

Chapter 3

[3.1] Prove that PV^γ is constant for an ideal gas. The process is adiabatic.
Let $\gamma = C_p/C_v$.

Solution

$$dU = \delta Q - \delta W = -PdV$$

$$\delta Q = 0$$

$$\text{Let } U = f(V, T) \Rightarrow dU \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

Since $U = f(T)$ only for an ideal gas, $\left(\frac{\partial U}{\partial V} \right)_T = 0$ hence

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT. \text{ At constant volume, } dU = C_v dT \text{ thus}$$

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT = C_v dT = -PdV.$$

$$PV = RT \Rightarrow T = \frac{PV}{R} \text{ and}$$

$$dT = \frac{1}{R} d(PV) = \frac{1}{R} (PdV + VdP). \text{ Expanding,}$$

$$C_v \left[\frac{1}{R} (PdV + VdP) \right] = -PdV$$

$$C_v PdV + C_v VdP = -RPdV$$

$$C_v PdV + RPdV = -C_v VdP$$

$$PdV(C_v + R) = -C_v VdP.$$

$$\text{Since } C_p - C_v = R,$$

$$C_p PdV = -C_v VdP \Rightarrow C_p \frac{dV}{V} = -C_v \frac{dP}{P}.$$

$$C_p \int_{V_1}^{V_2} \frac{dV}{V} = -C_v \int_{P_1}^{P_2} \frac{dP}{P} \Rightarrow C_p \ln \left(\frac{V_2}{V_1} \right) = -C_v \ln \left(\frac{P_2}{P_1} \right).$$

$$\text{Hence, } \ln \left(\frac{V_2}{V_1} \right)^{C_p} = \ln \left(\frac{P_2}{P_1} \right)^{-C_v} \text{ thus}$$

$$\frac{(P_2)^{-C_v}}{(P_1)^{-C_v}} = \frac{V_2^{C_p}}{V_1^{C_p}} \Rightarrow \frac{P_1^{C_v}}{P_2^{C_v}} = \frac{V_2^{C_p}}{V_1^{C_p}} \text{ hence}$$

$$P_1^{C_v} V_1^{C_p} = P_2^{C_v} V_2^{C_p} \text{ or}$$

$$(P_1^{C_v} V_1^{C_p})^{1/C_v} = (P_2^{C_v} V_2^{C_p})^{1/C_v}$$

$$P_1 (V_1)^{C_p/C_v} = P_2 (V_2)^{C_p/C_v}, \text{ Letting } \gamma = C_p/C_v,$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma \text{ hence}$$

$$\underline{PV^\gamma = \text{constant.}}$$

[3.2] Compute the standard entropy of formation for the reaction $2H_2(g) + S_2(g) \rightarrow 2H_2S(g)$ from 300 to 800 K in 100 K increments. Plot the entropy as a function of temperature. What is the significance of the plot?

Solution

$$\begin{aligned} \underline{S_2(g)}: S_{T,S_2(g)}^0 [J/(mol \cdot K)] &= S_{298,S_2(g)}^0 + (S_{T,S_2(g)}^0 - S_{298,S_2(g)}^0) \\ &= 228.17 + \int_{298}^T \frac{C_p^{S_2(g)} dT}{T} \\ &= 228.17 + \int_{298}^T (47.069 - 3.4459 \times 10^{-3} T + 6.9404 \times 10^{-7} T^2 \\ &\quad - 2.3124 \times 10^2 T^{-0.5} - 2.2639 \times 10^4 T^{-2}) dT / T \\ &= 228.17 + 47.069 \ln\left(\frac{T}{298}\right) - 3.4459 \times 10^{-3} (T - 298) \\ &\quad + 3.4702 \times 10^{-7} (T^2 - 298^2) \\ &\quad + 4.6248 \times 10^2 \left(\frac{1}{\sqrt{T}} - \frac{1}{\sqrt{298}}\right) + 1.1320 \times 10^4 \left(\frac{1}{T^2} - \frac{1}{298^2}\right). \end{aligned}$$

Substituting for T in the above expression for $S_{T,S_2(g)}^0$,

For $S_2(g)$:

$$\begin{array}{ll} (1 \text{ mol}) S_{300K,S_2(g)}^0 = 228.39 \text{ J/K} & (1 \text{ mol}) S_{600K,S_2(g)}^0 = 252.16 \text{ J/K} \\ (1 \text{ mol}) S_{400K,S_2(g)}^0 = 237.98 & (1 \text{ mol}) S_{700K,S_2(g)}^0 = 257.71 \\ (1 \text{ mol}) S_{500K,S_2(g)}^0 = 245.70 & (1 \text{ mol}) S_{800K,S_2(g)}^0 = 262.56 \end{array}$$

$$\begin{aligned} \underline{H_2(g)}: S_{T,H_2(g)}^0 [J/(mol \cdot K)] &= S_{298,H_2(g)}^0 + (S_{T,H_2(g)}^0 - S_{298,H_2(g)}^0) \\ &= 130.68 + \int_{298}^T \frac{C_p^{H_2(g)} dT}{T} \\ &= 130.68 + \int_{298}^T (7.4424 + 11.707 \times 10^{-3} T - 13.899 \times 10^{-7} T^2 \\ &\quad + 4.1017 \times 10^2 T^{-0.5} - 51.041 \times 10^4 T^{-2}) dT / T \\ &= 130.68 + 7.4424 \ln\left(\frac{T}{298}\right) + 11.707 \times 10^{-3} (T - 298) - 6.950 \times 10^{-7} \times \\ &\quad (T^2 - 298^2) - 8.2034 \times 10^2 \left(\frac{1}{\sqrt{T}} - \frac{1}{\sqrt{298}}\right) + 25.521 \times 10^4 \left(\frac{1}{T} - \frac{1}{298^2}\right). \end{aligned}$$

