

Fundamental Principles and Equations for a Closed System

Ref: C H P Lupis, Chemical Thermodynamics of Materials, North-Holland, 1983, Chapter I.

Lecture 04

4. Application to the Stability of Phases for One-Component System

4.1 The Gibbs Free Energy Function

At any given temperature T and pressure P , a system is in equilibrium when it has reached the minimum value of its Gibbs free energy. Thus, the phase α is more stable than the phase β if $G^\alpha < G^\beta$.

It should, however, be noted that if $G^\alpha < G^\beta$ at any T and P , the inequality may be reversed at some other temperature T' and pressure P' . So it is important to know the temperature and pressure dependences of the Gibbs free energy of a phase.

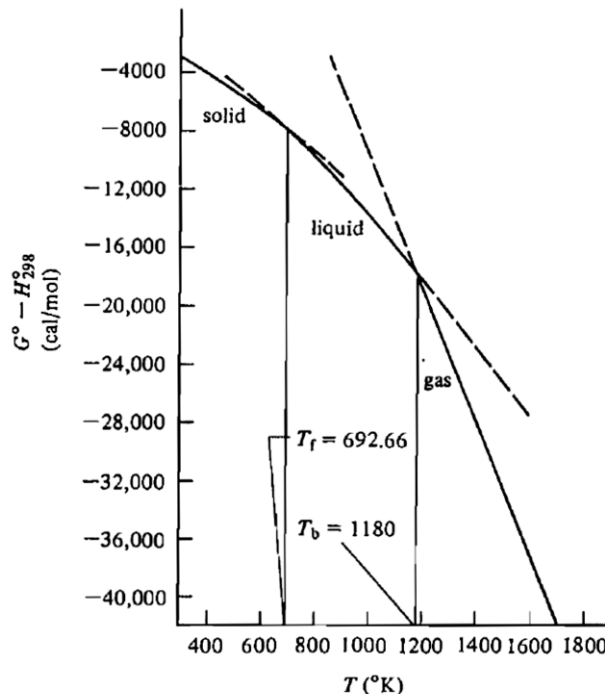
Unlike $S = S(T)$ and $H = H(T)$, the temperature dependence of G does not have any discontinuity in its values for phase transformations: at the melting point $G^s = G^l$, and at the boiling point $G^l = G^g$.

The slopes of the curves are always negative, since $dG = -SdT + VdP$, and

$$\left(\frac{\partial G}{\partial T}\right)_P = -S < 0 \quad (4.1)$$

The curvatures are negative also from the fact that

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{C_P}{T} < 0 \quad (4.2)$$



Temperature dependence of the Gibbs free energy of Zn in the solid, liquid and gas phases. The solid lines correspond to the stable phases and the dashed lines to the metastable phases.

The change in the slope of G at a transformation temperature corresponds to the ΔS of this transformation.

At any transition temperature

$$\Delta G^{\alpha \rightarrow \beta} = 0 = \Delta H^{\alpha \rightarrow \beta} - T^{\alpha \rightarrow \beta} \Delta S^{\alpha \rightarrow \beta}$$

$$\Delta H^{\alpha \rightarrow \beta} = T^{\alpha \rightarrow \beta} \Delta S^{\alpha \rightarrow \beta} \quad (4.3)$$

This expression is useful in estimating heats of melting or heats of vaporisation knowing the melting or boiling temperature, since the entropies of melting and vaporisation are often readily estimated.

