

Chapter 4

- [4.1] An ideal gas undergoes an isothermal process from an initial State 1: (P_1, V_1, T) to a final State 2: (P_2, V_2, T) . Prove

$$\Delta G_T = RT \ln(P_2/P_1).$$

Solution

$$dG = VdP - SdT, \quad V = RT/P$$

$$\begin{aligned} dG &= \frac{RT}{P} dP \Rightarrow \Delta G_T = RT \int_{P_1}^{P_2} dP/P \\ &= \underline{RT \ln(P_2/P_1)}. \end{aligned}$$

- [4.2] The initial state of one mole of a monatomic ideal gas is $P_1 = 5$ atm and $T_1 = 300$ K. Calculate the entropy change of the gas for:
- an isothermal decrease in pressure to 1 atm.
 - a constant volume decrease in the pressure to 1 atm.

Solution

- (a) Since the process is isothermal and the pressure change is known, use $S = f(P, T)$

$$ds = \left(\frac{\partial S}{\partial P} \right)_T dP + \left(\frac{\partial S}{\partial T} \right)_P dT$$

$$\text{Also, } \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P = R/P$$

$$\Delta S = \int_{S_1}^{S_2} dS = -R \int_5^1 dP/P = -8.3144 \ln(0.2) = \underline{13.38 \text{ J}/(\text{mol} \cdot \text{K})}.$$

- (b) Use $S = f(T, V)$

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

From [3-13],

$$\int_{S_1}^{S_2} dS = \Delta S = C_V \int_{300}^{T_2} dT/T$$

$$\text{Where } T_2 = \frac{P_2}{P_1} T_1 = 1/5 \times 300 = 60$$

$$\begin{aligned} \Delta S &= 3/2R \int_{300}^{60} dT/T \\ &= \underline{\underline{-20.07 \text{ J}/(\text{mol} \cdot \text{K})}}. \end{aligned}$$

[4.3] Prove by two methods that at constant temperature,
 $\Delta H_{\text{isothermal}} = 0$
 for an ideal gas, regardless of the pressure path.

Solution

Method 1

$$\text{Let } H=U+PV$$

$$dH = dU + d(PV)$$

For an ideal gas, $U = f(T)$ only,
 hence $dU = 0$ at constant temperature.

Also, since $PV = RT$,

$d(PV) = d(RT) = 0$. Substituting,

$$\int_{H_1}^{H_2} dH = \underline{\underline{\Delta H = 0}}.$$

Method 2

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

Substituting [3-7],

$$\left(\frac{\partial H}{\partial P}\right)_T dP = T ds + V dP. \text{ Dividing by } dP \text{ and holding } T \text{ constant,}$$

$$(1) \left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V. \text{ Substituting [4-23],}$$

$$(2) \left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P + V. \text{ From the ideal gas equation,}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = R/P. \text{ Substituting into the expression above,}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -TR/P + V = 0. \text{ Hence,}$$

$$\int_{H_1}^{H_2} dH = \underline{\underline{\Delta H = 0}}.$$

[4.4] Prove that at constant temperature,

$$\Delta S'_{\text{isothermal}} = -nR \ln(P_2/P_1)$$

for n moles of an ideal gas.

Solution

Let $S' = f(P, T)$,

$$dS' = \left(\frac{\partial S'}{\partial P}\right)_T dP + \left(\frac{\partial S'}{\partial T}\right)_P dT$$

$$\text{From [4-23], } \left(\frac{\partial S'}{\partial P}\right)_T = -\left(\frac{\partial V'}{\partial T}\right)_P$$

Substituting the last expression into the equation for dS' gives

$$dS' = -\left(\frac{\partial V'}{\partial T}\right)_P dP. \text{ For an ideal gas, } V' = \frac{nRT}{P} \text{ and therefore}$$

$$\left(\frac{\partial V'}{\partial T}\right)_P = \frac{\partial}{\partial T} \left(\frac{nRT}{P}\right)_P = \frac{nR}{P}. \text{ Hence, } dS' = -\frac{nR}{P} dP \Rightarrow \int_{S'_1}^{S'_2} dS' = -nR \int_{P_1}^{P_2} dP/P$$

or

$$\Delta S'_{\text{isothermal}} = \underline{\underline{-nR \ln\left(\frac{P_2}{P_1}\right)}}.$$

[4.5] Calcium boils at 1440°C . The standard free energy of vaporization of liquid calcium is given by

$$\Delta G_T^0 \text{ (cal/mol)} = 41,030 + 5.83T \log(T) - 42.23T,$$

where $\log = \log_{10}$ (personal communication, 1959, R. Schuhmann, Jr., Department of Metallurgical Engineering, Purdue University, West Lafayette, Indiana).

(a) Find the linear Gibbs free energy equation of the form

$$\Delta G_T^0 = a + bT$$

which approximates the above equation as closely as possible near 1500 K.

- (b) Calculate the boiling point from the linear equation and compare with the actual value.

Solution

$$\begin{aligned} \text{(a)} \quad \Delta G^0 &= 41,030 + 5.83T \log(T) - 42.23T \\ &= 41,030 + 2.53T \ln(T) - 42.23T \end{aligned}$$

From [4-25],

$$\left(\frac{\partial \Delta G^0}{\partial T}\right)_P = -\Delta S^0 = 2.53 \left[T \left(\frac{\partial \ln(T)}{\partial T}\right)_P + \ln(T) \left(\frac{\partial T}{\partial T}\right)_P \right] - 42.23$$

$$\begin{aligned} \Delta S^0 &= -2.53[1 + \ln(T)] + 42.23 \\ &= -2.53 \ln(T) - 2.53 + 42.23 \\ &= -2.53 \ln(T) + 39.70 \end{aligned}$$