Substituting for T in the above expression for $S_{T,H_2S(g)}^0$,

For $H_2(g)$:

$$\begin{array}{ll} (2 \text{ mol}) S_{300K,H_2(g)}^0 = 261.74 \text{ J/K} & (2 \text{ mol}) S_{600K,H_2(g)}^0 = 302.20 \text{ J/K} \\ (2 \text{ mol}) S_{400K,H_2(g)}^0 = 278.48 & (2 \text{ mol}) S_{700K,H_2(g)}^0 = 311.26 \\ (2 \text{ mol}) S_{500K,H_2(g)}^0 = 291.52 & (2 \text{ mol}) S_{800K,H_2(g)}^0 = 391.12 \end{array}$$

$$\begin{aligned} \underline{H_2S(g)}: S_{T,H_2S(g)}^0 [J/(mol \cdot K)] &= S_{298,H_2S(g)}^0 + (S_{T,H_2S(g)}^0 - S_{298,H_2S(g)}^0) \\ &= 205.80 + \int_{298}^T \frac{C_p^{H_2S(g)} dT}{T} = 205.80 + \int_{298}^T \frac{(29.37 + 15.40 \times 10^{-3} T) dT}{T} \\ &= 205.80 + 29.37 \ln\left(\frac{T}{298}\right) + 15.40 \times 10^{-3} (T - 298). \end{aligned}$$

Substituting for T in the above expression for $S_{T,H_2S(g)}^0$,

For $H_2S(g)$:

$$\begin{array}{ll} (2 \text{ mol}) S_{300K,H_2S(g)}^0 = 412.06 \text{ J/K} & (2 \text{ mol}) S_{600K,H_2S(g)}^0 = 462.00 \text{ J/K} \\ (2 \text{ mol}) S_{400K,H_2S(g)}^0 = 432.04 & (2 \text{ mol}) S_{700K,H_2S(g)}^0 = 474.14 \\ (2 \text{ mol}) S_{500K,H_2S(g)}^0 = 448.22 & (2 \text{ mol}) S_{800K,H_2S(g)}^0 = 485.06 \end{array}$$

$$\underline{2H_2(g) + S_2(g) \rightarrow 2H_2S(g)}: \Delta S^{0,f} = 2S_{H_2S(g)}^0 - S_{S_2(g)}^0 - 2S_{H_2(g)}^0$$

$$T = 300\text{K} : \Delta S^{o,f} = -78.07 \text{ J/K}$$

$$400\text{K} : \Delta S^{o,f} = -84.42$$

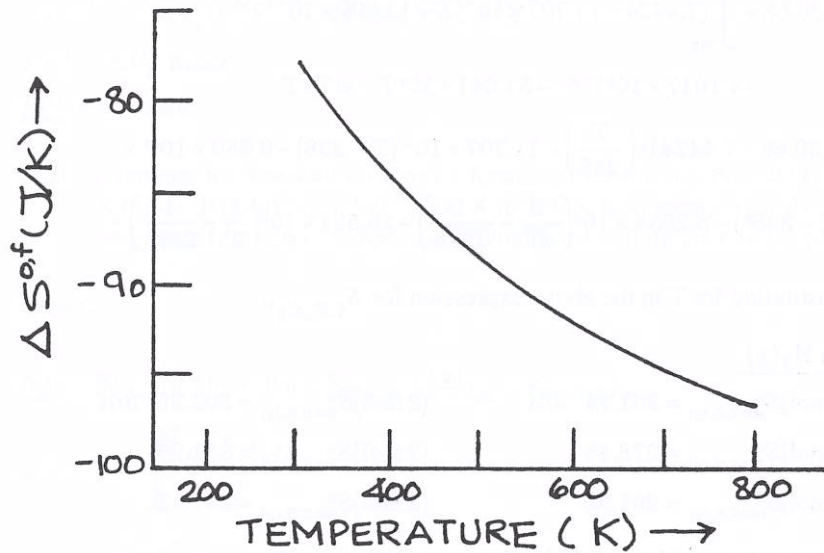
$$500\text{K} : \Delta S^{o,f} = -89.00$$

$$600\text{K} : \Delta S^{o,f} = -92.36 \text{ J/K}$$

$$700\text{K} : \Delta S^{o,f} = -94.83$$

$$800\text{K} : \Delta S^{o,f} = -96.62$$

$\Delta S^{o,f}_{\text{Reaction}}$ VS T (K)



The plot shows that $\Delta S^{o,f}(\text{reaction})$ decreases as the temperature increases (since $V_{\text{product}} < V_{\text{reactants}}$). The volume effect on $\Delta S^{o,f}$ becomes less dominant.

- [3.3] Compute the standard molar volume change for the reaction in Exercise Problem [3.2] from 300 K to 800 K in 100 degree increments. Plot the entropy change of the reaction as a function of molar volume change. What is the significance of the plot?

Solution

Assuming ideal gas,

$$PV^o = RT \Rightarrow V^o = \frac{RT}{P} \text{ where } V^o \text{ is standard molar volume of an ideal gas.}$$

$$= \frac{82.057 \text{ cm}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}} \left(\frac{T}{1 \text{ atm}} \right)$$

$$= \frac{82.057 \text{ cm}^3}{\text{mol} \cdot \text{K}} (T)$$

$$T = 300\text{K} : V^o = \frac{82.057 \text{ cm}^3}{\text{mol} \cdot \text{K}} (300 \text{ K}) = 24,617.1 \frac{\text{cm}^3}{\text{mol}}$$

