

## Chapter 3 Homework Solutions

- 3.1**  $n = 3 \text{ mol}$  ,  $T_1 = 25 \text{ }^\circ\text{C} = 298 \text{ K}$  ,  $T_2 = 125 \text{ }^\circ\text{C} = 398 \text{ K}$  ,  $p_1 = 1 \text{ atm}$  ,  $p_2 = 5 \text{ atm}$ .  
 $C_{p,m} = (5/2)R$

**The entropy changes for the heating and compression can be calculated separately and added.**

### Heat at constant pressure

$$\begin{aligned}\Delta S_1 &= nC_{p,m} \ln(T_2 / T_1) = n(5/2)R \ln(T_2 / T_1) \\ &= (3.0 \text{ mol})(5/2)(8.31 \text{ J} / \text{mol} \cdot \text{K}) \ln(398 / 298) = +18.0 \text{ J} / \text{K}\end{aligned}$$

### Compress at constant temperature.

Because  $T = \text{constant}$ ,  $p_2V_2 = p_1V_1 \rightarrow V_2 / V_1 = p_1 / p_2 = 1/5 = 0.20$

$$\Delta S_2 = nR \ln(V_2 / V_1) = (3 \text{ mol})(8.31 \text{ J} / \text{mol} \cdot \text{K}) \ln(0.20) = -40.1 \text{ J} / \text{K}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = +18.0 \text{ J/K} - 40.1 \text{ J/K} = -22.1 \text{ J/K}$$

In this particular example, the negative entropy change for compressing the sample is larger than the positive change for heating the sample, yielding a net negative  $\Delta S$ .

- 3.2**  $n = 3 \text{ mol}$  ,  $T_1 = 200 \text{ K}$  ,  $T_2 = 250 \text{ K}$  ,  $C_{v,m} = 27.5 \text{ J/mol-K}$   
 $C_{p,m} = C_{v,m} + R = 27.5 + 8.3 = 35.8 \text{ J/mol-K}$

$q = 0$  [Adiabatic]

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = 0 \text{ [for reversible Adiabatic process]}$$

$$w = \Delta U = nC_{v,m}(T_2 - T_1) = (3 \text{ mol})(27.5 \text{ J} / \text{mol} \cdot \text{K})(250 \text{ K} - 200 \text{ K}) = 4125 \text{ J} \approx 4.1 \text{ kJ}$$

$$\Delta H = nC_{p,m}(T_2 - T_1) = (3 \text{ mol})(35.8 \text{ J} / \text{mol} \cdot \text{K})(250 \text{ K} - 200 \text{ K}) = 5370 \text{ J} \approx 5.4 \text{ kJ}$$

- 3.3**  $T = 298 \text{ K}$  ,  $p_1 = 1 \text{ bar}$  ,  $V_2 = 2V_1$  ,  $n = 14 \text{ g} \cdot \frac{1 \text{ mol}}{28 \text{ g}} = 0.50 \text{ mol}$

### (a) Reversible Isothermal Expansion

$$\Delta S_{sys} = \Delta S = nR \ln(V_2 / V_1) = (0.50 \text{ mol})(8.31 \text{ J} / \text{mol} \cdot \text{K}) \ln(2V_1 / V_1) = +2.88 \text{ J} / \text{K}$$

$$\Delta S_{surr} = -\Delta S_{sys} = -2.88 \text{ J} / \text{K} \text{ because it's reversible and } \Delta S_{univ} = 0$$

**(b) Irreversible Isothermal Expansion against  $p_{\text{ex}} = 0$**

**System:** Cannot be calculated from actual process, which is irreversible. However,  $\Delta S_{\text{sys}} = +2.88 \text{ J/K}$  (part a) since S is a State Function

**Surroundings:**  $\Delta U_{\text{surr}} = 0$  (since isothermal)  
 $w_{\text{surr}} = 0$  (since  $p_{\text{ex}} = 0$ )  
 $q_{\text{surr}} = \Delta U_{\text{surr}} - w_{\text{surr}} = 0$   
Therefore,  $\Delta S_{\text{surr}} = 0$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = +2.88 + 0 = +2.88 \text{ J/K} > 0 \text{ (as expected for irreversible process)}$$