From [4-30],

$$\begin{aligned} \left[\frac{\partial(\Delta G^0/T)}{\partial T}\right]_P &= -\frac{\Delta H^0}{T^2} = -\frac{\partial\left(\frac{41,030}{T} + 2.53 \ln(T) - 42.23\right)}{\partial T} \\ &= \frac{-41,030}{T^2} + \frac{2.53}{T} \end{aligned}$$

$$\Delta H^0 = 41,030 - 2.53T$$

$$\Delta H^0|_{1500K} = 37,235$$

$$\Delta S^0|_{1500K} = 21.2$$

$$\Delta G^0(\text{cal/mol}) = \underline{37,235 - 21.2T}$$

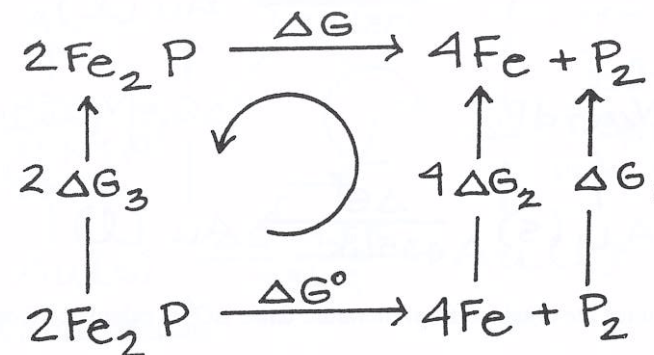
- (b) At the boiling point, liquid and vapor are at equilibrium, hence $\Delta G^0 = 0$:
 $0 = 37,235 - 21.2T$

$$T = \underline{1756 K} \left(\frac{1756 - 1440 - 273}{1440 + 273} \times 100 \approx 2.5\% \text{error} \right).$$

[4.6] Phosphorous bearing vanadium deposits of the western U.S. are a source of vanadium used in the steel industry as an alloy component. X-ray examination of a representative sample of raw material from these deposits reveals that the major impurity present in the ore is iron in the form of Fe_2P . A suggested method for removing the iron is to convert Fe_2P to Fe_3P and pure iron (ferrite) by vacuum distillation of the phosphorous and remove the iron magnetically. Assuming the best vacuum obtainable in a large scale operation is 10^{-2} mm Hg, estimate the operating temperature of a vacuum furnace required to accomplish this distillation.

Solution

(1) Set Up



(2) Sum

$$\Sigma \Delta G_{TL} = 0 = \Delta G^0 + \Delta G_1 + 4\Delta G_2 - \Delta G - 2\Delta G_3$$

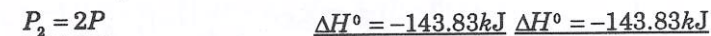
(3) Substitute

$$\Delta G_1 = RT \ln(P_2) = 8.3144T \ln\left(\frac{0.01}{760}\right)$$

$$\Delta G_2 = \Delta G_3 = 0$$

$$\Delta G = 0 \text{ (equilibrium)}$$

ΔG^0 is determined as follows:



$$\Delta S^0 = 2(72.38) - 4(27.28) - 218 = -182.4 \text{ kJ/(mol } P_2 \cdot \text{K)}$$

(4) Solve

$$\Delta G = 0 = -93.44T + 464,400 - 182.4T$$

$$T \approx 1684 \text{ K or } \underline{1411^\circ\text{C}}$$

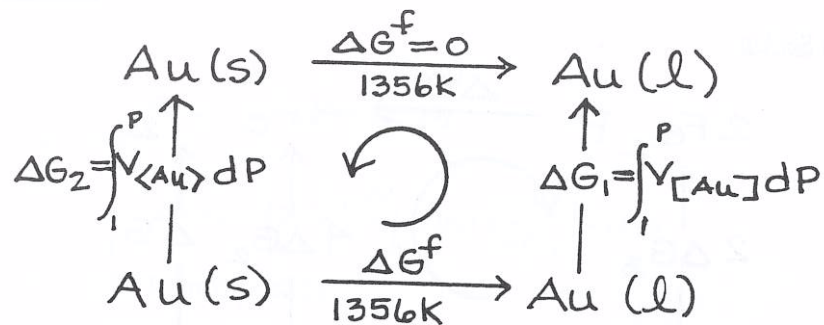
- [4.7] Estimate the pressure which must be applied to increase the melting point of pure Au by 20°C .

Solution

Three TL's are used to solve this problem.

TL #1 - Pressure

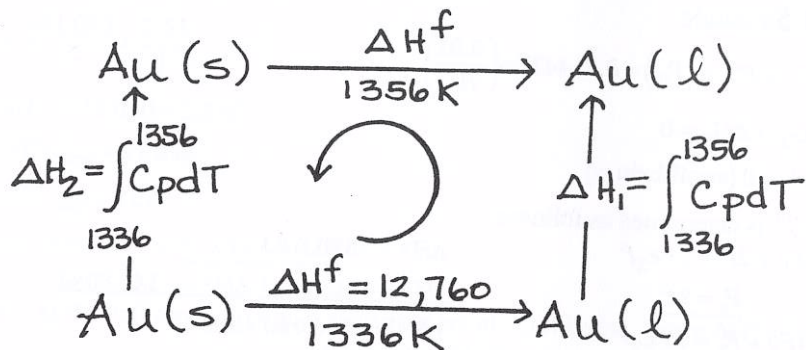
(1) Set up



Molar volumes are obtained from literature data. ΔG^f is calculated from TL #2 and #3.

