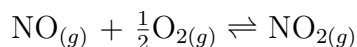


Chemistry 431  
Problem Set 9  
Fall 2023  
Solutions

1. Use Table 4.1 of the text to calculate the equilibrium constant of the reaction



at 25.°C and 35.°C.

**Answer:**

$$\begin{aligned}\Delta_{r,m}G^{\ominus} &= \Delta_{f,m}G^{\ominus}(\text{NO}_{2(g)}) - \Delta_{f,m}G^{\ominus}(\text{NO}_{(g)}) \\ &= 51.3 \text{ kJ mol}^{-1} - 87.6 \text{ kJ mol}^{-1} = -36.3 \text{ kJ mol}^{-1} \\ \Delta_{r,m}H^{\ominus} &= \Delta_{f,m}H^{\ominus}(\text{NO}_{2(g)}) - \Delta_{f,m}H^{\ominus}(\text{NO}_{(g)}) \\ &= 33.2 \text{ kJ mol}^{-1} - 91.3 \text{ kJ mol}^{-1} = -58.1 \text{ kJ mol}^{-1}\end{aligned}$$

At 25°C

$$\begin{aligned}K_P &= \exp\left\{-\frac{\Delta_{r,m}G^{\ominus}}{RT}\right\} \\ &= \exp\left\{\frac{36300 \text{ J mol}^{-1}}{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}\right\} = 2.30 \times 10^6 \\ \ln \frac{K_P(T_2)}{K_P(T_1)} &= \frac{\Delta_{r,m}H^{\ominus}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \\ \ln \frac{K_P(308)}{2.30 \times 10^6} &= \frac{-58100 \text{ J mol}^{-1}}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left(\frac{1}{298 \text{ K}} - \frac{1}{308 \text{ K}}\right) \\ K_p(308) &= 1.07 \times 10^6\end{aligned}$$

2. Consider the reaction



- (a) Show that if one starts with pure  $\text{PCl}_5$  and a fraction,  $\alpha$ , dissociates, the reaction quotient will be given by

$$Q_P = \frac{\alpha^2}{(1 - \alpha^2)} \frac{P}{P^{\ominus}}$$

**Answer:**

Let  $n$  = the initial number of moles of  $\text{PCl}_{5(g)}$

	$n_{\text{PCl}_5}$	$n_{\text{PCl}_3}$	$n_{\text{Cl}_2}$
initial	$n$	0	0
change	$-\alpha n$	$\alpha n$	$\alpha n$
equilibrium	$n(1 - \alpha)$	$\alpha n$	$\alpha n$

$$n_{\text{total}} = 2\alpha n + (1 - \alpha)n = (1 + \alpha)n$$

$$P_{\text{PCl}_5} = \chi_{\text{PCl}_5} P = \frac{1 - \alpha}{1 + \alpha} P$$

$$P_{\text{PCl}_3} = P_{\text{Cl}_2} = \chi_{\text{Cl}_2} = \frac{\alpha}{1 + \alpha} P$$

Then

$$\begin{aligned} Q_P &= \frac{(P_{\text{PCl}_3}/P^\ominus)(P_{\text{Cl}_2}/p^\ominus)}{P_{\text{PCl}_5}/p^\ominus} \\ &= \frac{[(\alpha/(1 + \alpha))(P/P^\ominus)]^2}{[(1 - \alpha)/(1 + \alpha)(P/P^\ominus)]} \\ &= \frac{\alpha^2}{1 - \alpha^2} \frac{P}{P^\ominus} \end{aligned}$$

- (b) At 250.°C the equilibrium constant for the reaction is  $K_P = 1.78$ . Calculate  $\alpha$  for  $P = 0.1$  bar and  $P = 1.0$  bar at equilibrium.

**Answer:**

$$K_P = \frac{\alpha^2}{1 - \alpha^2} \frac{P}{P^\ominus}$$

$$(1 - \alpha^2)K_P = \alpha^2 \frac{P}{P^\ominus}$$

$$\alpha^2 \left( \frac{P}{P^\ominus} + K_P \right) = K_P$$

$$\alpha = \left( \frac{K_P}{K_P + P/P^\ominus} \right)^{1/2}$$

$$\alpha(.1) = \left( \frac{1.78}{.1 + 1.78} \right)^{1/2} = 0.973$$

$$\alpha(1.) = \left( \frac{1.78}{2.78} \right)^{1/2} = 0.800$$

(c) Calculate  $\Delta_{r,m}G$  for an equimolar mixture at 1 bar pressure and 250.°C.