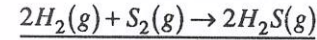
$$400\text{K} : V^o = 82.057(400) = 32,823$$

$$500\text{K} : V^o = 82.057(500) = 41,029$$

$$600\text{K} : V^o = 82.057(600) = 49,234$$

$$700\text{K} : V^o = 82.057(700) = 57,440$$

$$800\text{K} : V^o = 82.057(800) = 65,646$$



$$\Delta V^o = 2V^o_{\text{H}_2\text{S}(\text{g})} - 2V^o_{\text{H}_2(\text{g})} - (1)V^o_{\text{S}_2(\text{g})}$$

$$300\text{K} : \Delta V^o = -24,617 \text{ cm}^3/\text{mol}$$

$$400\text{K} : \Delta V^o = -32,823$$

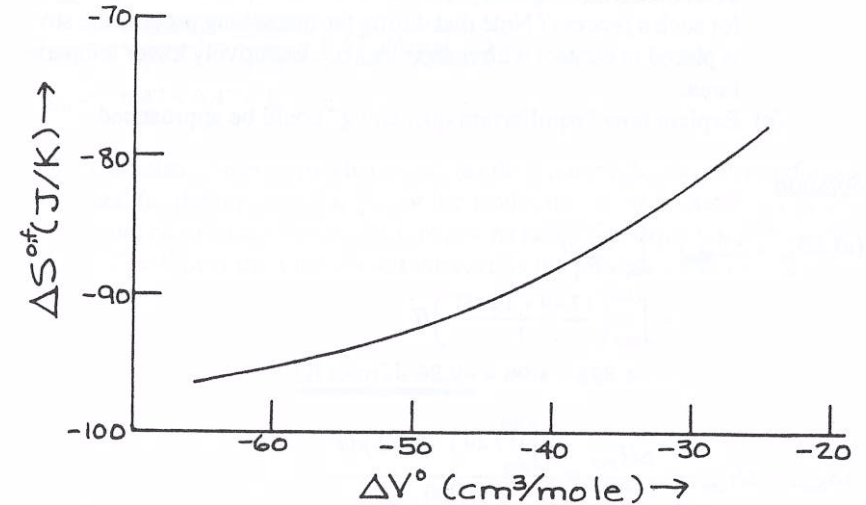
$$500\text{K} : \Delta V^o = -41,029$$

$$600\text{K} : \Delta V^o = -49,234 \text{ cm}^3/\text{mol}$$

$$700\text{K} : \Delta V^o = -57,440$$

$$800\text{K} : \Delta V^o = -65,646$$

$\Delta S^{o,f}_{\text{Reaction}}$ VS $\Delta V^o_{\text{Reaction}}$



The plot shows that $\Delta S^{o,f}(\text{reaction})$ decreases as $\Delta V^o(\text{reaction})$ decreases. This is consistent with the reduction in volume associated with the reaction as it proceeds in the direction indicated.

- [3.4] Use the entropy criteria to prove that liquid tantalum will solidify if the surroundings are at 20°C. Assume that the melt does not supercool.

Solution

$$Ta(s) \xrightarrow[T^f = 2980^\circ C]{\Delta H_f^f = 24,588} Ta(l)$$

For solidification, $\Delta H = -\Delta H^f$, hence

$$\Delta S_{Sys} = \frac{-24,588}{2980 + 273} = -7.56 \text{ J/mol}$$

$$\Delta S_{Surr} = \frac{24,588}{20 + 273} = 83.92$$

$$\Delta S_{Net} = -7.56 + 83.92 = \underline{76.36 \text{ J/(mol} \cdot \text{K)}} > 0 \text{ hence, Ta will solidify.}$$

[3.5] One mole of low carbon steel at 900 K is quenched and held in contact with a large reservoir of liquid lead at 700 K.

- (a) What is ΔS for the steel, for the reservoir, and for the universe (ΔS_{Net})? Use $C_p^{Fe(\alpha)}$ and assume that the reservoir is sufficiently large to maintain constant temperature.
- (b) If the steel had been quenched to an intermediate temperature of 800 K, then subsequently quenched to 700 K, what would ΔS_{Net} be for such a process? Note that during the quenching process the steel is placed in contact with reservoirs at consecutively lower temperatures.
- (c) Explain how “equilibrium quenching” could be approached.

Solution

$$\begin{aligned} \text{(a) } \Delta S_{Sys} = \Delta S_{Steel} &= \int_{T_1}^{T_2} \frac{C_p}{T} dT \\ &= \int_{900}^{700} \left(\frac{17.49 + .0248T}{T} \right) dT \\ &= -4.395 - 4.96 = \underline{-9.36 \text{ J/(mol} \cdot \text{K)}} \end{aligned}$$

$$\begin{aligned} \Delta S_{Surr} = \Delta S_{Res} &= -\frac{\Delta H_{Sys}}{T} = \frac{-\int_{900}^{700} (17.49 + .0248T) dT}{700} \\ &= 4.997 + 5.669 = \underline{10.67 \text{ J/(mol} \cdot \text{K)}} \end{aligned}$$

$$\Delta S_{Net} = \Delta S_{Univ} = \Delta S_{Sys} + \Delta S_{Surr} = -9.36 + 10.67 = \underline{1.31 \text{ J/(mol} \cdot \text{K)}}$$

$$\begin{aligned} \text{(b) } \Delta S_{Sys} &= \int_{900}^{800} \frac{(17.49 + .0248T)}{T} dT + \int_{800}^{700} \frac{(17.49 + .0248T)}{T} dT \\ &= -2.06 - 2.335 - 4.96 \approx -9.35 \end{aligned}$$

$$\begin{aligned} \Delta S_{Surr} &= \frac{\int_{900}^{800} (17.49 + .0248T) dT}{800} - \frac{\int_{800}^{700} (17.49 + .0248T) dT}{700} \\ &= 2.186 + 2.635 + 2.499 + 2.657 \approx 9.98 \\ \Delta S_{Net} = \Delta S_{Sys} + \Delta S_{Surr} &= -9.35 + 9.98 = \underline{0.63 \text{ J/(mol} \cdot \text{K)}} \end{aligned}$$

(c) From a) and b), it is noted that one intermediate quenching reduces ΔS_{Net} by more than 0.6 J/(mol · K). By quenching through an infinite number of intermediate temperatures, equilibrium quenching ($\Delta S_{Net} = 0$) could be achieved. In practice, this is an impossible process. Likewise, there is no practical reason to achieve “equilibrium quenching” since the objective in quenching is to obtain a non-equilibrium microstructure.