TL #2 - Enthalpy of fusion at 1356 K (see Example Problem 2-6)

(1) Set up



(2) & (3) Sum & Substitute

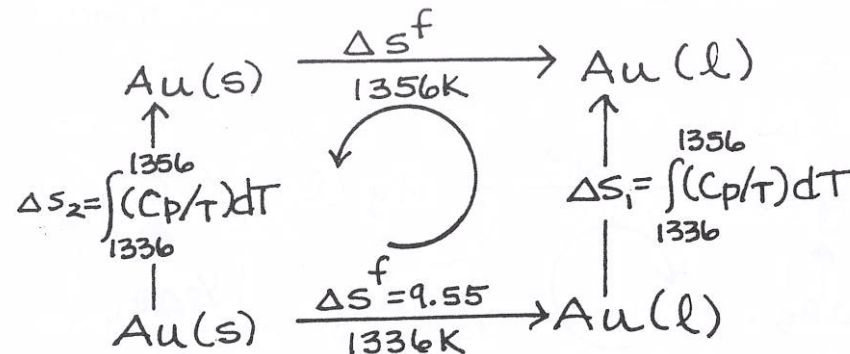
$$\begin{aligned}
 \Sigma \Delta H_{TL} = 0 &= 12,760 + \int_{1336}^{1356} 29.29 dT - \Delta H_{1356}^f - \int_{1336}^{1356} (23.68 + 5.19 \times 10^{-3} T) dT \\
 &= 12,760 + (29.29 \times 20) - \Delta H_{1356}^f - 613.6
 \end{aligned}$$

(4) Solve

$$\Delta H_{1356}^f = 12,732 \text{ J/mol.}$$

TL #3 - Entropy of fusion at 1356 K (see Example Problem 3-5)

(1) Set up



(2) & (3) Sum & Substitute

$$\Sigma \Delta S_{TL} = 0 = 9.55 + \int_{1336}^{1356} \frac{29.29}{T} dT - \Delta S_{1356}^f - \int_{1336}^{1356} \left(\frac{23.68}{T} + 5.19 \times 10^{-3} \right) dT$$

$$\Delta S_{1356}^f = 9.55 + 0.435 - 0.248 = 9.737 \text{ J/(mol} \cdot \text{K)} = 9.53$$

Calculating ΔG_{1356}^f from [4-8]:

$$\Delta G_{1356}^f = 12,732 - 1356(9.737) = -471.4 \text{ J/mol} = -190.68$$

Now, referring to TL #1: 9.53

(2) & (3) Sum & Substitute

$$\Sigma \Delta G_{TL} = -471.4 + V_{\text{Au}} \int_1^P dP - 0 - V_{\text{Au}} \int_1^P dP = 0$$

$$\text{Substituting } V_{\text{Au}} = \frac{M}{\rho} = \frac{1}{17.0} \times 197 = 11.59 \text{ cm}^3/\text{mol}$$

$$V_{\text{Au}} = \frac{1}{19.3} \times 197 = 10.207 \text{ cm}^3/\text{mol},$$

$$\Sigma \Delta G_{TL} = 0 = -471.4 + [11.59(P-1) - 10.207(P-1)] \times 0.1013$$

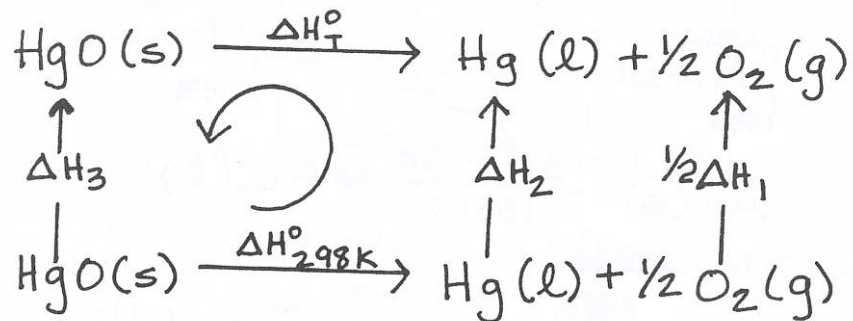
(4) Solve

$$P \approx \underline{3370 \text{ atm.}}$$

- [4.8] Assuming that ΔH° and ΔS° are independent of temperature, calculate the temperature at which solid HgO will dissociate into liquid Hg and $O_2(g)$ at 1 atm.

Solution

(1) Set Up



(2) & (3) Sum & Substitute

Since $\Delta C_p = 0$, $\int_{298}^T \Delta C_p dT = 0$, hence, the solution only requires standard data at 298K.

$$\sum \Delta H_{TL} = 0 = \Delta H_{298}^\circ - \Delta H_T^\circ$$

(4) Solve

$$\Delta H_T^\circ = 90.8 \text{ kJ/mol}$$

Applying the same TL in a similar manner for entropy: $\Delta S_T^\circ = \Delta S_{298}^\circ = 75.91 + 1/2 (205.02) - 70.3 = 108.12 \text{ J/(mol}\cdot\text{K)}$.

Using [4-11] and setting $\Delta G_T^\circ = 0$, $\Delta G_T^\circ = 0 = \Delta H_{298}^\circ - T\Delta S_{298}^\circ$

$$T = \frac{90,800}{108.12} = 839.8 \text{ K} \approx \underline{567^\circ\text{C}}$$

- [4.9] Thermodynamic analysis of the equilibrium state for carbon, chromium, and niobium carbide reveals that niobium is an effective alloying agent for limiting grain boundary precipitation of chromium carbide by preferentially removing carbon as niobium carbide.

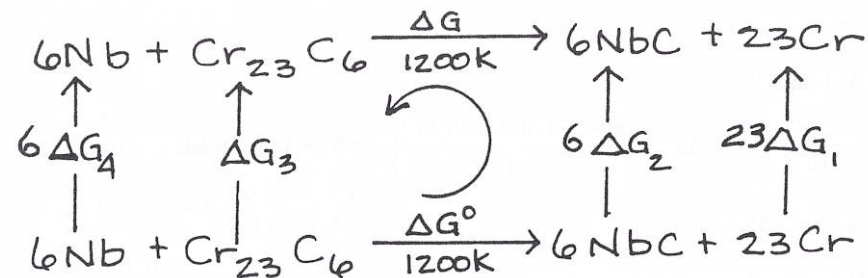
- (a) Write a single equation describing C-Nb-Cr equilibria neglecting solubility effects.
 (b) Confirm thermodynamically the alloying effect of Nb at 1200 K.

