G = \sum_i \mu_i n_i$$

Using First Law, and Euler Relation for the Energy, one can get the Gibbs-Duhem Equation:

$$SdT - VdP + \sum_i n_i d\mu_i = 0$$

The Gibbs-Duhem relation tells you that thermodynamic potentials in a system are not independent. A change in one of the potentials has to be accompanied by a corresponding change in the rest.

At constant temperature and pressure, the Gibbs-Duhem relation implies that, by knowing the thermodynamic behavior of one of the components, i of the system, it is possible to determine the behavior of the rest. To do this we have to do a *Gibbs-Duhem Integration*.

For a composite system, at constant pressure and temperature, (at mechanical and thermal equilibrium), the condition of equilibrium is such that the system minimizes its Gibbs free energy by changing its composition, n_i. For each component for which there is no constraint in its transfer across the composite system's internal boundaries, the equilibrium condition implies that:

$$
\begin{array}{ccccccc}
\mu_i^\alpha & = & \mu_i^\beta & = & \cdots & = & \mu_i^\phi \\
\mu_j^\alpha & = & \mu_j^\beta & = & \cdots & = & \mu_j^\phi \\
\vdots & & \vdots & & & & \vdots \\
\mu_k^\alpha & = & \mu_k^\beta & = & & = & \mu_k^\phi
\end{array}
$$

For all ϕ phases and k components.

Note that this equilibrium condition is valid, as long as the internal variables that can change are not coupled. For example, it is common that solids change their molar volume as their composition changes, so, in this case, the condition of all the chemical potential of i being equal in all phases is not the correct one.

When $\mu_i^\alpha > \mu_i^\beta$, and component i can pass across the α/β boundary, there will be a driving force for the mass flow of i, $\triangle \mu_i = \mu_i^\alpha - \mu_i^\beta$ until the system reaches an equilibrium state. $\mu_i^\beta = \mu_i^\alpha$. So $-dn_i^\alpha = dn_i^\beta$. Component i flows from the high chemical potential region to the low chemical potential region. The mass flow of i is parallel to *minus* the gradient of the chemical potential of component i.

Partial Molar Quantities
For any extensive quantity, Y, it is possible to define a corresponding partial quantity $\overline{Y_i}$:

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

Partial Pressures

When a gas is in equilibrium with a condensed phase, the activity of component i in the condensed phase is such that

$$a_i = \frac{p_i}{P_i}$$

where p_i is the partial pressure of component i in the gas mixture and P_i is the vapor pressure of i when you have a gas of pure component i over a condensed phase composed only of i.

In general,

$$a_i = \gamma_i x_i$$

where γ_i is called the activity coefficient of i.

Solutions

It is possible to define a change in the chemical potential μ_i of component i:

$$d\mu_i \left(P, T, x_i \right)_{P,T} = RT d \ln \left(a_i \right)$$

Where a_i is an *arbitrary* activity function that just makes life easier when trying to describe the thermodynamics of the system. We can integrate the previous equation on both sides, obtaining:

$$\mu_i \left(P, T, x_i \right)_{P,T} = \mu_i^* \left(P, T \right)_{P,T} + RT \ln \left(a_i \right)$$

where $\mu_i^* \left(T, P \right)$ is the reference state at the same P and T.

The standard state $\mu_i^0 \left(T, P = 1 \, atm. \right)$ is at $P = 1 \, atm..$

In general,

$$\mu_i^* - \mu_i^0 = \int_{P^0}^{P} \frac{\partial \mu_i}{\partial P} = \int_{P^0}^{P} \bar{V}_i$$

Since $\bar{V}_i \sim 0$ for condensed matter, $\mu_i^* \sim \mu_i^0$ for moderate pressures.

Problem 1

The boiling point of Li is 1620 K.

(a) What is the vapor pressure of liquid Li at 1000 K?

(b) Estimate the melting point of lithium from the data given.

Data:

Enthalpy of evaporation is 156 kJ/mol
Vapor pressure above solid Li is given by:

$$\ln(P) = 13.049 - \frac{19,314}{T}$$

Solution 1

(a) Integrate the Clausius-Clapeyron Equation

$$\frac{d\ln P^*}{d(1/T^*)} = -\frac{\Delta H}{R}$$

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

For this example, $P_1 = 1$ atm (at boiling), $T_1 = 1620K$, and $T_2 = 1000K$

$$\ln P_2 = \frac{-156,000}{8.314}\left[\frac{1}{1000} - \frac{1}{1620}\right]$$

$$P_2 = 7.6 \times 10^{-4} \text{ atm}$$

(b) At the melting point of Li, $P_{solid} = P_{liquid}$

$$13.049 - \frac{19,314}{T} = \frac{-156,000}{8.314}\left[\frac{1}{T} - \frac{1}{1620}\right]$$

$$1.47 = \frac{550.5}{T}$$

$$T = 375K$$