**Answer:**

$$\begin{aligned}\Delta_{r,m}G &= \Delta_{r,m}G^{\ominus} + RT \ln Q_P \\ &= -RT \ln K_P + RT \ln Q_P \\ &= -RT \ln K_P + RT \ln \frac{(P_{PCl_3}/P^{\ominus})(P_{Cl_2}/P^{\ominus})}{(P_{PCl_5}/P^{\ominus})} \\ &= -RT \ln K_P + RT \ln \left( \frac{P}{P^{\ominus}} \frac{(1/3)(1/3)}{1/3} \right) \\ &= (-8.3144 \text{ J mol}^{-1}\text{K}^{-1})(523\text{K})[\ln 1.78 - \ln(1/3)] = -7285 \text{ J mol}^{-1}\end{aligned}$$

(d) Calculate  $\Delta_{r,m}G$  for 20 per cent dissociation at 250.°C and 1 bar pressure.

**Answer:**

$$Q_P = \frac{.2^2}{1 - .2^2} = 0.0417$$

$$\Delta G_{r,m} = (-8.3144 \text{ J mol}^{-1}\text{K}^{-1})(523\text{K})[\ln 1.78 - \ln 0.0417] = -16323 \text{ J mol}^{-1}$$

3. The following results were obtained for the degree of dissociation,  $\alpha$ , of  $\text{CO}_2$  in the reaction



at a pressure of 1.0 bar:

T (°K)	$\alpha$
1000.	$2. \times 10^{-7}$
1400.	$1.27 \times 10^{-4}$
2000.	$1.55 \times 10^{-2}$

Calculate  $\Delta_{r,m}S^{\ominus}$  for the reaction at 1400.°K.

**Answer:**

Let  $n$  = initial number of moles of  $\text{CO}_{2(g)}$

	$n_{\text{CO}_2}$	$n_{\text{CO}}$	$n_{\text{O}_2}$
initial	$n$	0	0
change	$-\alpha n$	$\alpha n$	$\alpha n/2$
equilibrium	$n(1 - \alpha)$	$\alpha n$	$\alpha n/2$

$$n_{total} = (1 - \alpha)n + \alpha n + \frac{1}{2}\alpha n = \left(1 + \frac{\alpha}{2}\right)n$$

$$P_{CO_2} = \frac{2(1-\alpha)}{2+\alpha}P$$

$$P_{CO} = \frac{2\alpha}{2+\alpha}P$$

$$P_{O_2} = \frac{(1/2)\alpha}{1+(1/2)\alpha}P = \frac{\alpha}{2+\alpha}P$$

Then

$$\begin{aligned} K_P &= \frac{(P_{CO}/P^\circ)(P_{O_2}/P^\circ)^{1/2}}{P_{CO_2}/P^\circ} \\ &= \frac{(2\alpha/[2+\alpha])(\alpha/[2+\alpha])^{1/2}}{2(1-\alpha)/(2+\alpha)} \left(\frac{P}{P^\circ}\right)^{1/2} \\ &= \frac{\alpha^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}} \left(\frac{P}{P^\circ}\right)^{1/2} \end{aligned}$$

Then

$$K_P(1000\text{K}) = 6.32 \times 10^{-11}$$

$$K_P(1400\text{K}) = 1.01 \times 10^{-6}$$

$$K_P(2000\text{K}) = 1.38 \times 10^{-3}$$

$$\Delta_{r,m}G^\ominus(1400\text{K}) = -RT \ln K_P$$

$$= -(8.3144\text{J mol}^{-1}\text{K})(1400\text{K}) \ln(1.01 \times 10^{-6}) = 160.7\text{kJ mol}^{-1}$$

$$\ln \frac{K_P(1400\text{K})}{K_P(1000\text{K})} = \frac{\Delta_{r,m}H^\ominus}{R} \left( \frac{1}{1000\text{K}} - \frac{1}{1400\text{K}} \right)$$

$$\ln \frac{1.01 \times 10^{-6}}{6.32 \times 10^{-11}} = \frac{\Delta_{r,m}H^\ominus}{8.3144\text{J mol}^{-1}\text{K}} \left( \frac{1}{1000\text{K}} - \frac{1}{1400\text{K}} \right)$$

$$\Delta_{r,m}H^\ominus = 281.7\text{kJ mol}^{-1}$$

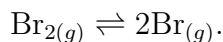
$$\Delta_{r,m}S^\ominus = \frac{\Delta_{r,m}H^\ominus - \Delta_{r,m}G^\ominus}{T}$$

$$= \frac{(281700 - 160700)\text{J mol}^{-1}}{1400\text{K}} = 86.43\text{J mol}^{-1}\text{K}^{-1}$$