Solution



(b) From TL analysis:

(1) Set Up



(2) Sum

$$\sum \Delta G_{TL} = \Delta G_{1200}^\circ + 23\Delta G_1 + 6\Delta G_2 - \Delta G_{1200} - 6\Delta G_4 - \Delta G_3 = 0$$

(3) Substitute All pure components, no solid solubility,

$$\Delta G_1 = \Delta G_2 = \Delta G_3 = \Delta G_4 = 0$$

$$\Delta G_{1200}^\circ = \Delta G_{1200}^\circ = 6\Delta G_{\text{NbC}}^\circ - \Delta G_{\text{Cr}_{23}\text{C}_6}^\circ$$

$$\begin{aligned} \Delta G_{1200}^\circ &= 6[-130,135 + 1.67(1200)] - 6[-68,540 - 6.44(1200)] \\ &= \underline{\underline{-311,200 \text{ J/mol} < 0}} \Rightarrow \text{NbC formation is favored.} \end{aligned}$$

- [4.10] Three equations for the oxidation of a metal M are given below. One of these equations is for the oxidation of solid M, one is for the oxidation of liquid M, and one is for the oxidation of gaseous M. Using the ΔG° data given, identify the reaction and the state of the reactant metal.



Solution

From [4-27], entropies for each reaction are:

Reaction (a)

$$\left(\frac{\partial \Delta G^\circ}{\partial T} \right)_P = -\Delta S^\circ = \frac{\partial(-290,400 + 46.1T)}{\partial T} \Big|_P = 46.1 \text{ cal/(mol}\cdot\text{K)}$$

$$\Delta S^\circ = -46.1$$

Reaction (b)

$$\left(\frac{\partial \Delta G^0}{\partial T}\right)_p = -\Delta S^0 = \frac{\partial(-358,754 + 102.6T)}{\partial T} \Big|_p = 102.6 \text{ cal}/(\text{mol}\cdot\text{K})$$

$$\Delta S^0 = -102.6$$

Reaction (c)

$$\left(\frac{\partial \Delta G^0}{\partial T}\right)_p = -\Delta S^0 = \frac{\partial(-298,400 + 55.4T)}{\partial T} \Big|_p = 55.4 \text{ cal}/(\text{mol}\cdot\text{K})$$

$$\Delta S^0 = -55.4$$

From the discussion in section 3.5,
 $\Delta S^0(\text{gas}) > \Delta S^0(\text{liquid}) > \Delta S^0(\text{solid})$
 hence, from the data above

ΔS^0 reaction (a) is solid M

ΔS^0 reaction (b) is gaseous M

ΔS^0 reaction (c) is liquid M

[4.11] For the reaction $\text{SiC}(s) \rightarrow \text{Si}(s) + \text{C}(s)$, $\Delta G_T^0 = 12,770 - 1.66T$ cal/mol from 298–1680 K. Using this data, determine:

- (a) ΔS^0 at 1000 K.
 (b) ΔH^0 at 1500 K.

Solution

From direct examination, the expression is identical to [4-11], hence ΔH^0 and ΔS^0 are constants over the applicable temperature range.

(a) $\Delta S^0_{1000\text{K}} = \underline{1.66 \text{ cal}/(\text{mol}\cdot\text{K})}$,

(b) $\Delta H^0_{1500\text{K}} = \underline{12,770 \text{ cal}/(\text{mol})}$.

[4.12] Using the general expression for $C_p - C_v$ given in Exercise Problem [1.3]:

(a) Show that $C_p - C_v = \alpha^2 VT/\beta$ for any substance.

(b) Use this expression to estimate $C_p - C_v$ for pure copper at 298 K.

Solution

(a) From Exercise Problem [1.3]:

$$C_p - C_v = T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial P}{\partial T}\right)_v$$

Using [1-2], [1-3], and the transformation formula [4-18],

$$\left(\frac{\partial V}{\partial T}\right)_p = \alpha V$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{-(\partial V/\partial T)_p}{(\partial V/\partial P)_T} = \frac{-\alpha V}{-\beta V}$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{\alpha}{\beta}$$

Substituting into the above expression,

$$\underline{C_p - C_v} = T(\alpha V) \left(\frac{\alpha}{\beta}\right) = \frac{\alpha^2 VT}{\beta}$$

(b) From Table B.1

$$\begin{aligned} C_p - C_v &= \frac{(16.5 \times 10^{-6})^2 \cdot \text{cm}^3 \cdot 298 \text{ K} \cdot \text{atm}}{\text{K}^2 \cdot 8.96 \text{ gm} \cdot 7.6 \times 10^{-6}} \\ &= \frac{0.0012 \text{ atm} \cdot \text{cm}^3}{\text{K} \cdot \text{gm}} \times \frac{1 \text{ mol} \cdot \text{K}}{82.057 \text{ atm} \cdot \text{cm}^3} \times \frac{8.3144 \text{ J}}{\text{mol} \cdot \text{K}} \times \frac{63.54 \text{ gm}}{\text{mol}} \\ &\approx \underline{0.01 \text{ J}/(\text{mol} \cdot \text{K})} \end{aligned}$$

[4.13] Use the data in Exercise Problem [3.8] and the Gibbs free energy criteria to confirm that solidification is spontaneous after supercooling.