**(c) Reversible Adiabatic Expansion**

$(dq_{\text{rev}})_{\text{sys}} = (dq_{\text{rev}})_{\text{surr}} = 0$   
Therefore,  $\Delta S_{\text{sys}} = 0$  and  $\Delta S_{\text{surr}} = 0$

**3.4**  $T_b = 62 \text{ }^\circ\text{C} = 335 \text{ K}$ ,  $\Delta_{\text{vap}}H^\circ = 29.4 \text{ kJ/mol} = 2.94 \times 10^4 \text{ J/mol}$

$$n = 240 \text{ g} / 119.4 \text{ g/mol} = 2.01 \text{ mol}$$

$$\Delta S_{\text{sys}} = \frac{q_{\text{sys}}}{T} = \frac{n\Delta_{\text{vap}}H^\circ}{T_b} = \frac{(2.01 \text{ mol})(2.94 \times 10^4 \text{ J/mol})}{335 \text{ K}} = +176.4 \text{ J/K}$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = \frac{-q_{\text{sys}}}{T} = \frac{-n\Delta_{\text{vap}}H^\circ}{T_b} = \frac{-(2.01 \text{ mol})(2.94 \times 10^4 \text{ J/mol})}{335 \text{ K}} = -176.4 \text{ J/K}$$

**3.5**  $T_b = 78 \text{ }^\circ\text{C} = 351 \text{ K}$ ,  $\Delta_{\text{vap}}H = 38.6 \text{ kJ/mol}$ ,  $p = 1 \text{ bar} = 100 \text{ kPa}$ ,  $n = 150 \text{ g} \cdot \frac{1 \text{ mol}}{46 \text{ g}} = 3.26 \text{ mol}$

The process is a condensation. Therefore, we need:

$$\Delta_{\text{cond}}H = -\Delta_{\text{vap}}H = -38.6 \text{ kJ/mol} = -3.86 \times 10^4 \text{ J/mol}$$

$$q = \Delta H = n \cdot \Delta_{\text{cond}}H = (3.26 \text{ mol})(-38.6 \text{ kJ/mol}) = -125.8 \text{ kJ}$$

$$w = -p(V_{\text{liq}} - V_{\text{gas}}) \approx +pV_{\text{gas}} = +nRT = (3.26 \text{ mol})(8.31 \times 10^{-3} \text{ kJ/mol} \cdot \text{K})(351 \text{ K}) \\ = +9.51 \text{ kJ} \approx 9.5 \text{ kJ}$$

$$\Delta U = q + w = -125.8 + 9.5 = -116.3 \text{ kJ}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{\Delta H}{T_b} = \frac{-125.8 \text{ kJ}}{351 \text{ K}} = -0.358 \text{ kJ/K} \cdot \frac{10^3 \text{ J}}{1 \text{ kJ}} = -358 \text{ J/K}$$

Note that  $\Delta S$  is negative as expected for a condensation because the entropy of the liquid is lower than the entropy of the gas.

**3.6**  $T_m = -114\text{ }^\circ\text{C} = 159\text{ K}$  ,  $\Delta_{\text{fus}}H = 9.45\text{ kJ/mol}$  ,  $p = 1\text{ bar} = 100\text{ kPa}$  ,  $n = 150\text{ g} \cdot \frac{1\text{ mol}}{46\text{ g}} = 3.26\text{ mol}$

The process is a crystallization. Therefore, we need:

$$\Delta_{\text{crys}}H = -\Delta_{\text{fus}}H = -9.45\text{ kJ/mol} = -9450\text{ J/mol}$$

$$q = \Delta H = n \cdot \Delta_{\text{crys}}H = (3.26\text{ mol})(-9.45\text{ kJ/mol}) = -30.8\text{ kJ}$$

$$w = -p(V_{\text{sol}} - V_{\text{liq}}) \approx 0 \text{ The volumes of liquids and solids are very small and can be ignored.}$$

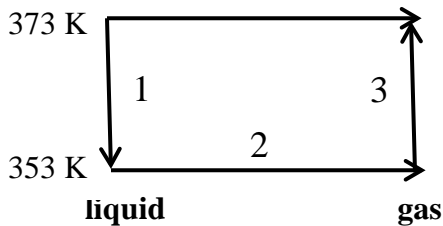
$$\Delta U = q + w = -30.8 + 0 = -30.8\text{ kJ}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{\Delta H}{T_b} = \frac{-30.8\text{ kJ}}{159\text{ K}} = -0.194\text{ kJ/K} \cdot \frac{10^3\text{ J}}{1\text{ kJ}} = -194\text{ J/K}$$

Note that  $\Delta S$  is negative as expected for a crystallization because the entropy of the solid is lower than the entropy of the liquid.

