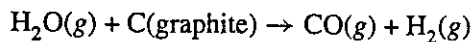


1. At one time, the gas used for cooking, called "water gas," was prepared as follows:



From the thermodynamic quantities listed in Appendix B, predict whether this reaction will occur at 298 K. If not, at what temperature will the reaction occur? Assume  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  are temperature independent.

*favor products*

The sign of  $\Delta_r G^\circ$  is used to determine if the reaction is ~~spontaneous~~ *favours products* when the reactants and products are in their standard states. If  $\Delta_r G^\circ$  is calculated via  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$ , the dependence of this quantity on temperature can also be assessed.

$$\begin{aligned}\Delta_r H^\circ &= \Delta_f \bar{H}^\circ [\text{CO}(g)] + \Delta_f \bar{H}^\circ [\text{H}_2(g)] - \Delta_f \bar{H}^\circ [\text{H}_2\text{O}(g)] - \Delta_f \bar{H}^\circ [\text{C}(\text{graphite})] \\ &= -110.5 \text{ kJ mol}^{-1} + 0 \text{ kJ mol}^{-1} - (-241.8 \text{ kJ mol}^{-1}) - 0 \text{ kJ mol}^{-1} \\ &= 131.3 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r S^\circ &= \bar{S}^\circ [\text{CO}(g)] + \bar{S}^\circ [\text{H}_2(g)] - \bar{S}^\circ [\text{H}_2\text{O}(g)] - \bar{S}^\circ [\text{C}(\text{graphite})] \\ &= 197.9 \text{ J K}^{-1} \text{ mol}^{-1} + 130.6 \text{ J K}^{-1} \text{ mol}^{-1} - 188.7 \text{ J K}^{-1} \text{ mol}^{-1} - 5.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 134.1 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = 131.3 \text{ kJ mol}^{-1} - (298 \text{ K}) (134.1 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) = 91.3 \text{ kJ mol}^{-1}$$

Since  $\Delta_r G^\circ > 0$ , the reaction is not spontaneous when all the reactants and products are in their standard states and at 298 K. The reaction is spontaneous when  $\Delta_r G^\circ < 0$ , that is, when

$$\Delta_r H^\circ - T \Delta_r S^\circ < 0$$

$$\Delta_r H^\circ < T \Delta_r S^\circ$$

$$T > \frac{\Delta_r H^\circ}{\Delta_r S^\circ} = \frac{131.3 \text{ kJ mol}^{-1}}{134.1 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}} = 979.1 \text{ K}$$

The lower limit of temperature, 979.1 K, is an estimate because  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  are not truly temperature independent, as assumed here.

6.26 The normal boiling point of ethanol is 78.3°C and its molar enthalpy of vaporization is 39.3 kJ mol<sup>-1</sup>. What is its vapor pressure at 30°C?

$$\begin{aligned}\ln \frac{P_2}{P_1} &= -\frac{\Delta_{\text{vap}} \bar{H}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \\ \ln \frac{P_2}{1 \text{ atm}} &= -\frac{39.3 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{303.2 \text{ K}} - \frac{1}{351.5 \text{ K}} \right) = -2.142 \\ P_2 &= (1 \text{ atm}) e^{-2.142} = 0.117 \text{ atm} = 88.9 \text{ torr}\end{aligned}$$

6.34 A sample of supercooled water freezes at  $-10^{\circ}\text{C}$ . What are the signs of  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  for this process? All the changes refer to the system.

$\Delta G$ : – because the process is spontaneous (constant temperature given and constant pressure assumed).

$\Delta H$ : – because freezing is an exothermic process.

$\Delta S$ : – because ice is more ordered than liquid water.

6.37 A closed, 7.8-L flask contains 1.0 g of water. At what temperature will half of the water be in the vapor phase. (*Hint*: Look up the vapor pressures of water in the inside back matter.)

Half of the water is 0.50 g, or  $\frac{0.50 \text{ g}}{18.02 \text{ g mol}^{-1}} = 0.0277 \text{ mol}$ . Find the temperature at which the pressure exerted by this much water in 7.8 L is equal to the vapor pressure of water. (The volume of the remaining 0.50 g of water is assumed negligible.) Assuming ideal gas behavior,

$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(0.0277 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) T \left(\frac{760 \text{ mmHg}}{1 \text{ atm}}\right)}{7.8 \text{ L}} \\ &= (0.221 \text{ mmHg K}^{-1}) T \\ &= (0.221 \text{ mmHg }^{\circ}\text{C}^{-1})(t + 273^{\circ}\text{C}) \\ &= (0.221 \text{ mmHg }^{\circ}\text{C}^{-1}) t + 60.3 \text{ mmHg} \end{aligned}$$

Now refer to the ~~inside back matter of the text~~ <sup>table</sup> to find a temperature and vapor pressure that satisfy this equation.