Solution

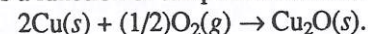
$$\Delta G = \Delta H - T\Delta S$$

$$= -12,136 - 803(-11.53)$$

$$= \underline{-2877 \text{ J/mol} < 0 \Rightarrow \text{spontaneous.}}$$

[4.14] (a) Starting with [4-13], use [4-27] and [4-30] to compute ΔS^0 and ΔH^0 , respectively, as a function of temperature.

(b) Use the results from (a) and Appendix A, Table A.4 to obtain ΔH^0 and ΔS^0 as a function of temperature for the reaction



Compare the results at $T = 298 \text{ K}$ with the data in Appendix A, Table A.1.

Solution

$$(a) \Delta S_T^0 : \Delta G_T^0 = A + \frac{B}{2.303} T \ln(T) + CT$$

$$\left(\frac{\partial \Delta G_T^0}{\partial T} \right)_P = -\Delta S_T^0 = \frac{B}{2.303} [T \cdot 1/T + \ln(T)] + C$$

$$-\Delta S_T^0 = \frac{B}{2.303} [1 + \ln(T)] + C$$

$$\Delta S_T^0 = \frac{B}{2.303} [\ln(1/T) - 1] - C$$

$$\Delta H_T^0 : \frac{\Delta G_T^0}{T} = A/T + \frac{B}{2.303} \ln(T) + C$$

$$\left. \frac{\partial(\Delta G_T^0/T)}{\partial T} \right|_P = -A/T^2 + \frac{B}{2.303} \cdot 1/T = -\frac{\Delta H_T^0}{T^2}$$

$$\Delta H_T^0 = A - \frac{BT}{2.303}$$

$$(b) \Delta S_T^0 \text{ and } \Delta S_{298}^0:$$

$$(Table A.4: Derived Equation) \left\{ \begin{array}{l} \Delta S_T^0 = -\frac{16.4}{2.303} [\ln(1/T) - 1] - 123.44 \\ \quad = 7.12 \ln(T) - 116.3 \\ \Delta S_{298}^0 = \underline{\underline{-75.74 \text{ J}/(\text{mol} \cdot \text{K})}} \end{array} \right.$$

$$(Table A.1) \left\{ \begin{array}{l} \Delta S_{298}^0 = 93.94 - \frac{205.2^2}{2} - 2(33.35) \\ \quad = \underline{\underline{-75.27 \text{ J}/(\text{mol} \cdot \text{K})}} \end{array} \right.$$

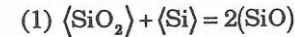
$$\Delta H_T^0 \text{ and } \Delta H_{298}^0:$$

$$(Table A.4: Derived Equation) \left\{ \begin{array}{l} \Delta H_T^0 = -169,470 + \frac{16.4T}{2.303} \\ \quad = -169,470 + 7.12T \\ \Delta H_{298}^0 \approx \underline{\underline{-167,350 \text{ J/mol}}} \end{array} \right.$$

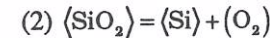
$$(Table A.1) \left\{ \Delta H_{298}^0 = \underline{\underline{-167,380 \text{ J/mol}}} \right.$$

[4.15] The thermodynamics of SiO is important in many materials applications because of its high vapor pressure. Develop an expression for the Gibbs free energy of formation of SiO(l), $\Delta G_{\text{SiO}(l)}^{0,f}$, as a function of temperature between 298–1700 K using the data in Appendix A, Table A.4.

Solution

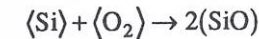


$$\Delta G^0 = 697,539 + 53.98T \log(T) - 518.45T \text{ J/mol,}$$



$$\Delta G^{0,f} = 881,235 + 12.55T \log(T) - 218.51T \text{ J/mol}$$

$$(3) = (1) - (2).$$



$$\Delta G^{0,f} = -183,696 + 41.3T \log(T) - 300T$$

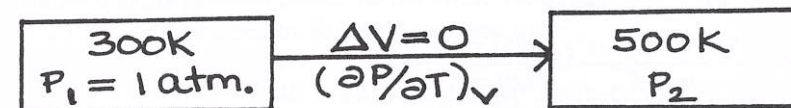
$$\Delta G_{\text{SiO}(l)}^{0,f} (\text{J/mol}) = \underline{\underline{-91,848 + 20.72T \log(T) - 150T}}$$

[4.16] One mole of a metal, m, at 1 atm pressure is heated at constant volume from 300 to 500 K. Calculate the hydrostatic pressure that results from such a process. What is the work done? Assume C_p is constant over the temperature interval. $\alpha_m = 5 \times 10^{-5} \text{ K}^{-1}$, and $\beta_m = 8 \times 10^{-6} \text{ atm}^{-1}$.

Solution

Since the process is constant volume, the path may be expressed by the

partial derivative $\left(\frac{\partial P}{\partial T} \right)_V$:



From [4-18],

$$\left(\frac{\partial P}{\partial T} \right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} \text{ and applying [1-2] and [1-3], } \left(\frac{\partial P}{\partial T} \right)_V = \frac{\alpha}{\beta}$$

Expanding and integrating,

$$\int_1^{P_2} dP = \frac{\alpha}{\beta} \int_{300}^{500} dT = \frac{5 \times 10^{-5}}{8 \times 10^{-6}} (200)$$

$$P_2 \approx \underline{1251 \text{ atm}};$$

$$W = \int PdV = \underline{0}.$$

[4.17] Referring to Exercise Problem [4.16], calculate the entropy change for the same process. Let $C_p^m = 20.9 \text{ J/(mol}\cdot\text{K)}$, $V_m = 6 \text{ cm}^3/\text{(gm mol)}$.