**3.7**  $T_1 = 100\text{ }^\circ\text{C} = 373\text{ K}$  (actual boiling point)

$T_2 = 80\text{ }^\circ\text{C} = 353\text{ K}$  (normal boiling point)



$\Delta S_{\text{sys}}$

We must calculate  $\Delta S_{\text{sys}}$  via a reversible path (see diagram above).

This path is:

- (1) Cool the liquid from  $T_1$  to  $T_2$  (the normal boiling point)
- (2) Vaporize the liquid reversibly at  $T_2$
- (3) Heat the gas back to  $T_1$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = C_{p,m}(l) \ln(T_2/T_1) + \frac{\Delta_{\text{vap}}H(T_2 = 353)}{T_2} + C_{p,m}(g) \ln(T_1/T_2)$$

$$\Delta S = (138.7\text{ J/mol}\cdot\text{K}) \ln(353/373) + \frac{35.7 \times 10^3\text{ J/mol}}{353\text{ K}} + (35.1\text{ J/mol}\cdot\text{K}) \ln(373/353)$$

$$= -7.64\text{ J/mol}\cdot\text{K} + 101.1\text{ J/mol}\cdot\text{K} + 1.93\text{ J/mol}\cdot\text{K}$$

$$= +95.39\text{ J/mol}\cdot\text{K} \approx +95.4\text{ J/mol}\cdot\text{K}$$

## $\Delta S_{\text{surr}}$

We will calculate the entropy change of the surroundings as  $q_{\text{surr}}/T_1(373)$ . However, to determine  $q_{\text{surr}}$ , we will have to know  $\Delta_{\text{vap}}H(T_1=373 \text{ K})$ . We can determine that from the same process (above).

$$\begin{aligned}\Delta_{\text{vap}}H(T_1) &= \Delta H_1 + \Delta H_2 + \Delta H_3 = C_{p,m}(l)[T_2 - T_1] + \Delta_{\text{vap}}H(T_2) + C_{p,m}(g)[T_1 - T_2] \\ \Delta_{\text{vap}}H(T_1) &= (138.7 \text{ J/mol}\cdot\text{K})[353 \text{ K} - 373 \text{ K}] + \Delta_{\text{vap}}H(353 \text{ K}) + (35.1 \text{ J/mol}\cdot\text{K})[373 \text{ K} - 353 \text{ K}] \\ &= -2774 \text{ J/mol} + 35.7 \times 10^3 \text{ J/mol} + 702 \text{ J/mol} \\ &= +33630 \text{ J/mol} \\ \Delta S_{\text{surr}} &= \frac{q_{\text{surr}}}{T_1} = \frac{-q_{\text{sys}}}{T_1} = \frac{-\Delta_{\text{vap}}H(T_1)}{T_1} = \frac{-33630 \text{ J/mol}}{373 \text{ K}} \\ &= -90.16 \text{ J/mol}\cdot\text{K} \approx -90.2 \text{ J/mol}\cdot\text{K}\end{aligned}$$

## $\Delta S_{\text{univ}}$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = +95.4 - 90.2 = +5.2 \text{ J/mol}\cdot\text{K}$$

$\Delta S_{\text{univ}} > 0$  as expected for the spontaneous vaporization of a superheated liquid.