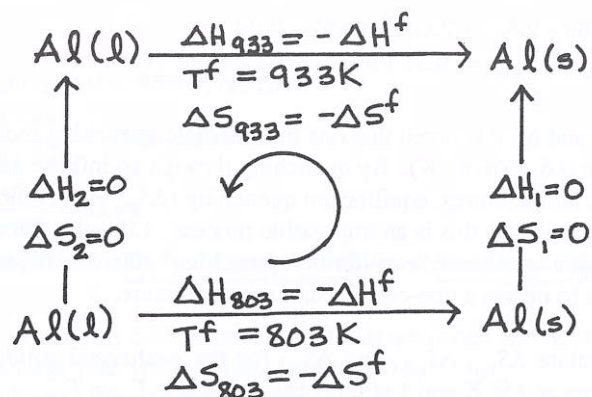
[3.6] Calculate ΔS_{Sys} , ΔS_{Surr} , and ΔS_{Net} for the isothermal solidification of lithium at 453 K and 1 atm pressure. Assume $T_{Sys} = T_{Surr}$.

Solution

$$\begin{aligned} \Delta S_{Sys} &= \frac{-\Delta H^f}{T^f} = \frac{-2929}{453} = \underline{-6.47 \text{ J/(mol} \cdot \text{K)}} \\ \Delta S_{Surr} &= \frac{-(-\Delta H^f)}{T^f} = \frac{2929}{453} = \underline{6.47 \text{ J/(mol} \cdot \text{K)}} \\ \Delta S_{Net} &= -6.47 + 6.47 = \underline{0}. \end{aligned}$$

[3.7] Calculate the entropy change of: (a) the system, (b) the surroundings, and (c) the universe (ΔS_{Net}) for the isothermal solidification of 1 gram atom of Al supercooled 130°C below its normal freezing point. Assume $\Delta C_p = 0$ over the supercooled interval. Is the process spontaneous?

Solution

 (1) Set Up Applying one loop for ΔH and ΔS :

 (2) Sum

$$\Sigma \Delta H_{TL} = 0 = \Delta H_{803} + \Delta H_1 - \Delta H_{933} - \Delta H_2$$

$$\Delta H_{803} = \Delta H_{933} = -10,461 \text{ J/mol}$$

$$\Sigma \Delta S_{TL} = 0 = \Delta S_{803} + \Delta S_1 - \Delta S_{933} - \Delta S_2$$

$$\Delta S_{803} = \Delta S_{933}$$

 (3) & (4) Substitute/Solve

$$(a) \Delta S_{Sys} = \Delta S_{803} = \frac{-10,461}{933} = \underline{\underline{-11.21 \text{ J/(mol} \cdot \text{K)}}}$$

$$(b) \Delta S_{Surr} = \frac{-(-10,461)}{803} = \underline{\underline{13.03 \text{ J/(mol} \cdot \text{K)}}}$$

$$(c) \Delta S_{Net} = \Delta S_{Sys} + \Delta S_{Surr} = -11.21 + 13.03 \\ = \underline{\underline{1.82 \text{ J/(mol} \cdot \text{K)} > 0 \Rightarrow \text{spontaneous.}}}$$

 [3.8] Repeat Exercise Problem [3.7] using heat capacity data from Appendix A, Table A.3A. What is the percent error in ΔS_{Net} assuming $\Delta C_p = 0$?

Solution

Referring to the loop in Exercise Problem [3.7],

$$\Sigma \Delta H_{TL} = 0 = \Delta H_{803} + \Delta H_1 - \Delta H_{933} - \Delta H_2$$

$$\Delta H_{Sys} = \Delta H_{803} = \Delta H_{933} - \Delta H_1 + \Delta H_2$$

$$= -10,461 - \int_{803}^{933} (20.67 + 12.39 \times 10^{-3} T) dT + \int_{803}^{933} 29.29 dT$$

$$= -10,461 - 5483 + 3808 = -12,136 \text{ J/mol}$$

$$\Sigma \Delta S_{TL} = 0 = \Delta S_{803} + \Delta S_1 - \Delta S_{933} - \Delta S_2$$

$$\Delta S_{803} = \Delta S_{933} - \Delta S_1 + \Delta S_2$$

$$(a) \Delta S_{Sys} = \Delta S_{803} = -11.21 - \int_{803}^{933} \frac{(20.67 + 12.39 \times 10^{-3} T)}{T} dT + \int_{803}^{933} 29.29 \frac{dT}{T} \\ = -11.21 - 4.71 + 4.39 = \underline{\underline{-11.53 \text{ J/(mol} \cdot \text{K)}}}$$

$$(b) \Delta S_{Surr} = \frac{12,136}{803} = \underline{\underline{15.11 \text{ J/(mol} \cdot \text{K)}}}$$

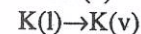
$$(c) \Delta S_{Net} = -11.53 + 15.11 = \underline{\underline{3.58 \text{ J/(mol} \cdot \text{K)} > 0 \Rightarrow \text{spontaneous}}}$$

$$\% \text{ Error} = \frac{3.58 - 1.82}{1.82} \times 100 \approx \underline{\underline{100\%}}$$

[3.9] Calculate the entropy change for the vaporization of potassium at 950 K and 0.447 bar. Illustrate calculations using two methods.

Solution

Method (1)



$$\Delta S^{l \rightarrow v} = S_v - S_l = 4.8129 - 2.7313$$

$$\approx \underline{\underline{2.08 \text{ kJ/(kg} \cdot \text{K)}}}$$

Method (2)

$$\Delta S^{l \rightarrow v} = \frac{h_v - h_l}{950} = \frac{2750.4 - 771.4}{950}$$

$$\approx \underline{\underline{2.08 \text{ kJ/(kg} \cdot \text{K)}}}$$

[3.10] Use the entropy criteria to confirm that liquid and potassium vapor are in equilibrium at 950 K and 0.447 bar.

Solution

$$\Delta S_{Net} = \Delta S_{Sys} + \Delta S_{Surr}$$

$$= 4.8129 - 2.7313 + \frac{[-(2750.4 - 771.4)]}{950}$$

$$\approx \underline{\underline{0}}$$

- [3.11] A single crystal of the amphibole tremolite at 298 K undergoes a volume expansion of $105.5 \times 10^{-3} \text{ cm}^3/\text{mol}$ during heating at $P^0 = 1 \text{ atm}$.
- Calculate the temperature shift associated with the volume change. Assume $\alpha V_{1\text{atm}, 298\text{K}}$ is constant over the temperature interval.
 - Use the result from (a) to calculate the corresponding change in entropy.