$t^{\circ}\text{C}$	$P_{\text{H}_2\text{O}}/\text{mmHg}$	$[(0.221 \text{ mmHg }^{\circ}\text{C}^{-1}) t + 60.3 \text{ mmHg}]/\text{mmHg}$
40	55.32	69.1
45	71.88	70.2
50	92.51	71.4

The closest agreement is for  $t = 45^{\circ}\text{C}$ . At this temperature, half of the water will be in the vapor phase.

6.40 The molar entropy of argon (Ar) is given by

$$\bar{S}^\circ = (36.4 + 20.8 \ln T) \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate the change in Gibbs energy when 1.0 mole of Ar is heated at constant pressure from 20°C to 60°C. (Hint: Use the relation  $\int \ln x dx = x \ln x - x$ .)

$\Delta G^\circ$  can be evaluated by using the relation

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

At constant pressure,

$$\begin{aligned} dG &= -SdT \\ \int_{G_1}^{G_2} dG &= - \int_{T_1}^{T_2} SdT \\ \Delta G &= - \int_{293.2 \text{ K}}^{333.2 \text{ K}} (1 \text{ mol}) [(36.4 + 20.8 \ln T) \text{ J K}^{-1} \text{ mol}^{-1}] dT \\ &= - [36.4T + 20.8 (T \ln T - T)]_{293.2}^{333.2} \text{ J} \\ &= - \{ [36.4 (333.2) + 20.8 (333.2 \ln 333.2 - 333.2)] \\ &\quad - [36.4 (293.2) + 20.8 (293.2 \ln 293.2 - 293.2)] \} \text{ J} \\ &= -6.24 \times 10^3 \text{ J} \end{aligned}$$

9.5 Consider the reaction



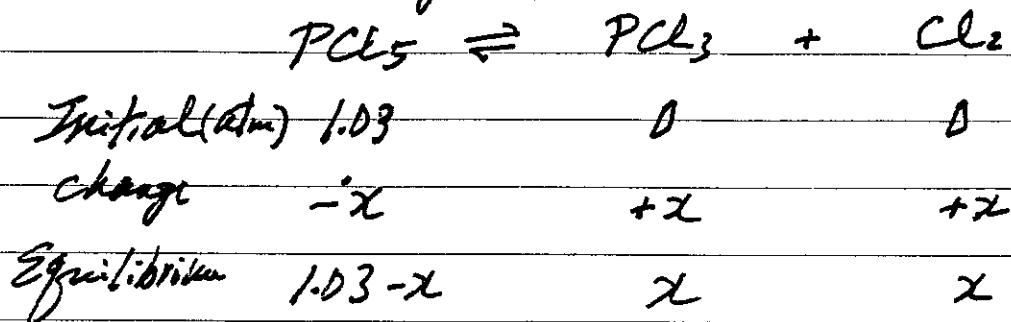
for which  $K_p = 1.05$  at 250°C. A quantity of 2.50 g of  $\text{PCl}_5$  is placed in an evacuated flask of volume 0.500 L and heated to 250°C. (a) Calculate the pressure of  $\text{PCl}_5$  if it did not dissociate. (b) Calculate the partial pressure of  $\text{PCl}_5$  at equilibrium. (c) What is the total pressure at equilibrium? (d) What is the degree of dissociation of  $\text{PCl}_5$ ? (The degree of dissociation is given by the fraction of  $\text{PCl}_5$  that has undergone dissociation.)

(a) Assume  $\text{PCl}_5$  behaves ideally. If it did not dissociate, its pressure would be

$$\begin{aligned} P_{\text{PCl}_5} &= \frac{nRT}{V} = \frac{\left(\frac{2.50 \text{ g}}{208.22 \text{ g mol}^{-1}}\right) (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (523.2 \text{ K})}{0.500 \text{ L}} \\ &= 1.031 \text{ atm} = 1.03 \text{ atm} \end{aligned}$$