- 3.8**  $n = 3$  moles,  $T_1 = 298 \text{ K}$ ,  $S_m^\circ(298) = 192.45 \text{ J/mol}\cdot\text{K}$ ,  
 $S^\circ(298) = nS_m^\circ(298) = (3 \text{ mol})(192.45 \text{ J/mol}\cdot\text{K}) = 577.35 \text{ J/K}$   
 $S^\circ(T_2) = S^\circ(298) + \Delta S$ ,

$$C_{p,m} = a + bT + \frac{c}{T^2} \quad a = 29.8 \quad , \quad b = 2.5 \times 10^{-2} \quad , \quad c = -1.6 \times 10^5$$

$$\begin{aligned}\Delta S &= \int_{T_1}^{T_2} \frac{nC_{p,m}}{T} dT = \int_{T_1}^{T_2} \frac{n\left(a + bT + \frac{c}{T^2}\right)}{T} dT \\ &= na \int_{T_1}^{T_2} \frac{1}{T} dT + nb \int_{T_1}^{T_2} dT + nc \int_{T_1}^{T_2} \frac{1}{T^3} dT \\ &= na [\ln(T)]_{T_1}^{T_2} + nb [T]_{T_1}^{T_2} - \frac{nc}{2} \left[ \frac{1}{T^2} \right]_{T_1}^{T_2} \\ &= na \ln(T_2/T_1) + nb(T_2 - T_1) - \frac{nc}{2} \left[ \frac{1}{T_2^2} - \frac{1}{T_1^2} \right]\end{aligned}$$

**(a)  $T_2 = 100 \text{ }^\circ\text{C} = 373 \text{ K}$**

$$\begin{aligned}\Delta S &= (3)(29.8) \ln(373/298) + (3)(2.5 \times 10^{-2})(373 - 298) - \frac{(3)(-1.6 \times 10^5)}{2} \left[ \frac{1}{(373)^2} - \frac{1}{(298)^2} \right] \\ &= 23.32 \text{ J/K}\end{aligned}$$

$$S^\circ(T_2) = S^\circ(298) + \Delta S = 577.35 + 23.32 = 600.67 \approx 601 \text{ J/mol}\cdot\text{K}$$

(b)  $T_2 = 500\text{ }^\circ\text{C} = 773\text{ K}$

$$\Delta S = (3)(29.8)\ln(773/298) + (3)(2.5 \times 10^{-2})(773 - 298) - \frac{(3)(-1.6 \times 10^5)}{2} \left[ \frac{1}{(773)^2} - \frac{1}{(298)^2} \right]$$
$$= 118.53\text{ J/mol}\cdot\text{K}$$

$$S^\circ(T_2) = S^\circ(298) + \Delta S = 577.35 + 118.53 = 695.88 \approx 696\text{ J/mol}\cdot\text{K}$$

3.9  $T_1 = 600\text{ }^\circ\text{C} = 873\text{ K}$  ,  $n = 100\text{ g} \cdot \frac{1\text{ mol}}{38\text{ g}} = 2.63\text{ mol}$  ,  $p_1 = 2\text{ bar} \cdot \frac{100\text{ kPa}}{1\text{ bar}} = 200\text{ kPa}$

$$C_{p,m} = a - \frac{b}{T} \quad a = 39.6\text{ J/mol}\cdot\text{K} \quad \text{and} \quad b = 2.5 \times 10^3\text{ J/mol}$$

$$C_{v,m} = C_{p,m} - R = a - \frac{b}{T} - R = (a - R) - \frac{b}{T} = a' - \frac{b}{T} \quad a' = a - R = 39.6 - 8.31 = 31.3\text{ J/mol}\cdot\text{K}$$

$$V_1 = \frac{nRT_1}{p_1} = \frac{(2.63\text{ mol})(8.31\text{ kPa}\cdot\text{L/mol}\cdot\text{K})(873\text{ K})}{200\text{ kPa}} = 95.4\text{ L}$$

(a) **Cool at constant pressure**

$$T_2 = 300\text{ }^\circ\text{C} = 573\text{ K}$$

$$\Delta U = \int_{T_1}^{T_2} nC_{v,m}dT = n \int_{T_1}^{T_2} \left( a' - \frac{b}{T} \right) dT = na'[T]_{T_1}^{T_2} - nb[\ln(T)]_{T_1}^{T_2}$$
$$= na'[T_2 - T_1] - nb \ln(T_2/T_1)$$
$$= (2.63\text{ mol})(31.3\text{ J/mol}\cdot\text{K})[573\text{ K} - 873\text{ K}] - (2.63\text{ mol})(2.5 \times 10^3\text{ J/mol}) \ln(573/873)$$
$$= -24700\text{ J} + 2770\text{ J} = -21930\text{ J} \approx -21.9\text{ kJ}$$