Solution

(a) $P^0 = 1 \text{ atm}, T_1 = 298 \text{ K}$.

$$\alpha V_{1\text{atm}, 298} = \left(\frac{\partial V}{\partial T} \right)_{1\text{atm}} \Rightarrow \alpha V_{1\text{atm}, 298} dT = dV \text{ or}$$

$$\alpha V_{1\text{atm}, 298} (T_2 - T_1) = \Delta V \Rightarrow \Delta T = \frac{\Delta V}{\alpha V_{1\text{atm}, 298}} \text{ or}$$

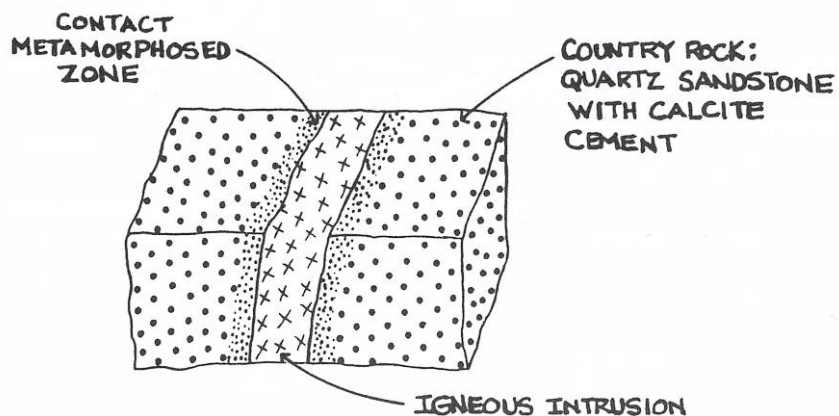
$$\Delta T = \frac{105.5 \times 10^{-3} \text{ cm}^3/\text{mol}}{8.45 \times 10^{-3} \text{ cm}^3/(\text{mol} \cdot \text{K})} = \underline{12.49 \text{ K}}$$

(b) Since $P^0 = 1 \text{ atm}$ is constant, $\Delta S = \int_{T_1}^{T_2} \frac{C_p dT}{T}$
 $\Rightarrow T_2 = 298 \text{ K} + 12.49 \text{ K} = 310.49 \text{ K}$

$$\Delta S = \int_{298}^{310.49} (1.2144 + 2.6528 \times 10^{-5} T - 12,362.0 T^{-2} - 7.3885 T^{-0.5}) \frac{dT}{T}$$

$$= \underline{2.73 \times 10^{-2} \text{ kJ}/(\text{mol} \cdot \text{K})}$$

- [3.12] A quartz sandstone with calcite cement is intruded by molten igneous rock as shown below.



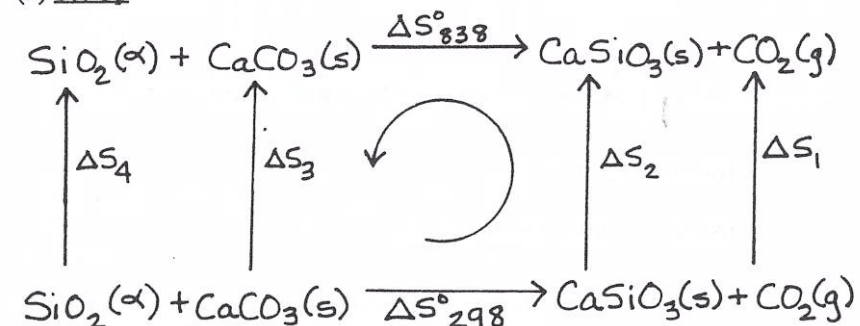
The country rock (sandstone) adjacent to the intrusion undergoes "contact metamorphism" as a consequence of heat transfer from the intrusion. The contact metamorphic reaction is:
 $\text{SiO}_2(s) + \text{CaCO}_3(s) \rightarrow \text{CaSiO}_3(s) + \text{CO}_2(g)$
 $\alpha\text{-Quartz}$ Calcite Wollastonite
 Calculate ΔS^0 for this reaction at 565°C .

Solution

$$\Delta S_{298}^0 = \sum n S_{298}^0(\text{Products}) - \sum n S_{298}^0(\text{Reactants})$$

$$= 82.01 + 213.8 - 41.46 - 88.7 = 165.65 \text{ J}/(\text{mol} \cdot \text{K})$$

(1) Set Up



(2) Sum

$$\sum \Delta S_{TL} = 0 = \Delta S_{298}^0 + \Delta S_1 + \Delta S_2 - \Delta S_{838}^0 - \Delta S_3 - \Delta S_4 \text{ or}$$

$$\Delta S_{838}^0 = \Delta S_{298}^0 + \int_{298}^{838} \frac{\Delta C_p dT}{T} \text{ where } \Delta C_p = \sum n_i C_p^i(\text{Products}) - \sum n_i C_p^i(\text{Reactants})$$

(3) Substitute

$$\Delta C_p = (1)C_p^{\text{CaSiO}_3(s)} + (1)C_p^{\text{CO}_2(g)} - (1)C_p^{\text{SiO}_2(\alpha)} - (1)C_p^{\text{CaCO}_3(s)}$$

The coefficients of C_p are taken from Tables A.3A and A.3B in Appendix A and arranged as follows:

	a	b	c	d	e
$C_p^{CaSiO_3(s)}$	111.25	14.373×10^{-3}	—	0.1694×10^2	-277.79×10^4
$C_p^{CO_2(g)}$	87.820	-2.6442×10^{-3}	—	-9.9886×10^2	70.641×10^4
$-C_p^{SiO_2(s)}$	-44.60	-37.754×10^{-3}	—	—	100.18×10^4
$-C_p^{CaCO_3(s)}$	-99.715	-26.920×10^{-3}	—	—	215.76×10^4
	a=54.755	b = -52.9452×10^{-3}	—	d = -9.8192×10^2	e = 108.791×10^4

Hence, ΔC_p [J/(mol·K)] = $55.295 - 52.9452 \times 10^{-3} T - 9.8192 \times 10^2 T^{-0.5} + 108.791 \times 10^4 T^{-2}$.