4. Given the following table for the thermodynamic properties of bromine at 298K

	$\Delta_{f,m}H^\ominus$ (kJ mol <sup>-1</sup> )	$\Delta_{f,m}G^\ominus$ (kJ mol <sup>-1</sup> )
Br <sub>2</sub> (ℓ)	0	0
Br <sub>2</sub> (g)	30.9	3.1
Br(g)	111.9	82.4

calculate the degree of dissociation  $\alpha$  of gas-phase  $\text{Br}_2$  at 2000.K and a total pressure of 5.00 bar according to the reaction



**Answer:**

$$\Delta_{r,m}G^\ominus = 2(82.4 \text{ kJ mol}^{-1}) - 3.1 \text{ kJ mol}^{-1} = 161.7 \text{ kJ mol}^{-1}$$

$$K_P(298) = e^{-\Delta_{r,m}G^\ominus/RT} = \exp\left\{-\frac{161700 \text{ J mol}^{-1}}{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}\right\} = 4.54 \times 10^{-29}$$

$$\Delta_{r,m}H^\ominus = 2(111.9 \text{ kJ mol}^{-1}) - 30.9 \text{ kJ mol}^{-1} = 192.9 \text{ kJ mol}^{-1}$$

$$\ln \frac{K(T_2)}{K(T_1)} = \frac{\Delta_{r,m}H^\ominus}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{K(2000)}{4.54 \times 10^{-29}} = \frac{192900 \text{ J mol}^{-1}}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left( \frac{1}{298 \text{ K}} - \frac{1}{2000 \text{ K}} \right)$$

$$K(2000) = 2.70$$

	$n_{\text{Br}_2}$	$n_{\text{Br}}$
initial	$n$	0
change	$-\alpha n$	$2\alpha n$
equilibrium	$n(1 - \alpha)$	$2\alpha n$

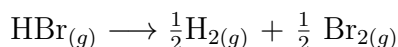
$$n_{\text{tot}} = n(1 + \alpha)$$

$$K_P = \frac{(P_{\text{Br}}/P^\ominus)^2}{(P_{\text{Br}_2}/P^\ominus)} = \frac{(2\alpha/(1 + \alpha))^2 P}{(1 - \alpha)/(1 + \alpha) P^\ominus}$$

$$= \frac{4\alpha^2}{1 - \alpha^2}(5) = 2.70$$

$$\frac{\alpha^2}{1 - \alpha^2} = 0.135 \quad \alpha = 0.345$$

5. Hydrogen bromide dissociates according to the reaction



Use Table 4.1 of the text to find the degree of dissociation of HBr at 35.°C and 2.0 bar pressure.

**Answer:**

$$\Delta_{r,m}G^\ominus = \frac{1}{2}(3.1 \text{ kJ mol}^{-1}) - (-53.4 \text{ kJ mol}^{-1}) = 54.95 \text{ kJ mol}^{-1}$$

$$\Delta_{r,m}H^{\ominus} = \frac{1}{2}(30.9 \text{ kJ mol}^{-1}) - (-36.3 \text{ kJ mol}^{-1}) = 51.75 \text{ kJ mol}^{-1}$$

$$K_P(298) = \exp \left\{ -\frac{\Delta_{r,m}G^{\ominus}}{RT} \right\}$$

$$= \exp \left\{ -\frac{54950 \text{ J mol}^{-1}}{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})} \right\} = 2.33 \times 10^{-10}$$

$$\ln \frac{K_P(308)}{2.33 \times 10^{-10}} = \frac{51750 \text{ J mol}^{-1}}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left( \frac{1}{298 \text{ K}} - \frac{1}{308 \text{ K}} \right)$$

$$K_P(308) = 4.59 \times 10^{-10}$$

Let  $n$ =initial number of moles of HBr

	$n_{HBr}$	$n_{H_2}$	$n_{Br_2}$
initial	$n$	0	0
change	$-\alpha n$	$\alpha n/2$	$\alpha n/2$
equilibrium	$n(1 - \alpha)$	$\alpha n/2$	$\alpha n/2$

$$n_{total} = \alpha n + (1 - \alpha)n = n$$

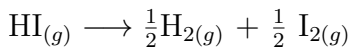
$$P_{HBr} = (1 - \alpha)P$$

$$P_{H_2} = P_{Br_2} = \frac{\alpha}{2}P$$

$$K_P = \frac{[(\alpha/2)^{1/2}]^2}{1 - \alpha} = \frac{\alpha}{2(1 - \alpha)}$$

$$\alpha = \frac{2K_P}{1 + 2K_P} = \frac{(2)(4.59 \times 10^{-10})}{1 + (2)(4.59 \times 10^{-10})} = 9.18 \times 10^{-10}$$

6. Hydrogen iodide gas dissociates according to the reaction



At 0.°C and 1.0 bar pressure, the degree of dissociation is  $\alpha = .40$ , and at 100.°C,  $\alpha = .88$ . Assuming  $\Delta_{r,m}H^{\ominus}$  to be independent of temperature, calculate  $\Delta_{r,m}H^{\ominus}$ ,  $\Delta_{r,m}G^{\ominus}$  and  $\Delta_{r,m}S^{\ominus}$  for the reaction at 0.°C.