$$\Delta H = \int_{T_1}^{T_2} nC_{p,m}dT = n \int_{T_1}^{T_2} \left( a - \frac{b}{T} \right) dT = na[T]_{T_1}^{T_2} - nb[\ln(T)]_{T_1}^{T_2}$$
$$= na[T_2 - T_1] - nb \ln(T_2/T_1)$$
$$= (2.63\text{ mol})(39.6\text{ J/mol}\cdot\text{K})[573\text{ K} - 873\text{ K}] - (2.63\text{ mol})(2.5 \times 10^3\text{ J/mol}) \ln(573/873)$$
$$= -31240\text{ J} + 2770\text{ J} = -28470\text{ J} \approx -28.5\text{ kJ}$$

$$q = \Delta H = -28.5\text{ kJ} \quad (\text{because } p = \text{constant})$$

$$w = \Delta U - q = -21.9 - (-28.5) = +6.6\text{ kJ}$$

$$\begin{aligned}
\Delta S &= \int_{T_1}^{T_2} \frac{nC_{p,m}}{T} dT = n \int_{T_1}^{T_2} \left( \frac{a}{T} - \frac{b}{T^2} \right) dT = na [\ln T]_{T_1}^{T_2} - nb \left[ -\frac{1}{T} \right]_{T_1}^{T_2} \\
&= na \ln(T_2 / T_1) + nb \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \\
&= (2.63 \text{ mol})(39.6 \text{ J / mol} \cdot \text{K}) \ln(573 / 873) + (2.63 \text{ mol})(2.5 \times 10^3 \text{ J / mol}) \left[ \frac{1}{573 \text{ K}} - \frac{1}{873 \text{ K}} \right] \\
&= -43.85 \text{ J / K} + 3.94 \text{ J / K} \approx -39.9 \text{ J / K}
\end{aligned}$$

**(b) Cool at constant volume**

$$T_2 = 300 \text{ }^\circ\text{C} = 573 \text{ K}$$

$$\Delta U = \int_{T_1}^{T_2} nC_{v,m} dT \approx -21.9 \text{ kJ} \quad \text{See part (a)}$$

$$\Delta H = \int_{T_1}^{T_2} nC_{p,m} dT \approx -28.5 \text{ kJ} \quad \text{See part (a)}$$

$$w = 0 \quad (\text{because } V = \text{constant})$$

$$q = \Delta U = -21.9 \text{ kJ} \quad (\text{because } V = \text{constant})$$

$$\begin{aligned}
\Delta S &= \int_{T_1}^{T_2} \frac{nC_{v,m}}{T} dT = n \int_{T_1}^{T_2} \left( \frac{a'}{T} - \frac{b}{T^2} \right) dT = na' [\ln T]_{T_1}^{T_2} - nb \left[ -\frac{1}{T} \right]_{T_1}^{T_2} \\
&= na' \ln(T_2 / T_1) + nb \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \\
&= (2.63 \text{ mol})(31.3 \text{ J / mol} \cdot \text{K}) \ln(573 / 873) + (2.63 \text{ mol})(2.5 \times 10^3 \text{ J / mol}) \left[ \frac{1}{573 \text{ K}} - \frac{1}{873 \text{ K}} \right] \\
&= -34.66 \text{ J / K} + 3.94 \text{ J / K} \approx -30.7 \text{ J / K}
\end{aligned}$$

(c) Isothermal Compression to  $p_2 = 5 \text{ bar}$

$$T = T_1 = 600 \text{ }^\circ\text{C} = 873 \text{ K}$$

$$\Delta U = \int_{T_1}^{T_1} nC_{V,m}dT = 0$$

$$\Delta H = \int_{T_1}^{T_1} nC_{p,m}dT = 0$$

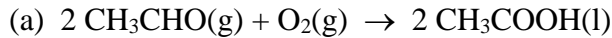
$$\text{Isothermal: } p_2V_2 = p_1V_1 \rightarrow \frac{V_2}{V_1} = \frac{p_1}{p_2} = \frac{2 \text{ bar}}{5 \text{ bar}} = 0.40$$

$$w = -nRT \ln(V_2/V_1) = -(2.63 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})(873 \text{ K}) \ln(0.40) \\ = +17,500 \text{ J} = 17.5 \text{ kJ}$$