(4) Solve

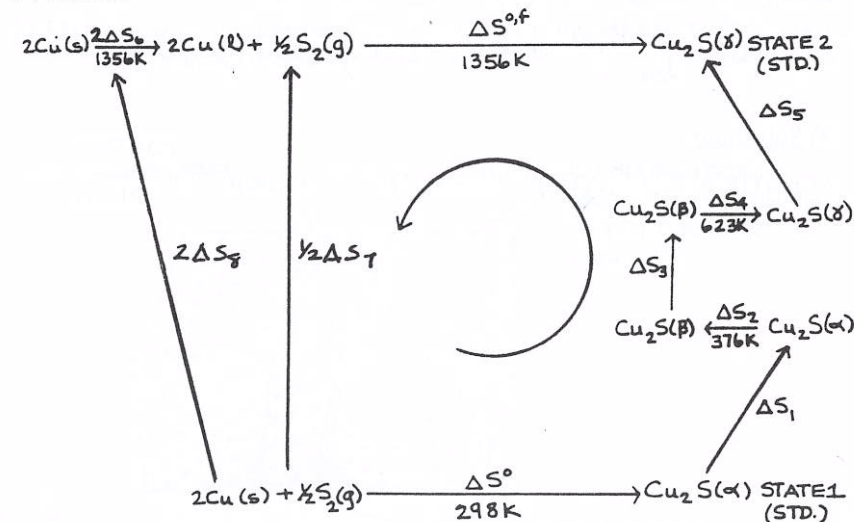
$$\Delta S_{565^\circ C}^o = 165.65 + \int_{298}^{838} (55.295 - 52.9452 \times 10^{-3} T - 9.8192 \times 10^2 T^{-1/2} + 108.791 \times 10^4 T^{-2}) \frac{dT}{T}$$

$$= 165.65 - 11.99 = \underline{154 \text{ J/(mol} \cdot \text{K)}}.$$

[3.13] Calculate the standard entropy of formation for the reaction in Exercise Problem [2.13] at 1356 K.

Solution

(1) Set Up



(2) Sum

$$\sum \Delta S_{TL} = 0 = \Delta S_{298}^o + \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 - \Delta S_{1356}^{o,f} - 2\Delta S_6 - \frac{1}{2} \Delta S_7 - 2\Delta S_8$$

which upon rearranging gives

$$\Delta S_{1356}^{o,f} = \Delta S_{298}^o + \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 - 2\Delta S_6 - \frac{1}{2} \Delta S_7 - 2\Delta S_8.$$

(3) Substitute

The data from Appendix A, Tables A.1, A.2, A.3A, and A.3B is substituted into $\Delta S_{1356}^{o,f}$ above:

$$\Delta S_{1356}^{o,f} = [1 \text{ mol} [120.75 \text{ J/(mol} \cdot \text{K)}] - 0.5 \text{ mol} [228.17 \text{ J/(mol} \cdot \text{K)}] - 2 \text{ mol} [33.15 \text{ J/(mol} \cdot \text{K)}]] + \int_{298}^{376} (1 \text{ mol}) C_p^{Cu_2S(a)} \frac{dT}{T} + \frac{(1 \text{ mol})(3849 \text{ J/mol})}{376 \text{ K}} + \int_{376}^{623} (1 \text{ mol}) C_p^{Cu_2S(\beta)} \frac{dT}{T} + (1 \text{ mol}) \left(\frac{836.8 \text{ J/mol}}{623 \text{ K}} \right) + \int_{623}^{1356} (1 \text{ mol}) C_p^{Cu_2S(a)} \frac{dT}{T} - (2 \text{ mol}) \left(\frac{13.054 \text{ kJ/mol}}{1356 \text{ K}} \right) - \int_{298}^{1356} (0.5 \text{ mol}) C_p^{S_2(g)} \frac{dT}{T} - \int_{298}^{1356} (2 \text{ mol}) C_p^{Cu(s)} \frac{dT}{T}.$$

(4) Solve

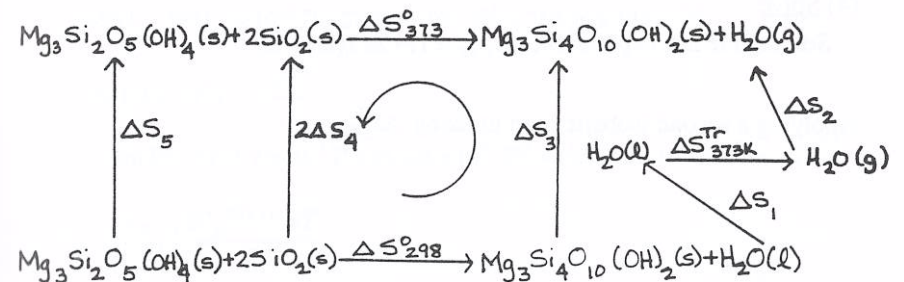
Upon integrating and completing all calculations,

$$\Delta S_{1356K}^{o,f} = \underline{122.2 \text{ J/(mol} \cdot \text{K)}}.$$

[3.14] Calculate the standard entropy change for the reaction in Exercise Problem [2.10] at temperature T where 373 K < T < 800 K. No phase changes occur.