9.5 cont'd

(b) The partial pressure of  $\text{PCl}_5$  at equilibrium can be determined using  $K_p$ . We write



$$K_p = 1.05 = \frac{x^2}{1.03 - x}$$

$$x^2 + 1.05x - 1.08 = 0$$

$$x = 0.64 \quad \text{or} \quad x = -1.69 \text{ (impossible)}$$

Therefore, at equilibrium

$$P_{\text{PCl}_5} = 1.03 - x = 1.03 - 0.64 = 0.39 \text{ atm}$$

(c) The total pressure  $P_T$  at equilibrium is given by the sum of the partial pressures

$$P_T = P_{\text{Cl}_2} + P_{\text{PCl}_3} + P_{\text{PCl}_5}$$

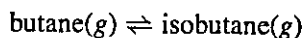
$$= [(1.03 - x) + x + x] \text{ atm}$$

$$= 1.03 + x = 1.67 \text{ atm}$$

$$\text{(d) degree of dissociation of } \text{PCl}_5 = \frac{0.64 \text{ atm}}{1.03 \text{ atm}} = 0.62 \text{ or } 62\%$$

9.42 Many hydrocarbons exist as structural isomers, which are compounds that have the same molecular formula but different structures. For example, both butane and isobutane have the same molecular formula:  $C_4H_{10}$ . Calculate the mole percent of these molecules in an equilibrium mixture at  $25^\circ\text{C}$ , given that the standard Gibbs energy of formation of butane is  $-15.9 \text{ kJ mol}^{-1}$  and that of isobutane is  $-18.0 \text{ kJ mol}^{-1}$ . Does your result support the notion that straight-chain hydrocarbons (that is, hydrocarbons in which the C atoms are joined along a line) are less stable than branch-chain hydrocarbons?

The isomerization process can be expressed as



First calculate  $\Delta_r G^\circ$ , from which the equilibrium constant  $K_p$  is obtained.

$$\begin{aligned} \Delta_r G^\circ &= \Delta_f \bar{G}^\circ [\text{isobutane}] - \Delta_f \bar{G}^\circ [\text{butane}] \\ &= -18.0 \text{ kJ mol}^{-1} - (-15.9 \text{ kJ mol}^{-1}) \\ &= -2.1 \text{ kJ mol}^{-1} \\ \ln K_p &= -\frac{\Delta_r G^\circ}{RT} \\ &= -\frac{-2.1 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 0.848 \\ K_p &= 2.33 \end{aligned}$$

The equilibrium constant is a ratio between the pressures of isobutane and butane. The pressure of each gas is proportional to number of moles of gas at constant  $T$  and  $V$ . Therefore,

$$K_p = \frac{P_{\text{isobutane}}}{P_{\text{butane}}} = \frac{n_{\text{isobutane}}}{n_{\text{butane}}} = 2.33$$

According to the above expression, for each mole of butane, there are 2.33 moles of isobutane.

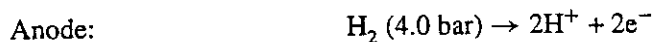
$$\text{Mole percent of isobutane} = \frac{2.33}{3.33} \times 100\% = 70\%$$

$$\text{Mole percent of butane} = 1 - 70\% = 30\%$$

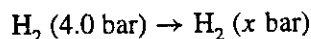
These results support the notion that straight-chain hydrocarbons like butane are less stable than branch-chain hydrocarbons like isobutane.

- 10.10 Consider a concentration cell consisting of two hydrogen electrodes. At 25°C the cell emf is found to be 0.0267 V. If the pressure of hydrogen gas at the anode is 4.0 bar, what is the pressure of hydrogen gas at the cathode?

Let the pressure of hydrogen gas at the cathode be  $x$  bars. The half reactions are



The overall reaction is



Since this is a concentration cell,  $E^\circ = 0 \text{ V}$ . The emf for the cell is

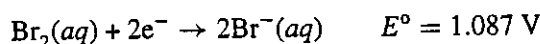
$$E = E^\circ - \frac{0.0257 \text{ V}}{\nu} \ln \frac{x}{4.0}$$

$$0.0267 \text{ V} = 0 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{x}{4.0}$$

$$x = 0.50 \text{ bar}$$

- 10.11 An electrochemical cell consists of a half-cell in which a piece of platinum wire is dipped into a solution that is 2.0 M in KBr and 0.050 M in Br<sub>2</sub>. The other half-cell consists of magnesium metal immersed in a 0.38 M Mg<sup>2+</sup> solution. (a) Which electrode is the anode and which is the cathode? (b) What is the emf of the cell? (c) What is the spontaneous cell reaction? (d) What is the equilibrium constant of the cell reaction? Assume that the temperature is 25°C.