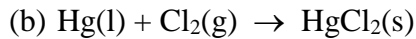
$$q = \Delta U - w = 0 - w = -17.5 \text{ kJ}$$

$$\Delta S = nR \ln(V_2/V_1) = (2.63 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K}) \ln(0.40) = -20.0 \text{ J/K}$$

3.10



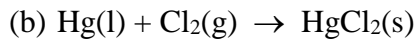
$$\Delta_r S^\circ = [2 S_m^\circ(\text{CH}_3\text{COOH})] - [2 S_m^\circ(\text{CH}_3\text{CHO}) + 1 S_m^\circ(\text{O}_2)] \\ = [(2 \text{ mol})(159.8 \text{ J/mol}\cdot\text{K})] - [(2 \text{ mol})(250.3 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol})(205.1 \text{ J/mol}\cdot\text{K})] \\ = -386.1 \text{ J/K}$$



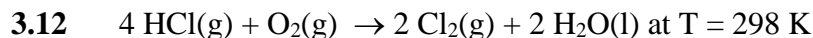
$$\Delta_r S^\circ = [1 S_m^\circ(\text{HgCl}_2)] - [1 S_m^\circ(\text{Hg}) + 1 S_m^\circ(\text{Cl}_2)] \\ = [(1 \text{ mol})(146.0 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol})(76.0 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol})(223.1 \text{ J/mol}\cdot\text{K})] \\ = -153.1 \text{ J/K}$$

3.11 (a)  $2 \text{ CH}_3\text{CHO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{ CH}_3\text{COOH}(\text{l})$

$$\Delta_r G^\circ = [2 \Delta_f G_m^\circ(\text{CH}_3\text{COOH})] - [2 \Delta_f G_m^\circ(\text{CH}_3\text{CHO}) + 1 \Delta_f G_m^\circ(\text{O}_2)] \\ = [(2 \text{ mol})(-389.9 \text{ kJ/mol})] - [(2 \text{ mol})(-128.9 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] \\ = -522.0 \text{ kJ}$$



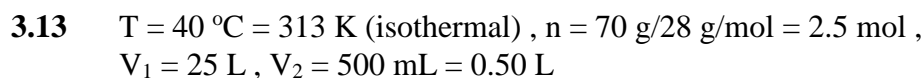
$$\Delta_r G^\circ = [1 \Delta_f G_m^\circ(\text{HgCl}_2)] - [1 \Delta_f G_m^\circ(\text{Hg}) + 1 \Delta_f G_m^\circ(\text{Cl}_2)] \\ = [(1 \text{ mol})(-178.6 \text{ kJ/mol})] - [(1 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] \\ = -178.6 \text{ kJ}$$



$$\begin{aligned}\Delta_r S^\circ &= [2 S_m^\circ(\text{Cl}_2) + 2 S_m^\circ(\text{H}_2\text{O})] - [4 S_m^\circ(\text{HCl}) + 1 S_m^\circ(\text{O}_2)] \\ &= [(2 \text{ mol})(69.9 \text{ J/mol} \cdot \text{K}) + (2 \text{ mol})(223.1 \text{ J/mol} \cdot \text{K})] \\ &\quad - [(4 \text{ mol})(186.9 \text{ J/mol} \cdot \text{K}) + (1 \text{ mol})(205.1 \text{ J/mol} \cdot \text{K})] \\ &= -366.7 \text{ J/K} = -0.3667 \text{ kJ/K}\end{aligned}$$