Solution

$$S = f(T, P)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Using the differential form of [3-10] and applying [4-23],

$$dS = \frac{C_p dT}{T} \Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha V$$

$$\therefore \int_{S_1}^{S_2} dS = \Delta S = \int_{300}^{500} \frac{C_p}{T} dT - \alpha V \int_1^{1251} dP$$

Where V (assumed) $\neq f(P)$

$$\begin{aligned} \Delta S &= 20.9 \ln\left(\frac{500}{300}\right) - \frac{5 \times 10^{-5} \times 6 \text{ cm}^3}{\text{mol} \cdot \text{K}} (1251 \text{ atm}) \\ &= 10.68 - \frac{5 \times 10^{-5} \times 6 \text{ cm}^3}{\text{mol} \cdot \text{K}} \times \frac{1251 \text{ atm} \times \text{J}}{9.869 \text{ cm}^3 \cdot \text{atm}} \\ &= 10.68 - 0.038 = \underline{10.64 \text{ J/(mol}\cdot\text{K)}}. \end{aligned}$$

[4.18] Use the Gibbs free energy criteria to confirm that liquid potassium and its vapor are in equilibrium at 950 K and 0.447 bar.

Solution

(Table D.2)

$$\begin{aligned} \Delta g_{vi} &= \Delta h_{vi} - T \Delta s_{vi} \\ &= (2750.4 - 771.4) - 950(4.8129 - 2.7313) \text{ kJ/kg} \\ &= 1979 - 1978 \approx \underline{0}. \end{aligned}$$

[4.19] Use [3-6] to confirm the value of $u_g - u_l$ in Appendix D, Table D.2, at 900 K and 0.251 bar.

Solution

$$\int du = T \int ds - P \int dv$$

$$\begin{aligned} \Delta u &= 900(4.9175 - 2.6874) - \frac{0.2510}{10} (7180 - 1.438) \\ &= \underline{1827 \text{ kJ/kg}} \text{ (check)}. \end{aligned}$$

[4.20] Referring to Exercise Problems [4.16] and [4.17], estimate the enthalpy change for the same process if $V_m = 10 \text{ cm}^3/\text{mol}$. State any assumptions in making the calculations.

Solution

From [4-33],

$$\begin{aligned} \Delta H &= C_p \int_{300}^{500} dT + V \int_1^{1251} (1 - \alpha T) dP \\ &= 20.9 \int_{300}^{500} dT + \frac{10 \text{ cm}^3}{\text{mol}} \times \frac{0.101 \text{ J} \cdot \text{atm}}{\text{cm}^3 \cdot \text{atm}} \times \int_1^{1251} (1 - 5 \times 10^{-5} T) dP \end{aligned}$$

Since the functional dependence between T and P is unknown, a rigorous solution to the problem cannot be obtained. However, since $5 \times 10^{-5} T \ll 1$, proceed by neglecting the last term:

$$\begin{aligned} \Delta H &= 20.9(200) + 10 \times .101 \times 1250 \\ &= \underline{5440 \text{ J/mol}}, \text{ } V_m \text{ and } \alpha_m \text{ are assumed constant.} \end{aligned}$$

Note: If the substance were an ideal gas for which the equation of state is known, the pressure term would disappear since $(1 - \alpha T) = (1 - 1) = 0$. In such a case, a rigorous solution is obtained. This illustrates the importance of identifying reasonable assumptions in determining thermodynamic properties of condensed states for which equations of state are empirical and limited in application.

- [4.21] Using the standard enthalpy and entropy changes computed in Exercise Problems [2.10] and [3.14] for the reaction
 $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4(s) + 2\text{SiO}_2(s) \rightarrow \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2(s) + \text{H}_2\text{O}(g)$,
 calculate ΔG_T^0 at temperature T where $373 \text{ K} < T < 800 \text{ K}$. No phase changes occur.

Solution

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0$$

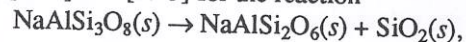
$$\Delta G_T^0 \text{ (J/mol)} =$$

$$\begin{aligned} &(-69.42 \times 10^{-8} T^3 - 2.59 T^2 + 4672.2 T - 3.70 \times 10^7 T^{-1} + 4672.17 T - 2.59 T^2 \\ &- 6.94 \times 10^{-7} T^3 - 131,264 T^{0.5} - 82,315) - T(-771.17 + 4672.2 \ln(T) - 5.17 T \\ &- 10.41 \times 10^{-7} T^2 + 131.26 \times 10^3 T^{-0.5} - 389.32 \times 10^3 T^{-2}). \end{aligned}$$

Collecting like terms :

$$\Delta G_T^0 \text{ (J/mol)} = -82,315 - 4672.2 T \ln(T) + 5.44 \times 10^3 T + 2.58 T^2 + 3.47 \times 10^{-7} T^3 - 3.66 \times 10^7 T^{-1} - 2.63 \times 10^5 T^{0.5}.$$

- [4.22] Using the standard enthalpy and entropy changes computed in Exercise Problems [2.12] and [3.15] for the reaction



calculate ΔG_T^0 at temperature T where $298 \text{ K} < T < 844 \text{ K}$. No phase changes occur.

Solution

$$\Delta G_T^0 \text{ (J/mol)} = (53.21 \times 10^3 - 238.21 T + 7.04 \times 10^{-2} T^2 - 7.57 \times 10^{-6} T^3 + 4.92 \times 10^6 T^{-1} + 8.74 \times 10^3 T^{0.5}) - T(1762.21 - 238.21 \ln(T) + 140.749 \times 10^{-3} T - 113.61 \times 10^{-7} T^2 - 87.384 \times 10^2 T^{-0.5} + 24.596 \times 10^5 T^{-2}).$$

Collecting like terms:

$$\begin{aligned} \Delta G_T^0 \text{ (J/mol)} = & 53.21 \times 10^3 - 2000.4 T + 238.21 T \ln(T) - \\ & 70.349 \times 10^{-3} T^2 + 3.791 \times 10^{-6} T^3 + \\ & 17.478 \times 10^3 T^{0.5} + 2460.4 \times 10^3 T^{-1}. \end{aligned}$$

- [4.23] The sorosilicate lawsonite, $\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}(s)$, is a common constituent of metamorphic rocks formed at low temperature and high pressure. Assuming the molar volume of this mineral is independent of pressure, calculate the molar isothermal Gibbs free energy change for lawsonite subjected to a reversibly applied pressure increase from 1 to 5 bar at 298 K.