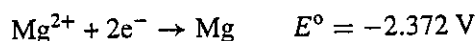
(a) The reduction reaction for the Pt | Br<sub>2</sub>, Br<sup>-</sup> half cell is



The emf for this half cell is

$$E = E^\circ - \frac{0.0257 \text{ V}}{\nu} \ln \frac{[\text{Br}^-]^2}{[\text{Br}_2]} = 1.087 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(2.0)^2}{0.050} = 1.0307 \text{ V}$$

The reduction reaction for the Mg<sup>2+</sup> | Mg half cell is



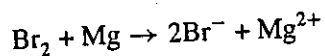
The emf for this half cell is

$$E = E^\circ - \frac{0.0257 \text{ V}}{\nu} \ln \frac{1}{[\text{Mg}^{2+}]} = -2.372 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{1}{0.38} = -2.3844 \text{ V}$$

The cell reaction that would occur is one with a positive  $E$ . This is possible if Mg<sup>2+</sup> | Mg is the anode and Pt | Br<sub>2</sub>, Br<sup>-</sup> is the cathode.

(b)  $E = 1.0307 \text{ V} - (-2.3844 \text{ V}) = 3.415 \text{ V}$

(c) The spontaneous cell reaction is



(d)  $E^\circ$  for the cell is

$$E^\circ = 1.087 \text{ V} - (-2.372 \text{ V}) = 3.459 \text{ V}$$

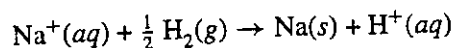
Therefore, the equilibrium constant is

$$K = \exp\left(\frac{\nu F E^\circ}{RT}\right) = \exp\left[\frac{2(96500 \text{ C mol}^{-1})(3.459 \text{ V})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.2 \text{ K})}\right] = e^{269.3} = 9.03 \times 10^{116}$$

**10.44** Use the data in Appendix B and the convention that  $\Delta_f \bar{G}^\circ[\text{H}^+(\text{aq})] = 0$  to determine the standard reduction potentials for sodium and fluorine. (Like sodium, fluorine also reacts violently with water.)

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To determine the standard reduction potential for sodium, consider the following reaction



The standard Gibbs energy for this reaction is

$$\begin{aligned} \Delta_r G^\circ &= \Delta_f \bar{G}^\circ[\text{Na}(\text{s})] + \Delta_f \bar{G}^\circ[\text{H}^+(\text{aq})] - \Delta_f \bar{G}^\circ[\text{Na}^+(\text{aq})] - \frac{1}{2} \Delta_f \bar{G}^\circ[\text{H}_2(\text{g})] \\ &= 0 \text{ kJ mol}^{-1} + 0 \text{ kJ mol}^{-1} - (-261.9 \text{ kJ mol}^{-1}) - \frac{1}{2}(0 \text{ kJ mol}^{-1}) \\ &= 261.9 \text{ kJ mol}^{-1} \end{aligned}$$

The standard emf for the reaction is

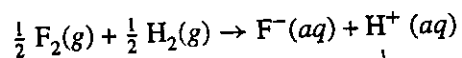
$$E^\circ = -\frac{\Delta_r G^\circ}{\nu F} = -\frac{261.9 \times 10^3 \text{ J mol}^{-1}}{96500 \text{ C mol}^{-1}} = -2.71 \text{ V}$$

Since  $E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ , where the half-reactions are



the reduction potential of Na is  $-2.71 \text{ V}$ .

To determine the standard reduction potential for fluorine, consider the following reaction



The standard Gibbs energy for this reaction is

$$\begin{aligned} \Delta_r G^\circ &= \Delta_f \bar{G}^\circ [\text{F}^-(aq)] + \Delta_f \bar{G}^\circ [\text{H}^+(aq)] - \frac{1}{2} \Delta_f \bar{G}^\circ [\text{F}_2(g)] - \frac{1}{2} \Delta_f \bar{G}^\circ [\text{H}_2(g)] \\ &= -276.5 \text{ kJ mol}^{-1} + 0 \text{ kJ mol}^{-1} - \frac{1}{2} (0 \text{ kJ mol}^{-1}) - \frac{1}{2} (0 \text{ kJ mol}^{-1}) \\ &= -276.5 \text{ kJ mol}^{-1} \end{aligned}$$

The standard emf for the reaction is

$$E^\circ = -\frac{\Delta_r G^\circ}{\nu F} = -\frac{-276.5 \times 10^3 \text{ J mol}^{-1}}{96500 \text{ C mol}^{-1}} = 2.87 \text{ V}$$

Since  $E^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$ , where the half-reactions are



the reduction potential of  $\text{F}_2$  is 2.87 V