**Answer:**

As in the previous problem

$$K_P = \frac{\alpha}{2(1 - \alpha)}$$

$$K_P(273) = 0.333 \quad K_P(373) = 3.67$$

$$\Delta_{r,m}G^{\ominus} = -RT \ln K_P = -(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(273 \text{ K}) \ln 0.333 = 2496 \text{ J}$$

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = \frac{\Delta_{r,m}H^{\ominus}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{3.67}{0.33} = \frac{\Delta_{r,m}H^{\ominus}}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left( \frac{1}{273 \text{ K}} - \frac{1}{373 \text{ K}} \right)$$

$$\Delta_{r,m}H^{\ominus} = 20318 \text{ J mol}^{-1}$$

$$\Delta_{r,m}S^{\ominus} = \frac{\Delta_{r,m}H^{\ominus} - \Delta_{r,m}G^{\ominus}}{T}$$

$$= \frac{20318 \text{ J mol}^{-1} - 2496 \text{ J mol}^{-1}}{273 \text{ K}} = 65.28 \text{ J mol}^{-1}\text{K}^{-1}$$

7. The gas  $\text{NO}_2$  dissociates according to the reaction



One mole of  $\text{NO}_{2(g)}$  is placed in a vessel, and the gas is allowed to come to equilibrium such that the total pressure is kept fixed at 1.0 bar. The ratio  $P_{\text{NO}}/P_{\text{NO}_2}$  is measured as a function of temperature and equals .872 at 700K and 2.50 at 800K. Calculate  $\Delta_{r,m}H^{\ominus}$ ,  $\Delta_{r,m}G^{\ominus}$  and  $\Delta_{r,m}S^{\ominus}$  for the reaction at 700K.

**Answer:** Let

$$r = \frac{P_{\text{NO}}}{P_{\text{NO}_2}}$$

	$n_{\text{NO}_2}$	$n_{\text{NO}}$	$n_{\text{O}_2}$
initial	$n$	0	0
change	$-\alpha n$	$\alpha n$	$\alpha n/2$
equilibrium	$n(1 - \alpha)$	$\alpha n$	$\alpha n/2$

Then

$$n_{\text{tot}} = n(1 - \alpha) + \alpha n + \frac{\alpha}{2}n = \left(1 + \frac{\alpha}{2}\right)n$$

$$P_{\text{NO}} = \frac{\alpha}{1 + \alpha/2}P \quad P_{\text{NO}_2} = \frac{1 - \alpha}{1 + \alpha/2}P$$

$$r = \frac{\alpha}{1 - \alpha}$$

or

$$\alpha = \frac{r}{1 + r}$$

Then

$$\text{at 700 K } \alpha = 0.47 \quad \text{and at 800 K } \alpha = 0.71$$

Now

$$K_P = \frac{(P_{O_2}/P^\circ)^{1/2}(P_{NO}/P^\circ)}{P_{NO_2}/P^\circ} = \frac{(\alpha/2)^{1/2}\alpha}{(1 + \alpha/2)^{1/2}(1 - \alpha)} \left(\frac{P}{P^\circ}\right)^{1/2}$$

Then

$$K_P(700) = 0.38 \quad K_P(800) = 1.27$$

$$\Delta_{r,m}G^\ominus = -RT \ln K_P = -(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(700 \text{ K}) \ln 0.38 = 5631 \text{ J}$$

$$\ln \frac{1.27}{0.38} = \frac{\Delta_{r,m}H^\ominus}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left( \frac{1}{700 \text{ K}} - \frac{1}{800 \text{ K}} \right)$$

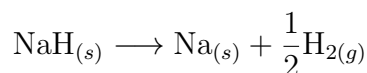
$$\Delta_{r,m}H^\ominus = 56180 \text{ J}$$

$$\Delta_{r,m}S^\ominus = \frac{56180 \text{ J mol}^{-1} - 5631 \text{ J mol}^{-1}}{700 \text{ K}} = 72.71 \text{ J mol}^{-1}\text{K}^{-1}$$

8. The standard molar enthalpy of formation and molar Gibbs free energy of formation of solid sodium hydride (NaH) at 298K are given by

$$\Delta_{f,m}H^\ominus = -56.3 \text{ J mol}^{-1} \quad \Delta_{f,m}G^\ominus = -33.5 \text{ J mol}^{-1}.$$

Given the reaction



Calculate the temperature at which the pressure of hydrogen in equilibrium with NaH<sub>(s)</sub> and Na<sub>(s)</sub> is 0.01 bar.