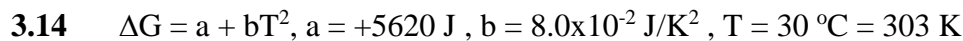
$$\begin{aligned}\Delta_r H^\circ &= [2 \Delta_f H^\circ(\text{Cl}_2) + 2 \Delta_f H^\circ(\text{H}_2\text{O})] - [4 \Delta_f H^\circ(\text{HCl}) + 1 \Delta_f H^\circ(\text{O}_2)] \\ &= [(2 \text{ mol})(0 \text{ kJ/mol}) + (2 \text{ mol})(-285.8 \text{ kJ/mol})] \\ &\quad - [(4 \text{ mol})(-92.3 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] \\ &= -202.4 \text{ kJ}\end{aligned}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = -202.4 \text{ kJ} - (298 \text{ K})(-0.3667 \text{ kJ/K}) = -93.1 \text{ kJ}$$



Because  $T = \text{constant}$ ,  $p_2 V_2 = p_1 V_1 \rightarrow p_2 / p_1 = V_1 / V_2 = 25 / 0.50 = 50$ .

$$\Delta G = nRT \ln(p_2 / p_1) = (2.5 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(313 \text{ K}) \ln(50) = 25,440 \text{ J} \approx 25.4 \text{ kJ}$$

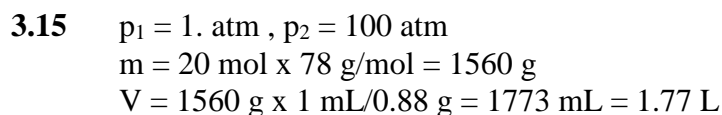


$$dG = -SdT + Vdp = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

$$\text{Therefore: } S = -\left(\frac{\partial G}{\partial T}\right)_p$$

$$\text{For a reaction (process), this can be written as: } \Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_p$$

$$\text{Therefore, } \Delta S = -\left(\frac{\partial [a + bT^2]}{\partial T}\right)_p = 0 - 2bT = -2(8.0 \times 10^{-2} \text{ J/K}^2)(303 \text{ K}) = -48.5 \text{ J/K}$$



$$\Delta G = \int_{p_1}^{p_2} V dp = V(p_2 - p_1) \quad [\text{For solid or liquid, } V \approx \text{constant}]$$

$$\Delta G = (1.77 \text{ L})(100 \text{ atm} - 1 \text{ atm}) = 175.2 \text{ L} \cdot \text{atm} \frac{101 \text{ J}}{1 \text{ L} \cdot \text{atm}} = 1.77 \times 10^4 \text{ J} = 17.7 \text{ kJ}$$



**3.16**  $n = 20 \text{ mol}$  ,  $T = 298 \text{ K}$  ,  $p_1 = 1 \text{ atm}$  ,  $p_2 = 100 \text{ atm}$

$$\begin{aligned}\Delta G &= \int_{p_1}^{p_2} V dp = \int_{p_1}^{p_2} \frac{nRT}{p} dp = nRT \ln(p_2 / p_1) \\ &= (20. \text{mol})(8.31 \text{ J} / \text{mol} \cdot \text{K})(298 \text{ K}) \ln(100 / 1) = 2.28 \times 10^5 \text{ J} = 228 \text{ kJ}\end{aligned}$$

**Note:** It is not surprising that  $\Delta G$  for the pressure increase in  $\text{H}_2(\text{g})$  is much greater than for  $\text{C}_6\text{H}_6(\text{l})$  because the volumes of gases are much greater than the volumes of liquids (and solids).

**3.17**  $\Delta G^\circ = 6.0 \times 10^3 \text{ J/mol} = 6.0 \times 10^3 \text{ kPa} \cdot \text{L/mol}$        $\Delta V_m = -15 \text{ mL/mol} = -1.5 \times 10^{-2} \text{ L/mol}$

At equilibrium:  $\Delta G = \Delta G^\circ + \Delta V_m (p - p^\circ) = 0$

$$(p - p^\circ) = -\frac{\Delta G^\circ}{\Delta V_m} = -\frac{6 \times 10^3 \text{ kPa} \cdot \text{L} / \text{mol}}{-1.5 \times 10^{-2} \text{ L} / \text{mol}} = 4.0 \times 10^5 \text{ kPa}$$

$$p = 4.0 \times 10^5 \text{ kPa} + p^\circ = 4.0 \times 10^5 \text{ kPa} + 100 \text{ kPa} = 4.0 \times 10^5 \text{ kPa} \times 1 \text{ bar} / 100 \text{ kPa} = 4,000 \text{ bar}.$$