

12.10: Problems

1. For any change in a reversible system, we have $dG = -SdT + VdP$. Consider two systems, α and β , where system α can be converted to system β . (Below, we will let α and β be the solid and liquid phases of the same pure substance, but this is not a necessary restriction.) For incremental changes in temperature and pressure, represented by dT and dP , we have

$$dG_{\alpha} = V_{\alpha}dP - S_{\alpha}dT$$

$$\text{and } dG_{\beta} = V_{\beta}dP - S_{\beta}dT$$

We can subtract to find

$$d(G_{\beta} - G_{\alpha}) = (V_{\beta} - V_{\alpha})dP - (S_{\beta} - S_{\alpha})dT$$

or

$$d(\Delta_{\alpha \rightarrow \beta} G) = (\Delta_{\alpha \rightarrow \beta} V)dP - (\Delta_{\alpha \rightarrow \beta} S)dT$$

which we usually write as

$$d(\Delta G) = \Delta VdP - \Delta SdT$$

Here $\Delta_{\alpha \rightarrow \beta} X$ (or ΔX) is the change in the state function X that occurs when system α is converted to system β . For many interconvertible systems, it is a good approximation to say that $\Delta_{\alpha \rightarrow \beta} S$ (or ΔS) and $\Delta_{\alpha \rightarrow \beta} V$ (or ΔV) are constant for modest changes in temperature or pressure. Then, representing the pressure and temperature in the initial and final states as (P_1, T_1) and (P_2, T_2) , respectively, the **change** in $\Delta_{\alpha \rightarrow \beta} G$ (or ΔG) can be obtained by integration:

$$\int_{P_1, T_1}^{P_2, T_2} d(\Delta G) = -\Delta S \int_{T_1}^{T_2} dT + \Delta V \int_{P_1}^{P_2} dP$$

or

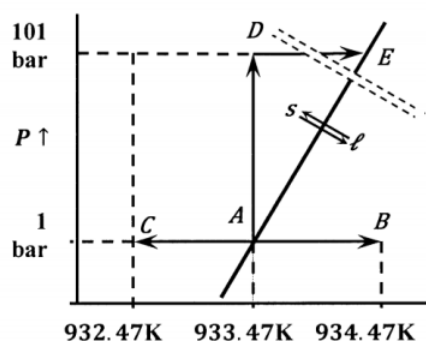
$$\Delta(\Delta G) = \Delta G(P_2, T_2) - \Delta G(P_1, T_1) = -\Delta S(T_2 - T_1) + \Delta V(P_2 - P_1)$$

Note that α and β need not be in equilibrium with one another at either the condition specified by (P_1, T_1) or that specified by (P_2, T_2) .

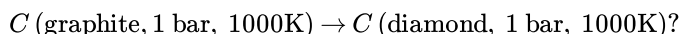
However, in the important special case that α and β are in equilibrium at (P_1, T_1) , we have $\Delta_{\alpha \rightarrow \beta} G(P_1, T_1) = \Delta G(P_1, T_1) = 0$. Then

$$\Delta(\Delta G) = \Delta G(P_2, T_2) = -\Delta S(T_2 - T_1) + \Delta V(P_2 - P_1)$$

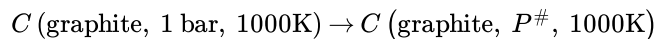
Consider the application of these observations to the case where α and β are solid and liquid aluminum metal, respectively. At one bar, aluminum melts at 933.47 K. At the melting point, the enthalpy of fusion is $\Delta_{fus} \bar{H} = +10.71 \text{ kJ mol}^{-1}$. The atomic weight of aluminum is $26.9815 \text{ g mol}^{-1}$. The density of liquid aluminum at the melting point is 2.375 g cm^{-3} ; the molar volume of the liquid is therefore $1.1361 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$. At 20 °C, the density of solid aluminum is 2.70 g cm^{-3} , and the molar volume is $0.9993 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$. Assuming the molar volume of the solid to be independent of temperature, the change in the molar volume that occurs when aluminum melts is $\Delta_{fus} \bar{V} = 1.368 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$.