**Answer:**

$$K_P = \left(\frac{P_{H_2}}{P^\circ}\right)^{1/2}$$

$$K_P(298 \text{ K}) = \exp\left(-\frac{\Delta_{f,m}G^\ominus}{RT}\right) = \exp\left(-\frac{33500 \text{ J mol}^{-1}}{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}\right) = 1.34 \times 10^{-6}$$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_{r,m}H^\ominus}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{0.01^{1/2}}{1.34 \times 10^{-6}}\right) = \frac{56300 \text{ J mol}^{-1}}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left(\frac{1}{298 \text{ K}} - \frac{1}{T}\right)$$

$$T = 589 \text{ K}$$

9. Solid ammonium chloride at 600.K is allowed to come to equilibrium with equimolar amounts of gas phase hydrogen chloride (HCl) and ammonia (NH<sub>3</sub>) according to the reaction



Given the table of thermodynamic data valid at 298.K



Substance	$\Delta_{f,m}H^{\ominus}$ kJ mol <sup>-1</sup>	$\Delta_{f,m}G^{\ominus}$ kJ mol <sup>-1</sup>
NH <sub>3(g)</sub>	-45.9	-16.5
HCl <sub>(g)</sub>	-92.3	-95.3
NH <sub>4</sub> Cl <sub>(s)</sub>	-314.4	-202.9

calculate the partial pressures of ammonia and hydrogen chloride gas in equilibrium with the solid ammonium chloride at 600K.

**Answer:**

$$\begin{aligned}\Delta_{r,m}H^{\ominus} &= \Delta_{f,m}H^{\ominus}(\text{NH}_3(g)) + \Delta_{f,m}H^{\ominus}(\text{HCl}(g)) - \Delta_{f,m}H^{\ominus}(\text{NH}_4\text{Cl}(s)) \\ &= -45.9 \text{ kJ mol}^{-1} - 92.3 \text{ kJ mol}^{-1} - (-314.4 \text{ kJ mol}^{-1}) = 176.2 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_{r,m}G^{\ominus} &= \Delta_{f,m}G^{\ominus}(\text{NH}_3(g)) + \Delta_{f,m}G^{\ominus}(\text{HCl}(g)) - \Delta_{f,m}G^{\ominus}(\text{NH}_4\text{Cl}(s)) \\ &= -16.5 \text{ kJ mol}^{-1} - 95.3 \text{ kJ mol}^{-1} - (-202.9 \text{ kJ mol}^{-1}) = 91.1 \text{ kJ mol}^{-1}\end{aligned}$$

$$K_P(298 \text{ K}) = \exp\left(-\frac{91100 \text{ J mol}^{-1}}{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}\right) = 1.08 \times 10^{-16}$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta_{r,m}H^{\ominus}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln \frac{K_P(600 \text{ K})}{1.08 \times 10^{-16}} = \frac{176200 \text{ J mol}^{-1}}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left(\frac{1}{298 \text{ K}} - \frac{1}{600 \text{ K}}\right)$$

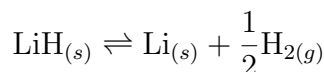
$$K_P(600 \text{ K}) = 0.38 = \frac{P_{\text{HCl}}}{P^{\circ}} \frac{P_{\text{NH}_3}}{P^{\circ}}$$

$$P_{\text{HCl}} = P_{\text{NH}_3} = P$$

$$\left(\frac{P}{P^{\circ}}\right)^2 = 0.38$$

$$P_{\text{HCl}} = P_{\text{NH}_3} = P = 0.62 \text{ bar}$$

10. The equilibrium pressure of hydrogen gas in the presence of solid lithium hydride and lithium metal according to the reaction



is 0.0213 bar at 1000. K and 0.801 bar at 1200. K. Assuming the enthalpy change for the process is temperature independent, calculate the equilibrium pressure of H<sub>2(g)</sub> in the presence of of solid LiH and Li at 1100. K.

**Answer:**

$$K_P = \left(\frac{P}{P^{\circ}}\right)^{1/2} \quad K_P(1000) = 0.146 \quad K_P(1200) = 0.895$$

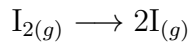
$$\ln \frac{K_P(T_2)}{K_P(T_1)} = \frac{\Delta_{r,m}H^\ominus}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{0.895}{0.146} = \frac{\Delta_{r,m}H^\ominus}{R} \left( \frac{1}{1000. \text{ K}} - \frac{1}{1200. \text{ K}} \right) \quad \frac{\Delta_{r,m}H^\ominus}{R} = 10879. \text{ K}$$

$$\ln \frac{K_P(1100)}{0.146} = 10879. \text{ K} \left( \frac{1}{1000. \text{ K}} - \frac{1}{1100. \text{ K}} \right)$$

$$K_P(1100) = 0.393 = \left( \frac{P}{P^\ominus} \right)^{1/2} \quad P = 0.154 \text{ bar}$$