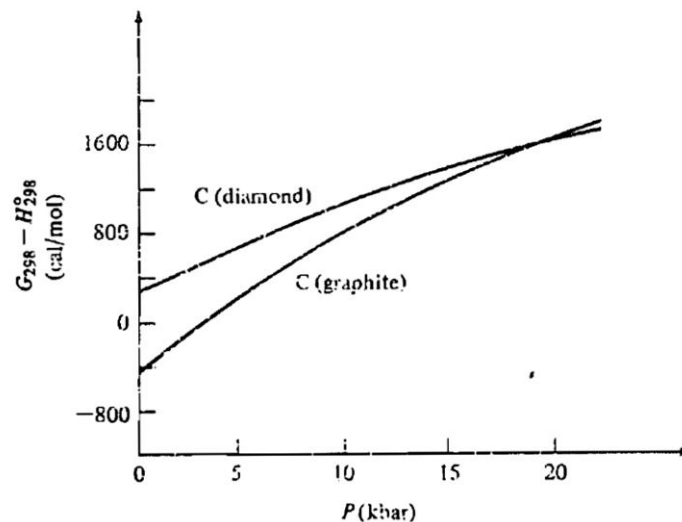
To study the pressure dependence of the Gibbs free energy, we note that

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad (4.4)$$

and

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_P = \left(\frac{\partial V}{\partial P}\right)_T = -V\beta \quad (4.5)$$

Thus, the plot G vs P shows curves of positive slope but negative curvatures. High pressures favours phases of low volumes, i.e., of high density.



Pressure dependence of Gibbs free energy of carbon in graphite and diamond structures

4.2 Clausius-Clapeyron equation

The phases α and β coexist when $G^\alpha = G^\beta$. Then it can be found that

$$\frac{dT}{dP} = \frac{\Delta V^{\alpha \rightarrow \beta}}{\Delta S^{\alpha \rightarrow \beta}} = \frac{T^{\alpha \rightarrow \beta} \Delta V^{\alpha \rightarrow \beta}}{\Delta H^{\alpha \rightarrow \beta}} \quad (4.6)$$

This is known as the Clausius-Clapeyron equation.

The value of (dT/dP) for the fusion of silver is of the order of 0.004 K/atm. The value is substantially similar for other elements. So the melting temperatures are not significantly affected by minor variations in pressure.

The changes in boiling temperatures are much larger than changes in melting temperatures since the corresponding ΔV is more than four orders of magnitude higher (V^g is 22414 cc/mol at 273 K). For example, in the case of water at $P=1$ atm, dT/dP is 28.01 K/atm.

Problem:

Determine the rate of change in melting and boiling temperatures of silver with pressure at their transformation temperatures. Given data: $T_F = 1234$ K, $T_b = 2470$ K, $V_S = 10.9$ cc/mol, $v_L = 11.3$ cc/mol, $V_G = 22414$ cc/mol at 273 K, $\Delta H^F = 2855$ cal/mol, $\Delta H^G = 61510$ cal/mol.

Solution

Fusion of Silver:

$$\begin{aligned}\frac{dT}{dP} &= \frac{T_F \Delta V^{S \rightarrow L}}{\Delta H^F} = \frac{(1234 \text{ K})(0.4 \text{ cc/mol})}{2855 \text{ cal/mol}} = 0.17 \text{ K cc/cal} \\ &= \left(0.17 \frac{\text{K cc}}{\text{cal}}\right) \left(\frac{1.987 \text{ cal}}{82.06 \text{ cc atm}}\right) = 0.004 \text{ K/atm}\end{aligned}$$

Boiling of Silver:

$$\text{Volume of silver gas at 2470 K} = \left(\frac{2470}{273}\right) \left(22414 \frac{\text{cc}}{\text{mol}}\right) = 202793 \text{ cc/mol}$$

$$\begin{aligned}\frac{dT}{dP} &= \frac{T_b \Delta V^{L \rightarrow G}}{\Delta H^G} = \frac{(2470 \text{ K})(202793 - 11.3 \text{ cc/mol})}{61510 \text{ cal/mol}} = 8142.9 \text{ K cc/cal} \\ &= \left(8142.9 \frac{\text{K cc}}{\text{atm}}\right) \left(\frac{1.987 \text{ cal}}{82.06 \text{ cc atm}}\right) = 197.2 \text{ K/atm}\end{aligned}$$

