

of the factor $(n - 1)$ in the exponent of the above equation, where n can be greater than 10^3 ; this resulted in explosions in the early days of polymer chemistry.

(c) The van't Hoff relation gives (approximately)

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta h^\circ}{kT^2} = \frac{(n - 1)\Delta\varepsilon_0}{kT^2},$$

so the slope of $\ln K$ versus T gets steeper as n gets larger. Hence, the formation of longer chains is more sensitive to temperature than that of shorter chains.

6. Hydrogen ionization.

A hydrogen atom can ionize in the gas phase:

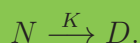


Calculate the equilibrium constant K for temperature $T = 5000$ K. There is no rotational or vibrational partition function for H, H^+ , or e^- , but there are spin partition functions: $q_s = 1$ for H^+ and $q_s = 2$ for e^- . $\Delta D = -311$ kcal mol $^{-1}$.

$$\begin{aligned} K_p &= \frac{q_{\text{H}^+} q_{e^-}}{q_{\text{H}}} e^{-\Delta\varepsilon_0/kT} \\ &= kT \frac{\left(\frac{2\pi m_{\text{H}^+} kT}{h^2}\right)^{3/2} \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} e^{-\Delta\varepsilon_0/kT}}{\left(\frac{2\pi m_{\text{H}} kT}{h^2}\right)^{3/2}} \\ &= kT \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} e^{-\Delta\varepsilon_0/kT} \\ &= \frac{(8.21 \times 10^{-5} \text{ m}^3 \text{ atm K}^{-1} \text{ mol}^{-1})(5000 \text{ K})}{6.02 \times 10^{23} \text{ molecules mol}^{-1}} \\ &\quad \left[\frac{(2\pi)(9.11 \times 10^{-31} \text{ kg})(1.38 \times 10^{-23} \text{ J K}^{-1})(5000 \text{ K})}{(6.626 \times 10^{-34} \text{ J s})^2} \right]^{3/2} e^{-311,000/9935} \\ &= (6.82 \times 10^{-25} \text{ m}^3 \text{ atm})(8.53 \times 10^{26} \text{ m}^{-3})(2.54 \times 10^{-14}) \\ &= 1.48 \times 10^{-11} \text{ atm.} \end{aligned}$$

8. Pressure denaturation of proteins.

For a typical protein, folding can be regarded as involving two states, native (N) and denatured (D):



At $T = 300 \text{ K}$, $\Delta\mu^\circ = 10 \text{ kcal mol}^{-1}$. Applying about 10,000 atm of pressure can denature a protein at $T = 300 \text{ K}$. What is the volume change Δv for the unfolding process?

We assume here that with the added 10,000 atm pressure, $K_2 = 1 \implies \Delta\mu_2^\circ = 0$. Therefore, following Example 13.8,

$$\begin{aligned} \Delta v &= v_D - v_N = -\frac{RT(\ln K_2 - \ln K_1)}{\Delta p} = -\frac{RT\left(-\frac{\Delta\mu_2^\circ}{RT} - \frac{\Delta\mu_1^\circ}{RT}\right)}{\Delta p} \\ &= -\frac{(0 + 10,000) \text{ cal mol}^{-1}}{10,000 \text{ atm}} \left(\frac{8.21 \times 10^{-5} \text{ m}^3 \text{ atm K}^{-1} \text{ mol}^{-1}}{2 \text{ cal K}^{-1} \text{ mol}^{-1}}\right) \\ &\quad \times \left(\frac{10^{10} \text{ \AA}}{1 \text{ m}}\right)^3 \left(\frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ molecules}}\right) \\ &= 68 \text{ \AA}^3 \text{ molecule}^{-1}. \end{aligned}$$

Since a protein may have about 100 amino acids, and each amino acid has a volume of about 100 \AA^3 , the volume of a protein is about 10^4 \AA^3 . Hence, Δv is a small change.

9. Clusters.

Sometimes isolated molecules of type A can be in a two-state equilibrium with a cluster of m monomers, $mA \xrightarrow{K} A_m$, where A_m represents an m -mer cluster.

- At equilibrium, what is the relationship between μ_1 , the chemical potential of the monomer, and μ_m , the chemical potential of A in the cluster?
- Express the equilibrium constant K in terms of the partition functions.