Solution

Since T & V are constant,

$$dG = VdP - SdT \Rightarrow$$

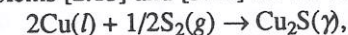
$$dG = VdP \text{ or } \int_{G_1}^{G_2} dG = V \int_{P_1}^{P_2} dP \Rightarrow$$

$$\Delta G = V\Delta P, \text{ hence from B.2,}$$

$$\begin{aligned} \Delta G &= \left(101.32 \frac{\text{cm}^3}{\text{mol}} \right) \left(\frac{4.184 \text{ J}}{41.3223 \text{ cm}^3 \cdot \text{atm}} \right) \left(\frac{1 \text{ atm}}{1.01325 \text{ bar}} \right) \Delta P \\ &= \left(10.125 \frac{\text{J}}{\text{mol} \cdot \text{bar}} \right) \Delta P \end{aligned}$$

$$\Delta P = 4 \text{ bar} : \Delta G = \left(10.125 \frac{\text{J}}{\text{mol} \cdot \text{bar}} \right) (4 \text{ bar}) = \underline{40.5 \text{ J/mol}}.$$

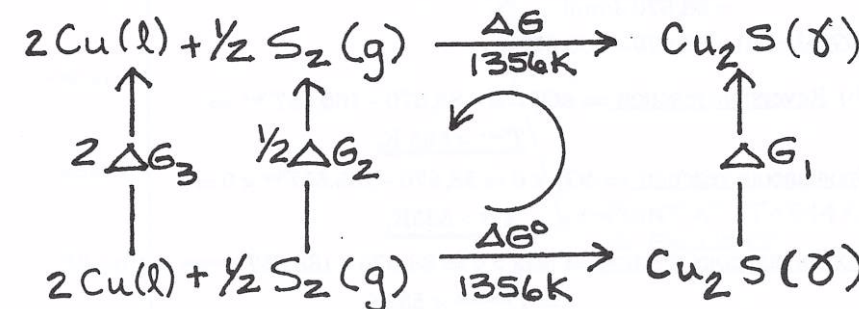
- [4.24] Using the standard enthalpy and entropy of formation computed in Exercise Problems [2.13] and [3.13] for the reaction



determine whether or not this reaction is spontaneous at 1356 K as written.

Solution

(1) Set Up



(2) Sum

$$\sum \Delta G_{TL} = 0 = \Delta G_{1356}^0 + \Delta G_1 - \Delta G_{1356} - \frac{1}{2} \Delta G_2 - 2\Delta G_3$$

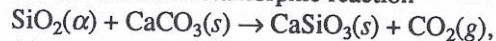
(3) Substitute

$$\begin{aligned}\Delta G_{1356}^{\circ} &= \Delta H_{1356}^{\circ} - 1356(\Delta S_{1356}^{\circ}) \\ &= -108,371 - 1356(122.244) \\ &= -274,260 \text{ J/mol} \\ \Delta G_1 &= \Delta G_2 = \Delta G_3 = 0\end{aligned}$$

(4) Solve

$$\underline{\Delta G_{1356}^{\circ}} = -274,260 \text{ J/mol} < 0 \Rightarrow \text{spontaneous.}$$

[4.25] For the contact metamorphic reaction



(a) Calculate the standard Gibbs free energy change at temperature $298 \text{ K} \leq T < 844 \text{ K}$. Assume $\Delta C_p = 0$ and use the value of ΔS_{298}° computed in Example Problem [3.12].

(b) Plot ΔG_T° as a function of T . Label line segments and points corresponding to a reversible reaction, a spontaneous reaction, and a nonspontaneous reaction as written.

Solution

Since $\Delta C_p = 0$, $\Delta G_T^{\circ} = \Delta H_{298}^{\circ} - T\Delta S_{298}^{\circ}$

$$\Delta S_{298}^{\circ} = 165.65 \text{ J/(mol} \cdot \text{K)}$$

$$\begin{aligned}\Delta H_{298}^{\circ} &= (1)\Delta H_{298, < \text{CaSiO}_3 >}^{\circ} + (1)\Delta H_{298, \text{CO}_2(g)}^{\circ} - (1)\Delta H_{298, < \text{SiO}_2 >}^{\circ} - (1)\Delta H_{298, < \text{CaCO}_3 >}^{\circ} \\ &= -1635.22 \text{ kJ/mol} - 393.51 \text{ kJ/mol} - (-910.7 \text{ kJ/mol}) - (-1206.7 \text{ kJ/mol}) \\ &= 88,670 \text{ J/mol}\end{aligned}$$

$$\Delta G_T^{\circ} (\text{J/mol}) = 88,670 - 165.65T.$$

(b) Reversible reaction $\Rightarrow \Delta G_T^{\circ} = 0 = 88,670 - 165.65T^{\text{Rev}} \Rightarrow$