Considering $V^g \gg V^{s \text{ or } l}$, the Clausius-Clapeyron equation for $\alpha \rightarrow g$ equilibrium can be expressed as

$$\frac{dT}{dP} = \frac{T^{\alpha \rightarrow g} \Delta V^g}{\Delta H^{\alpha \rightarrow g}} = \frac{RT^2}{P \Delta H^{\alpha \rightarrow g}} \quad (4.7)$$

$$\frac{dP}{P} = \frac{\Delta H^{\alpha \rightarrow g}}{RT^2} dT \quad (4.8)$$

If we further assume that the heat of vaporisation is not a strong function of pressure and temperature, then Eq.(4.8) is easily integrated and yields

$$\ln P = \frac{\Delta H^{\alpha \rightarrow g}}{R} \left(\frac{1}{T^{\alpha \rightarrow g}} - \frac{1}{T} \right) \quad (4.9)$$

Solution to Problems
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12. The van der Waals equation of state for an imperfect gas is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

where a and b are two constants independent of temperature.

(a) Calculate the expressions of $(\partial P/\partial T)_V$, $(\partial E/\partial V)_T$, and of the coefficient of compressibility $\beta = -(1/V)(\partial V/\partial P)_T$.

(b) Assume now that $a = 0$ (in this case the equation of state sometimes bears the name of Clausius) and calculate the coefficient of thermal expansion α , $(\partial H/\partial P)_T$, and the difference $C_p - C_v = \alpha^2 TV/\beta$. For $b = 22 \text{ cm}^3$, calculate the change in the molar enthalpy (in cal) of the gas when its pressure is changed from 1 to 1000 atm.

Solution

The van der Waals equation of state of an imperfect gas is given as

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$P + \frac{a}{V^2} = \frac{RT}{V - b}$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

(a)

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b} = \frac{1}{T} \left[P + \frac{a}{V^2} \right]$$

Since $dE = TdS - PdV$,

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P$$

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad (\text{Maxwell's relation})$$

$$\left(\frac{\partial E}{\partial V}\right)_T = T \frac{1}{T} \left[P + \frac{a}{V^2} \right] - P = \frac{a}{V^2}$$

Now the given equation of state

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Differentiating this with respect to P at constant T, we get

$$(V - b) \left[1 - \frac{2a}{V^3} \left(\frac{\partial V}{\partial P}\right)_T \right] + \left(P + \frac{a}{V^2}\right) \left(\frac{\partial V}{\partial P}\right)_T = 0$$

$$\left[-(V - b) \frac{2a}{V^3} + P + \frac{a}{V^2} \right] \left(\frac{\partial V}{\partial P}\right)_T + (V - b) = 0$$

$$\left[-\frac{2a}{V^2} + \frac{2ab}{V^3} + P + \frac{a}{V^2} \right] \left(\frac{\partial V}{\partial P}\right)_T = -(V - b)$$

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{(V-b)}{P - \frac{a}{V^2} + \frac{2ab}{V^3}}$$

$$\therefore \beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = \frac{(V-b)}{V\left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right)} = \frac{(V-b)}{PV - \frac{a}{V} + \frac{2ab}{V^2}}$$

(b)

Since $a = 0$, the given equation of state becomes

$$P(V-b) = RT$$

$$V-b = \frac{RT}{P}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

Now the coefficient of thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{VP} = \frac{1}{V} \left(\frac{V-b}{T}\right)$$

$$\therefore \alpha = \frac{1}{T} \left(\frac{V-b}{V}\right) = \frac{1}{T} \left(1 - \frac{b}{V}\right)$$

Since $dH = TdS + VdP$

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P + V \quad (\text{Maxwell's relation})$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{R}{P}\right) + V = -(V-b) + V = b$$

Now, we have seen previously in (a) that

$$\beta = \frac{(V-b)}{PV - \frac{a}{V} + \frac{2ab}{V^2}}$$

Putting $a = 0$, we get

$$\beta = \frac{V-b}{PV}$$

Then

$$C_P - C_V = \frac{TV\alpha^2}{\beta}$$

$$C_P - C_V = TV \left(\frac{R}{VP}\right)^2 \left(\frac{PV}{V-b}\right) = \frac{TR^2}{P(V-b)}$$

$$C_P - C_V = \frac{TR^2}{P} \left(\frac{P}{RT}\right) = R$$

Now, given that, $b = 22$ cc. Then

$$\left(\frac{\partial H}{\partial P}\right)_T = b = 22 \text{ cc}$$

$$\therefore dH = 22 dP$$

$$\Delta H = \int_1^{100} 22 dP = 22 (100 - 1) \text{ cc-atm/mol}$$

$$\Delta H = \left(2178 \frac{\text{cc-atm}}{\text{mol-K}}\right) \left(\frac{1.987 \text{ cal}}{82.06 \text{ cc-atm}}\right) = 52.73 \text{ cal/mol}$$