Solution

(1) Set Up



(2) Sum

$$\sum \Delta S_{TL} = 0 = \Delta S_{298}^0 + \Delta S_1 + \Delta S_{373}^{Tr} + \Delta S_2 + \Delta S_3 - \Delta S_{373}^0 - 2\Delta S_4 - \Delta S_5$$

(3) Substitute

$$\Delta S_{298}^0 = \sum nS_{298}^0(\text{Products}) - \sum nS_{298}^0(\text{Reactants}) \\ = 260.83 + 70.09 - 221.3 - 2(41.46) = 26.70 \text{ J/(mol} \cdot \text{K)}$$

$$\Delta S_{373}^{Tr} = \frac{\Delta H^{Tr}}{T^{Tr}} = \frac{41,090}{373} = 110.16 \text{ J/(mol} \cdot \text{K)}$$

$$\Delta S_1 = \int_{298}^{373} \frac{C_p^{H_2O(l)} dT}{T} = \int_{298}^{373} 75.44 \frac{dT}{T} = 16.94$$

$$\Delta S_2 = \int_{373}^{373} \frac{C_p^{H_2O(g)} dT}{T} = 0$$

$$\Delta S_3 = \int_{298}^{373} \frac{C_p^{\text{Calc}} dT}{T} = \int_{298}^{373} (5653.6 - 5271.7 \times 10^{-3} T + 27.291 \times 10^{-7} T^2 - 769.26 \times 10^2 T^{-0.5} \\ + 4021.1 \times 10^4 T^{-2}) \frac{dT}{T} = 9.48$$

$$2\Delta S_4 = \int_{298}^{373} 2C_p^{SiO_2(s)} \frac{dT}{T} = \int_{298}^{373} 2(44.60 + 37.754 \times 10^{-3} T \\ - 10.018 \times 10^5 T^{-2}) \frac{dT}{T} = 21.61$$

$$\Delta S_5 = \int_{298}^{373} \frac{C_p^{\text{Serp}} dT}{T} = \int_{298}^{373} (899.60 - 144.76 \times 10^{-3} T - 109.32 \times 10^2 T^{-0.5} \\ + 449.99 \times 10^4 T^{-2}) \frac{dT}{T} = 65.78$$

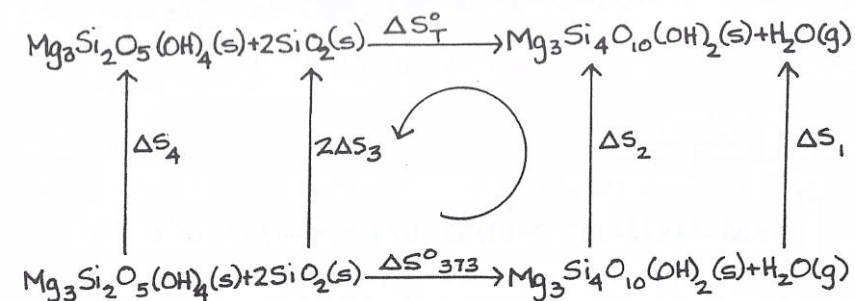
Substituting the above data into the expression for $\sum \Delta S_{TL} = 0$,

$$0 = 70.09 + 16.94 + 110.16 + 9.48 - \Delta S_{373}^0 - 21.61 - 65.78$$

(4) Solve

Solving the last expression, $\Delta S_{373K}^0 = 119.28 \text{ J/(mol} \cdot \text{K)}$.

Applying a second isobaric loop utilizing ΔS_{373K}^0 ,

(1) Set Up(2) Sum

$$\sum \Delta S_{TL} = 0 = \Delta S_{373}^0 + \Delta S_1 + \Delta S_2 - \Delta S_T^0 - 2\Delta S_3 - \Delta S_4$$

(3) Substitute

$$\Delta S_{373}^0 = 194.6 \text{ J/(mol} \cdot \text{K)}$$

$$\Delta S_1 \left(\frac{\text{J}}{\text{mol} \cdot \text{K}} \right) = \int_{373}^T C_p^{H_2O(g)} \frac{dT}{T} =$$

$$\int_{373}^T (7.368 + 27.468 \times 10^{-3} T - 48.117 \times 10^{-7} T^2 + 3.6174 \times 10^2 T^{-0.5} \\ - 22.316 \times 10^4 T^{-2}) \frac{dT}{T}$$

$$= 7.368 \ln(T) + 27.468 \times 10^{-3} T - 24.059 \times 10^{-7} T^2 - 7.2348 \times 10^2 T^{-0.5} \\ + 11.158 \times 10^4 T^{-2} - 17.55$$

$$\Delta S_2 = \int_{373}^T \frac{C_p^{\text{Calc}} dT}{T}$$

$$= \int_{373}^T (5653.6 - 5271.7 \times 10^{-3} T + 27.291 \times 10^{-7} T^2 - 769.26 \times 10^2 T^{-0.5} \\ + 4021.1 \times 10^4 T^{-2}) \frac{dT}{T}$$

$$= 5653.6 \ln(T) - 5271.7 \times 10^{-3} T + 13.646 \times 10^{-7} T^2 + 1538.52 \times 10^2 T^{-0.5} - 7821.83$$

$$2\Delta S_3 = \left(\int_{373}^T \right) \frac{2C_p^{SiO_2(s)} dT}{T}$$

Solution

$$\begin{aligned} \text{(a) } \eta &= \frac{\text{area } 123}{\text{area } a123b} \\ &= \frac{1/2(T_2 - T_1)(S_2 - S_1)}{1/2(T_2 - T_1)(S_2 - S_1) + T_1(S_2 - S_1)} \\ &= \left[\frac{(T_2 - T_1)}{(T_2 - T_1) + 2T_1} \right] \\ &= (T_2 - T_1)/(T_2 + T_1) \end{aligned}$$

$$\eta_{T_2=600K, T_1=300K} = \frac{300}{900} = 0.33 \text{ or } \underline{33\%}$$

$$\eta_{\text{Car}} = \frac{300}{600} = 0.50 \text{ or } \underline{50\%}$$

$$\text{(b) } \eta_{T_2=750K, T_1=300K} = \frac{450}{1050} = 0.43 \text{ or } \underline{43\%}$$

$$\eta_{\text{Car}} = \frac{450}{750} = 0.60 \text{ or } \underline{60\%}.$$

[3.17] The Carnot cycle efficiency is often used as a basis for estimating the effect of increasing operating input temperature and lowering rejection temperature on the efficiency of a power generating process. Curzon and Ahlborn (1975, p. 22-24) have shown that to achieve theoretical Carnot efficiency, heat transfer must take place through an infinitely small temperature differential, which in turn, requires infinite time. They derived the following modification to Carnot efficiency, which takes into account the necessary temperature differential that must exist across the high and low temperature heat transfer boundaries if the cycle is going to be completed in a reasonable time interval:

$$\eta_{\text{C.A.}} = 1 - \sqrt{T_L/T_H}.$$

Using the data given in Exercise Problem [3.16], calculate $\eta_{\text{C.A.}}$ and compare with η and η_{Car} obtained in the same problem.