$$\underline{T^{\text{Rev}} = 535 \text{ K,}}$$

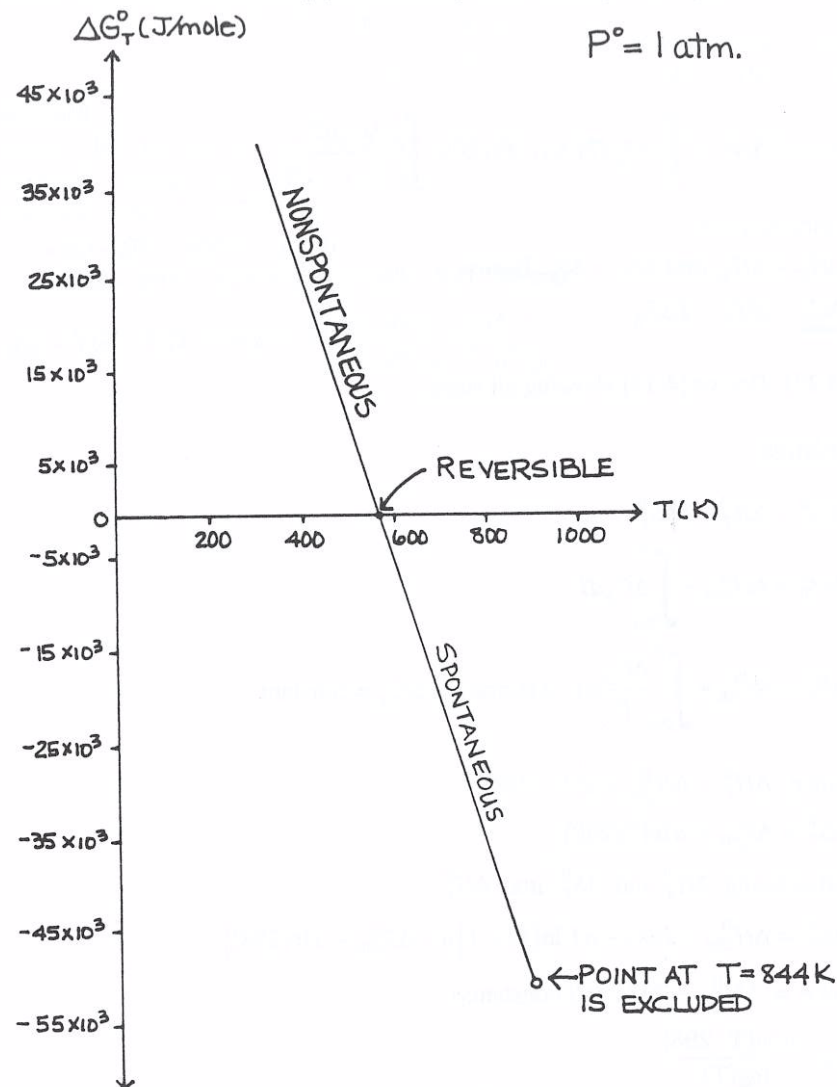
Spontaneous reaction $\Rightarrow \Delta G_T^{\circ} < 0 \Rightarrow 88,670 - 165.65T^{\text{Irr}} < 0 \Rightarrow$

$$\underline{T^{\text{Irr}} > 535 \text{ K;}}$$

Nonspontaneous reaction $\Rightarrow \Delta G_T^{\circ} > 0 \Rightarrow 88,670 - 165.65T^{\text{Nonspon.}} > 0$

$$\Rightarrow \underline{T^{\text{Nonspon.}} < 535 \text{ K.}}$$

ΔG_T° as a Function of T for the
Reaction $(\text{SiO}_2)_{\alpha} + < \text{CaCO}_3 > \rightarrow < \text{CaSiO}_3 > + \text{CO}_2(g)$
 $P^{\circ} = 1 \text{ atm.}$



[4.26] Show that the Gibbs free energy change for an isobaric chemical reaction occurring at a temperature T is

$$\Delta G_T = \Delta H_{T_1} - T\Delta S_{T_1}$$

when $\Delta C_p = 0$ in the temperature range between T_1 to T .

Solution

At constant pressure,

$$\Delta G_T = \Delta H_T - T\Delta S_T$$

$$\Delta H_T = \Delta H_{T_1} + \int_{T_1}^T \Delta C_p dT; \Delta S_T = \Delta S_{T_1} + \int_{T_1}^T \frac{\Delta C_p dT}{T}$$

Since $\Delta C_p = 0$,

$$\Delta H_T = \Delta H_{T_1} \text{ and } \Delta S_T = \Delta S_{T_1} \text{ Hence,}$$

$$\underline{\Delta G_T} = \Delta H_{T_1} - T\Delta S_{T_1}.$$

[4.27] Derive [4-13] showing all steps.

Solution

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0$$

$$\Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^T \Delta C_p dT$$

$$\Delta S_T^0 = \Delta S_{298}^0 + \int_{298}^T \frac{\Delta C_p}{T} dT. \text{ Assume } a = \Delta C_p = \text{constant,}$$

$$\text{hence, } \Delta H_T^0 = \Delta H_{298}^0 + a(T - 298)$$

$$\Delta S_T^0 = \Delta S_{298}^0 + a \ln(T/298)$$

Substituting ΔH_T^0 and ΔS_T^0 into ΔG_T^0 ,

$$\Delta G_T^0 = \Delta H_{298}^0 - 298a - aT \ln(T) + T[a - \Delta S_{298}^0 + a \ln(298)]$$

$$\text{Let } A = \Delta H_{298}^0 - 298a \text{ (all constants)}$$

$$B = \frac{-a \ln(T/298)}{\log(T)}$$

$$C = a - \Delta S_{298}^0 \text{ (all T terms)}$$

Substituting A, B, and C:

$$\underline{\Delta G_T^0} = A + B T \log(T) + CT.$$

[4.28] Derive [4-14] and show that

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P.$$

Solution

Let $G = H - TS$, $H = U + PV$, $dU = \delta Q - \delta W$, $\delta W = PdV$, and $dS = \delta Q/T$

$$dG = dH - d(TS) = d(U + PV) - d(TS)$$

$$dG = dU + d(PV) - d(TS)$$

$$= \delta Q - \delta W + d(PV) - d(TS)$$

$$= TdS - PdV + PdV + VdP - TdS - SdT. \text{ Hence,}$$

$$\underline{dG} = VdP - SdT. \text{ From [1-5], } -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P.$$