14. Phase a of a species A transforms in phase b at 55 K and 1 atm. The heat capacities of A in the structures a and b are, respectively, $C_p^{0\alpha} = 2.1 \times 10^{-5} T^3$ and $C_p^{0\beta} = 5.7 \times 10^{-5} T^3$ cal/K mol. Calculate the enthalpy and entropy of transformation at 55 K and 0 K, at 1 atm.

Solution

Entropy of any substance at temperature T is

$$S_T = S_0 + \int_0^T \frac{C_p}{T} dT$$

So the change in entropy for $\alpha \rightarrow \beta$ transformation

$$\begin{aligned} \Delta S_{55}^{\alpha \rightarrow \beta} &= S_{55}^{\beta} - S_{55}^{\alpha} \\ \Delta S_{55}^{\alpha \rightarrow \beta} &= \left[S_0^{\beta} + \int_0^{55} \frac{C_p^{\beta}}{T} dT \right] - \left[S_0^{\alpha} + \int_0^{55} \frac{C_p^{\alpha}}{T} dT \right] \end{aligned}$$

Given data: $C_p^{0\alpha} = 2.1 \times 10^{-5} T^3$, $C_p^{0\beta} = 5.7 \times 10^{-5} T^3$; $S_0^{\alpha} = 0$; $S_0^{\beta} = 0$ cal/mol-K.

Then

$$\Delta S_{55}^{\alpha \rightarrow \beta} = \left[0 + \frac{5.7 \times 10^{-5}}{3} (55^3) \right] - \left[0 + \frac{2.1 \times 10^{-5}}{3} (55^3) \right] = 2.0 \text{ cal/mol-K}$$

The change in free energy for $\alpha \rightarrow \beta$ transformation

$$\begin{aligned} \Delta G^{\alpha \rightarrow \beta} = 0 &= \Delta H^{\alpha \rightarrow \beta} - T^{\alpha \rightarrow \beta} \Delta S^{\alpha \rightarrow \beta} \\ \therefore \Delta H^{\alpha \rightarrow \beta} &= T^{\alpha \rightarrow \beta} \Delta S^{\alpha \rightarrow \beta} \end{aligned}$$

Then, at 55 K, the change in enthalpy for $\alpha \rightarrow \beta$ transformation

$$\therefore \Delta H_{55}^{\alpha \rightarrow \beta} = T^{\alpha \rightarrow \beta} \Delta S^{\alpha \rightarrow \beta} = 55 (2.0) = 110.0 \text{ cal/mol}$$

Now, at 0 K,

$$\Delta S_0^{\alpha \rightarrow \beta} = S_0^{\beta} - S_0^{\alpha} = 0$$

Since $d(\Delta H) = \Delta C_p dT$ and $\Delta C_p^{\alpha \rightarrow \beta} = C_p^{\beta} - C_p^{\alpha}$,

we have

$$\begin{aligned}\Delta H_{55}^{\alpha\rightarrow\beta} &= \Delta H_0^{\alpha\rightarrow\beta} + \int_0^{55} \Delta C_P^{\alpha\rightarrow\beta} dT \\ 110.0 &= \Delta H_0^{\alpha\rightarrow\beta} + \int_0^{55} (3.6 \times 10^{-5} T^3) dT \\ \therefore \Delta H_0^{\alpha\rightarrow\beta} &= 110.0 - \frac{3.6 \times 10^{-5}}{4} (55^4) = 27.64 \text{ cal/mol}\end{aligned}$$