11. When gas phase molecular iodine dissociates according to the reaction



at a total pressure of 0.50 bar, the degree of dissociation of the molecular iodine at equilibrium is  $\alpha = 3.45 \times 10^{-2}$  at 1000K and  $\alpha = 0.155$  at 1200K. Assuming the standard enthalpy change for the reaction is independent of temperature, calculate  $\Delta_{r,m}H^\ominus$ ,  $\Delta_{r,m}G^\ominus$  and  $\Delta_{r,m}S^\ominus$  for the dissociation reaction at 1000K.

**Answer:**

	$n_{\text{I}_2}$	$n_{\text{I}}$
initial	$n$	0
change	$-\alpha n$	$2\alpha n$
equilibrium	$n(1 - \alpha)$	$2\alpha n$

$$n_{\text{tot}} = (1 + \alpha)n$$

$$K_P = \frac{(P_{\text{I}}/P^\ominus)^2}{P_{\text{I}_2}/P^\ominus} = \frac{(2\alpha/(1 + \alpha)P/P^\ominus)^2}{(1 - \alpha)/(1 + \alpha)P/P^\ominus} = \frac{4\alpha^2}{1 - \alpha^2} \frac{P}{P^\ominus}$$

$$K_P(1000 \text{ K}) = 2.38 \times 10^{-3} \quad K_P(1200 \text{ K}) = 4.92 \times 10^{-2}$$

$$\ln \frac{K(1200 \text{ K})}{K(1000 \text{ K})} = \frac{\Delta_{r,m}H^\ominus}{R} \left( \frac{1}{1000 \text{ K}} - \frac{1}{1200 \text{ K}} \right)$$

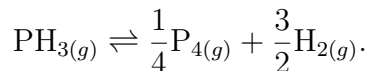
$$\ln \frac{4.92 \times 10^{-2}}{2.38 \times 10^{-3}} = \frac{\Delta_{r,m}H^\ominus}{R} \left( \frac{1}{1000 \text{ K}} - \frac{1}{1200 \text{ K}} \right)$$

$$\Delta_{r,m}H^\ominus = 151129 \text{ J mol}^{-1}$$

$$\Delta_{r,m}G^\ominus = -RT \ln K_P = -(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(1000 \text{ K}) \ln 2.38 \times 10^{-3} = 50224 \text{ J mol}^{-1}$$

$$\Delta_{r,m}S^\ominus = \frac{\Delta_{r,m}H^\ominus - \Delta_{r,m}G^\ominus}{T} = \frac{151129 \text{ J mol}^{-1} - 50224 \text{ J mol}^{-1}}{1000 \text{ K}} = 100.9 \text{ J mol}^{-1}\text{K}^{-1}$$

12. Phosphorous trihydride dissociates according to the gas-phase reaction



Measurements of the amount of phosphorous trihydride at equilibrium find that the degree of dissociation is  $\alpha = 0.934$  at  $25.0^\circ\text{C}$  and  $\alpha = 0.950$  at  $50.0^\circ\text{C}$  when the total pressure in each case is 2.00 bar. Calculate the entropy change for the reaction at  $25.0^\circ\text{C}$  assuming the enthalpy change for the reaction is temperature independent.

**Answer:**

Let  $n$  be the initial number of moles of  $\text{PH}_3$ . Then

	$n_{\text{PH}_3}$	$n_{\text{P}_4}$	$n_{\text{H}_2}$
initial	$n$	0	0
change	$-\alpha n$	$\alpha n/4$	$3\alpha n/2$
equilibrium	$n(1 - \alpha)$	$\alpha n/4$	$3\alpha n/2$

$$n_{\text{tot}} = n_{\text{PH}_3} + n_{\text{P}_4} + n_{\text{H}_2} = n(1 + 3\alpha/4)$$

$$K_P = \frac{(P_4/P^\ominus)^{1/4}(P_{\text{H}_2}/P^\ominus)^{3/2}}{P_{\text{PH}_3}/P^\ominus}$$

$$= \frac{\left(\frac{\alpha/4}{1 + 3\alpha/4}\right)^{1/4} \left(\frac{3\alpha/2}{1 + 3\alpha/4}\right)^{3/2}}{(1 - \alpha)/(1 + 3\alpha/4)} \left(\frac{P}{P^\ominus}\right)^{3/4}$$