(a) Use Equation (13.15) of the text with $a = m$, $b = 0$, $c = 1$ to get $\mu_m = m\mu_1$

(b) Equation (13.17) gives $K = \left(\frac{q_m}{q_1^m}\right) e^{-\Delta\epsilon_0/kT}$.

Chapter 14

Phase Equilibria

1. Applying the Clausius–Clapeyron equation.

- (a) The vapor pressure of water is 23 mmHg at $T = 300$ K and 760 mmHg at $T = 373$ K. Calculate the enthalpy of vaporization Δh_{vap} .
- (b) Assuming that each water has $z = 4$ nearest neighbors, calculate the interaction energy w_{AA} .

$$\begin{aligned} \text{(a)} \quad \ln\left(\frac{p_2}{p_1}\right) &= -\frac{\Delta h_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ &\Rightarrow \frac{\ln\left(\frac{760}{23}\right)}{\left(\frac{1}{373} - \frac{1}{300}\right)} (1.987 \text{ cal mol}^{-1}) = -\Delta h_{\text{vap}} \\ &\Rightarrow \Delta h_{\text{vap}} = 10.653 \text{ kcal mol}^{-1} \end{aligned}$$

(b) Since

$$\begin{aligned} -\frac{zw}{2} &= \Delta h_{\text{vap}}, \\ w &= -\frac{\Delta h_{\text{vap}}}{2} \approx -5.3 \text{ kcal mol}^{-1}. \end{aligned}$$

8. Sublimation of graphite.

The heat of sublimation of graphite is $\Delta h_{\text{sub}} = 716.7 \text{ kJ mol}^{-1}$. Use this number to estimate the strength of a carbon–carbon bond.

Equation (14.22) of the text applies to sublimation as well as to vaporization, so

$$\Delta h_{\text{sub}} = -\frac{zw_{AA}}{2}.$$

In graphite, carbon is in the sp^2 hybridization state, with three bonds and a delocalized π bond. For simplicity, we take $z = 4$ neighbors, so

$$w_{AA} = -\frac{\Delta h_{\text{sub}}}{2} = -358.35 \text{ kJ mol}^{-1} = -85.6 \text{ kcal mol}^{-1}$$

The experimental value of a C–C single bond is -342 kJ mol^{-1} , but it can typically vary from about -300 to -400 kJ mol^{-1} , depending on neighboring bond substituent effects.

9. Surface tension of mercury.

The surface tension of water is 72 erg cm^{-2} and that of liquid mercury is 487 erg cm^{-2} . If the water–water attraction is about 5 kcal mol^{-1} , what is the mercury–mercury attraction?

$$\begin{aligned} \frac{w_{AA_2}}{w_{AA_1}} &= \frac{\gamma_2}{\gamma_1} \\ \implies w_{AA_{\text{Hg}}} &= \left(\frac{487}{72}\right)(5 \text{ kcal mol}^{-1}) = 33 \text{ kcal mol}^{-1}. \end{aligned}$$

10. Squeezing ice.

Use the Clapeyron relation to compute the pressure that is required to lower the melting temperature of ice by 10 K. For water, $\Delta h = 6.008 \text{ kJ mol}^{-1}$ and $\Delta v = -1.64 \text{ cm}^3 \text{ mol}^{-1}$.

$$\begin{aligned} \int_{P_1}^{P_2} dP &= \frac{\Delta h}{\Delta v} \int_{T_1}^{T_2} \frac{dT}{T}, \\ P_2 &= P_1 + \frac{\Delta h}{\Delta v} \ln\left(\frac{T_2}{T_1}\right). \end{aligned}$$

The melting temperature of water at 1 atm is 273.15 K.

$$\begin{aligned} P_2 &= 1.013 \times 10^5 \text{ Pa} + \frac{6.008 \times 10^3 \text{ J}}{-1.64 \times 10^{-6} \text{ m}^3} \ln\left(\frac{263.15}{273.15}\right), \\ P_2 &= 1.366 \times 10^8 \text{ Pa} \left(\frac{1 \text{ atm}}{1.013 \times 10^5 \text{ Pa}}\right) = 1348 \text{ atm} = 0.137 \text{ kJ cm}^{-3}. \end{aligned}$$