- (a) What is $\Delta_{fus} \bar{V}$ at the melting point at one bar (point A on the diagram)?
- (b) Is the conversion of solid aluminum to liquid aluminum a reversible, spontaneous, or impossible process at (933.47 K, 1 bar)—that is, at point A?
- (c) What is $\Delta_{fus} \bar{S}$ at the melting point at one bar—that is, at point A?
- (d) What is $\Delta(\Delta_{fus} \bar{G})$ when the pressure and temperature go from (933.47 K, 1 bar) to (934.47 K, 1 bar)? (That is from point A to point B on the diagram.) What is $\Delta_{fus} \bar{G}$ at (934.47 K, 1 bar)?
- (e) Is the conversion of solid aluminum to liquid aluminum a reversible, spontaneous, or impossible process at (934.47 K, 1 bar)—that is, at point B?
- (f) What is $\Delta(\Delta_{fus} \bar{G})$ when the pressure and temperature go from (933.47 K, 1 bar) to (932.47 K, 1 bar)? (That is from point A to point C on the diagram.) What is $\Delta_{fus} \bar{G}$ at (932.47 K, 1 bar)?
- (g) Is the conversion of solid aluminum to liquid aluminum a reversible, spontaneous, or impossible process at (932.47 K, 1 bar)—that is, at point C?
- (h) What is $\Delta(\Delta_{fus} \bar{G})$ when the pressure and temperature go from (933.47 K, 1 bar) to (933.47 K, 101 bar)? (That is from point A to point D on the diagram.) What is $\Delta_{fus} \bar{G}$ at (933.47 K, 101 bar)?
- (i) Is the conversion of solid aluminum to liquid aluminum a reversible, spontaneous, or impossible process at (933.47 K, 101 bar)—that is, at point D?
- (j) If we maintain the pressure constant at 101 bar, how much would we have to change the temperature to just offset the change in $\Delta(\Delta_{fus} \bar{G})$ that occurred in part h? Note that this change will reach the conditions represented by point E on the diagram
- (k) Is the conversion of solid aluminum to liquid aluminum a reversible, spontaneous, or impossible process at point E?
- (l) What is $\Delta(\Delta_{fus} \bar{G})$ in going from point D (933.47 K, 101 bar) to point B (934.47 K, 1 bar)? Is this value equal to the difference between the Gibbs free energy of a mole of liquid aluminum at point B and a mole of solid aluminum at point D?
2. In the temperature interval $0.01 > t > -10$ C, the vapor pressure of water (in Pa) above pure ice is approximated by $\ln P = a + bt + ct^2$, where $a = 6.41532$, $b = 8.229 \times 10^{-2}$, $c = -3.2 \times 10^{-4}$, $t = T - 273.15$, and T is the temperature in degrees kelvin. Estimate the enthalpy of sublimation of ice at 273.15 K.
3. In the temperature interval $373.15 > T > 273.15$ K, the vapor pressure of water (in Pa) is approximated by $\ln P = a + bt + ct^2 + dt^3 + et^4$, where $a = 9.42095$, $b = 4.960 \times 10^{-2}$, $c = -1.7536 \times 10^{-4}$, $d = 6.02 \times 10^{-7}$, $e = -2.0 \times 10^{-9}$, $t = T - 323.15$, and T is the temperature in degrees kelvin. Estimate the enthalpy of vaporization of water at 323.15 K and 373.15 K.
4. The normal (1 atm) boiling point of acetone is 56.05 C. The enthalpy of vaporization at the normal boiling point is 29.10 kJ mol⁻¹. What is the entropy of vaporization of acetone at the normal boiling point? Estimate the vapor pressure of acetone at 25.0 C.
5. Two allotropic forms of tin, gray tin and white tin, are at equilibrium at 13.2 C and 1 atm. The density of gray tin is 5.769 g cm⁻³; the density of white tin is 7.265 g cm⁻³. Assume that the densities are independent of temperature. At 298.15 K and 1 bar, S° and C_P for gray tin are 44.1 J mol⁻¹ K⁻¹ and 25.8 J mol⁻¹ K⁻¹, respectively. For white tin, S° and C_P are 51.2 J mol⁻¹ K⁻¹ and 27.0 J mol⁻¹ K⁻¹, respectively. Estimate $\Delta \bar{S}$ and $\Delta \bar{V}$ for the conversion of gray tin to white tin at 13.2 C. At what temperature are gray tin and white tin at equilibrium at a pressure of 100 atm?
6. At 1000K, the standard Gibbs free energies of formation of graphite and diamond are 0.000 and +5.905 kJ mol⁻¹, respectively. At 298.15 K and 1.000 bar, the molar volumes of graphite and diamond are 5.46×10^{-6} m³ mol⁻¹ and 3.42×10^{-6} m³ mol⁻¹, respectively. Let $P^\#$ be the pressure at which graphite and diamond are at equilibrium at 1000 K.
- (a) What is the value of $\Delta \bar{G}$ for

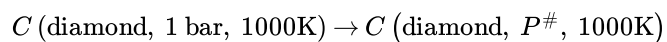


(b) Express $\Delta\bar{G}$ for



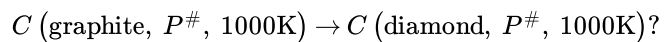
as a function of $P^\#$.

(c) Express $\Delta\bar{G}$ for



as a function of $P^\#$.

(d) What is the value of $\Delta\bar{G}$ for



(e) Assume that the molar volumes are independent of pressure and temperature. Estimate the value of the equilibrium pressure, $P^\#$.

Notes

See Robert Bruce Lindsay and Henry Margenau, *Foundations of Physics*, Dover Publications, Inc., New York, 1963, p 195.

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