$$K_P(298) = 19.7 \quad K_P(323) = 26.7$$

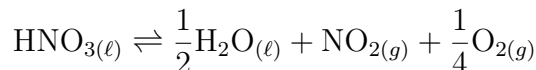
$$\ln \frac{K_2}{K_1} = \frac{\Delta_{r,m}H^\ominus}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{26.7}{19.7} = \frac{\Delta_{r,m}H^\ominus}{R} \left( \frac{1}{298 \text{ K}} - \frac{1}{323 \text{ K}} \right) \quad \Delta_{r,m}H^\ominus = 9733 \text{ J mol}^{-1}$$

$$\Delta_{r,m}G^\ominus = -RT \ln K_P = -(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K}) \ln 19.7 = -7385 \text{ J mol}^{-1}$$

$$\Delta_{r,m}S^\ominus = \frac{\Delta_{r,m}H^\ominus - \Delta_{r,m}G^\ominus}{T} = \frac{9733 \text{ J mol}^{-1} - (-7385 \text{ J mol}^{-1})}{298. \text{ K}} = 57.4 \text{ J mol}^{-1}\text{K}^{-1}$$

13. Liquid nitric acid dissociates into liquid-phase water and gas-phase nitrogen dioxide and oxygen according to the reaction



Pure nitric acid is injected into an evacuated flask, and it is found that at equilibrium, the total pressure of the gas phase species is  $3.92 \times 10^{-2}$  bar at 323. K and  $2.77 \times$

$10^{-2}$  bar at 308. K. Assuming the enthalpy change for the reaction is independent of temperature, calculate the entropy change  $\Delta_{r,m}S^{\ominus}$  for the reaction at 308. K.

**Answer:**

$$K_P = \left(\frac{P_{NO_2}}{P^{\ominus}}\right) \left(\frac{P_{O_2}}{P^{\ominus}}\right)^{1/4}$$

$$P_{tot} = P_{NO_2} + P_{O_2} = 5P_{O_2}$$

$$323. \text{ K} : P_{O_2} = \frac{1}{5}P_{tot} = 7.84 \times 10^{-3} \text{ bar} \quad P_{NO_2} = 4P_{O_2} = 3.14 \times 10^{-2} \text{ bar}$$

$$K_P(323) = (3.14 \times 10^{-2})(7.84 \times 10^{-3})^{1/4} = 9.33 \times 10^{-3}$$

$$308. \text{ K} : P_{O_2} = \frac{1}{5}P_{tot} = 5.54 \times 10^{-3} \text{ bar} \quad P_{NO_2} = 4P_{O_2} = 2.22 \times 10^{-2} \text{ bar}$$

$$K_P(308) = (2.22 \times 10^{-2})(5.54 \times 10^{-3})^{1/4} = 6.06 \times 10^{-3}$$

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = \frac{\Delta_{r,m}H^{\ominus}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

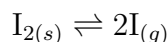
$$\ln \frac{(9.33 \times 10^{-3})}{(6.06 \times 10^{-3})} = \frac{\Delta_{r,m}H^{\ominus}}{R} \left( \frac{1}{308. \text{ K}} - \frac{1}{323. \text{ K}} \right)$$

$$\Delta_{r,m}H^{\ominus} = 23800. \text{ J mol}^{-1}$$

$$\Delta_{r,m}G^{\ominus} = -RT \ln K_P = -(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(308. \text{ K}) \ln 6.06 \times 10^{-3} = 13070 \text{ J mol}^{-1}$$

$$\Delta_{r,m}S^{\ominus} = \frac{\Delta_{r,m}H^{\ominus} - \Delta_{r,m}G^{\ominus}}{T} = \frac{23800 \text{ J mol}^{-1} - 13070 \text{ J mol}^{-1}}{308. \text{ K}} = 34.8 \text{ J K}^{-1}$$

14. At 750.K the pressure of atomic  $I_{(g)}$  in equilibrium with solid iodine according to the reaction



is 0.310 bar, and the pressure of atomic iodine associated with the same reaction at 850.K is 0.844 bar. Calculate the pressure of atomic, gas-phase iodine in equilibrium with solid  $I_2$  at 800.K.

**Answer:**

$$K(750) = P^2 = (0.310)^2 = 0.0961$$

$$K(850) = P^2 = (0.844)^2 = 0.712$$

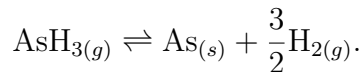
$$\ln \frac{K(T_2)}{K(T_1)} = \frac{\Delta_{r,m}H^{\ominus}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{0.712}{9.62 \times 10^{-2}} = \frac{\Delta_{r,m}H^{\ominus}}{R} \left( \frac{1}{750 \text{ K}} - \frac{1}{850 \text{ K}} \right) \quad \frac{\Delta_{r,m}H^{\ominus}}{R} = 12760 \text{ K}$$