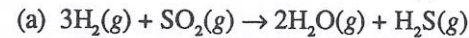
Solution

$$\text{a) } \eta_{\text{C.A.}} = 1 - \sqrt{\frac{300}{600}} = 0.293 \text{ or } \underline{29.3\%}$$

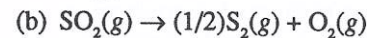
$$\text{b) } \eta_{\text{C.A.}} = 1 - \sqrt{\frac{300}{750}} = 0.293 \text{ or } \underline{36.8\%}$$

A comparison of Carnot efficiencies in Example Problem [3.16] indicates that alloy modification increases predicted efficiency from 50 to 60% because of the higher allowable T_2 . This is a 20% increase ($10/50 \times 100\% = 20\%$). A comparison of Curzon-Ahlborn efficiencies indicates that alloy modification increases predicted efficiency from 29.3 to 36.8% because of the higher allowable T_2 . This is a 25.6% increase ($7.5/29.3 \times 100\% = 25.6\%$). The C.A. equation gives an efficiency which is much closer to the actual value in [3.16] and provides a stronger case for alloy modification.

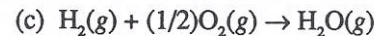
[3.18] A small amount of $\text{H}_2\text{S}(g)$ in volcanic gases promotes intense chemical weathering of rock in the vicinity of a volcanic vent. Calculate the standard entropy of formation associated with the production of $\text{H}_2\text{S}(g)$ from its elements at 600 K and 1 atm in $\text{kJ}/(\text{mol}\cdot\text{K})$ and $\text{cal}/(\text{mol}\cdot\text{K})$.



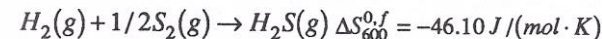
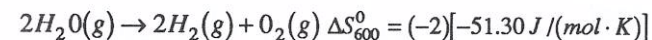
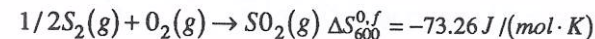
$$\Delta S_{600}^0 = -75.44 \text{ J}/(\text{mol}\cdot\text{K})$$



$$\Delta S_{600}^0 = 73.26 \text{ J}/(\text{mol}\cdot\text{K})$$



$$\Delta S_{600}^{0,f} = -51.30 \text{ J}/(\text{mol}\cdot\text{K})$$

Solution


$$\Delta S_{600}^{0,f} = -46.10 \text{ J}/(\text{mol}\cdot\text{K}) \times 1 \text{ kJ}/1000 \text{ J} = -46.10 \times 10^{-3} \text{ kJ}/(\text{mol}\cdot\text{K}). \text{ Also,}$$

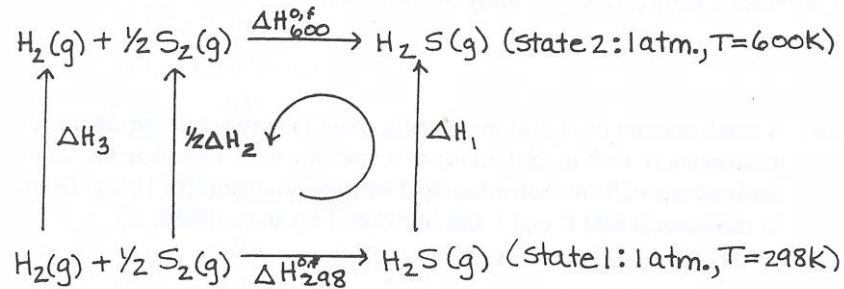
$$\Delta S_{600}^{0,f} = -46.10 \text{ J}/(\text{mol}\cdot\text{K}) \times 1 \text{ cal}/4.184 \text{ J} = -11.02 \text{ cal}/(\text{mol}\cdot\text{K}).$$

$$\Delta S_{600}^{0,f} = \underline{\underline{-46.1 \times 10^{-3} \text{ kJ}/(\text{mol}\cdot\text{K})}} = \underline{\underline{-11.02 \text{ cal}/(\text{mol}\cdot\text{K})}}.$$

[3.19] Show that $\text{H}_2\text{S}(g)$ spontaneously forms at 600 K. Refer to Exercise Problem [3.18]. Assume the surroundings are at 600 K. Use the heat capacity for $\text{S}_2(g)$ in Appendix A, Table A.3B.

Solution

(1) Set Up



(2) Sum

$$\Sigma \Delta H_{TL} = 0 = \Delta H_{298}^{0,f} + \Delta H_1 - \Delta H_{600}^{0,f} - \frac{1}{2}\Delta H_2 - \Delta H_3 \text{ or } \Delta H_{600}^{0,f} = \Delta H_{298}^{0,f} + \Delta H_1 - \frac{1}{2}\Delta H_2 - \Delta H_3$$

(3) & (4) Substitute/Solve Collecting terms and applying [2-16] and [2-17]:

$$\begin{aligned}
 \Delta H_{600}^{0,f} &= -84,872 + \int_{298}^{600} (-1.6069 + 5415.95 \times 10^{-6}T + 1042.88 \times 10^{-9}T^2 \\
 &\quad - 294.55T^{-0.5} + 521,729.5T^{-2})dT \\
 &= -87,936 \text{ J/mol.}
 \end{aligned}$$

$$\begin{aligned}
 \text{At } 600\text{K, } \Delta S_{Net}^0 &= \Delta S_{Sys}^0 + \Delta S_{Surr}^0 = \Delta S_{Sys}^0 + \frac{-\Delta H_{Sys}^0}{T_{Surr}} = -46.1 + \frac{-(-87,936)}{600} \\
 &= \underline{100.5 \text{ J/(mol} \cdot \text{K)} > 0 \Rightarrow \text{spontaneous.}}
 \end{aligned}$$