$$\ln \frac{K(800)}{9.62 \times 10^{-2}} = 12760 \text{ K} \left( \frac{1}{750 \text{ K}} - \frac{1}{800 \text{ K}} \right) \quad K(800) = 0.279$$

$$P(800) = K(800)^{1/2} = 0.528 \text{ bar}$$

15. Arsine ( $\text{AsH}_3$ ) gas dissociates into solid arsenic and hydrogen gas according to the reaction



At a total pressure of 3.00 bar, the equilibrium degrees of dissociation of arsine are found to be  $\alpha = 9.2 \times 10^{-5}$  at 223 K and  $\alpha = 6.9 \times 10^{-6}$  at 250K. Assuming the enthalpy of the reaction is independent of temperature, calculate  $\Delta_{r,m}S^\ominus$  for the reaction at 250K.

**Answer:**

$n_{\text{AsH}_3}$	$n_{\text{H}_2}$
$n_0$	0
$-\alpha n_0$	$3\alpha n_0/2$
$n_0(1 - \alpha)$	$3\alpha n_0/2$

$$n_{\text{tot}} = n_{\text{AsH}_3} + n_{\text{H}_2} = n_0(1 + \alpha/2)$$

$$K_P = \frac{\left(\frac{P_{\text{H}_2}}{P^\ominus}\right)^{3/2}}{\left(\frac{P_{\text{AsH}_3}}{P^\ominus}\right)} = \frac{\left(\frac{3\alpha/2}{1 + \alpha/2}\right)^{3/2}}{\left(\frac{1 - \alpha}{1 + \alpha/2}\right)} \sqrt{\frac{P}{P^\ominus}}$$

$$K_P(223) = 2.8 \times 10^{-6} \quad K_P(250) = 5.8 \times 10^{-8}$$

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = \frac{\Delta_{r,m}H^\ominus}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{5.8 \times 10^{-8}}{2.8 \times 10^{-6}} = \frac{\Delta_{r,m}H^\ominus}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left( \frac{1}{223 \text{ K}} - \frac{1}{250 \text{ K}} \right) \quad \Delta_{r,m}H^\ominus = -66500 \text{ J mol}^{-1}$$

$$\Delta_{r,m}G^\ominus = -RT \ln K_P = -(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(250 \text{ K}) \ln(5.8 \times 10^{-8}) = 34600 \text{ J mol}^{-1}$$

$$\Delta_{r,m}S^\ominus = \frac{\Delta_{r,m}H^\ominus - \Delta_{r,m}G^\ominus}{T} = -404 \text{ J mol}^{-1}\text{K}^{-1}$$

16. For the dissociation reaction of gas-phase tungsten hexafluoride into liquid tungsten and fluorine gas



when the total pressure is 2.00 bar, the degree of dissociation of  $\text{WF}_{6(g)}$  is measured to be  $\alpha = 0.221$  at  $T = 5650\text{K}$  and  $\alpha = 0.249$  at  $T = 5700\text{K}$ . Calculate the entropy change for the reaction at 5650. K.

**Answer:**

	$n_{WF_6}$	$n_{F_2}$
initial	$n$	0
change	$-\alpha n$	$3\alpha n$
equilibrium	$n(1 - \alpha)$	$3\alpha n$

$$n_{tot} = n(1 + 2\alpha)$$

$$\chi_{F_2} = \frac{3\alpha}{1 + 2\alpha} \quad \chi_{WF_6} = \frac{1 - \alpha}{1 + 2\alpha}$$

$$K = \frac{(P_{F_2}/P^\circ)^3}{P_{WF_6}/P^\circ} = \frac{\left(\frac{3\alpha}{1 + 2\alpha}\right)^3}{\frac{1 - \alpha}{1 + 2\alpha}} \left(\frac{P}{P^\circ}\right)^2$$

$$K(5650) = 0.720 \quad K(5700) = 0.989$$

$$\ln \frac{K(T_2)}{K(T_1)} = \frac{\Delta_{r,m}H^\ominus}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{0.989}{0.720} = \frac{\Delta_{r,m}H^\ominus}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left( \frac{1}{5650 \text{ K}} - \frac{1}{5700 \text{ K}} \right) \quad \Delta_{r,m}H^\ominus = 1702000 \text{ J mol}^{-1}$$

$$\Delta_{r,m}G^\ominus = -RT \ln K = -(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(5650 \text{ K}) \ln 0.720 = 15430 \text{ J mol}^{-1}$$

$$\Delta_{r,m}S^\ominus = \frac{\Delta_{r,m}H^\ominus - \Delta_{r,m}G^\ominus}{T}$$

$$= \frac{1702000 \text{ J mol}^{-1} - 15430 \text{ J mol}^{-1}}{5650 \text{ K}} = 299 \text{ J mol}^{-1}\text{K}^{-1}$$