

THE SECOND AND THIRD LAWS OF THERMODYNAMICS

3.1 THERMODYNAMIC EFFICIENCY, THE SECOND LAW AND ENTROPY

Starting with the definition of *thermodynamic efficiency* of a system for the conversion of thermal to mechanical energy

$$\eta = \frac{Q_H - Q_L}{Q_H} \quad [3-1]$$

it can easily be shown for a Carnot cycle as illustrated in Example Problem 3-1, that

$$\eta = \frac{T_H - T_L}{T_H} \quad [3-2]$$

All steps are reversible, the working substance is an ideal gas, and Q_H and T_H are the heat output from and absolute temperature of a high temperature *heat source* respectively. Q_L and T_L are the heat input to and absolute temperature of a low temperature *heat sink* respectively. The heat source and heat sink are *reservoirs* or masses so large that they can transmit or absorb, respectively, an unlimited amount of heat without experiencing a change in temperature.

It should be noted that the Carnot cycle represents maximum theoretical thermodynamic efficiency. A more realistic expression for Carnot efficiency, which takes into account the ΔT required for heat transfer, is discussed in Exercise Problem [3.17].

Rearranging [3-1] and [3-2] and eliminating η ,

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L} \quad \text{or} \quad \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0 \quad [3-3]$$

Generalizing [3-3] for smaller and smaller Carnot cycles,

$$\oint \frac{\delta Q^{\text{Rev}}}{T} = 0 \quad [3-4]$$

The ratio $\delta Q^{\text{Rev}}/T$ defines the thermodynamic function *entropy*, S , where

$$dS = \frac{\delta Q^{\text{Rev}}}{T} \quad [3-5]$$

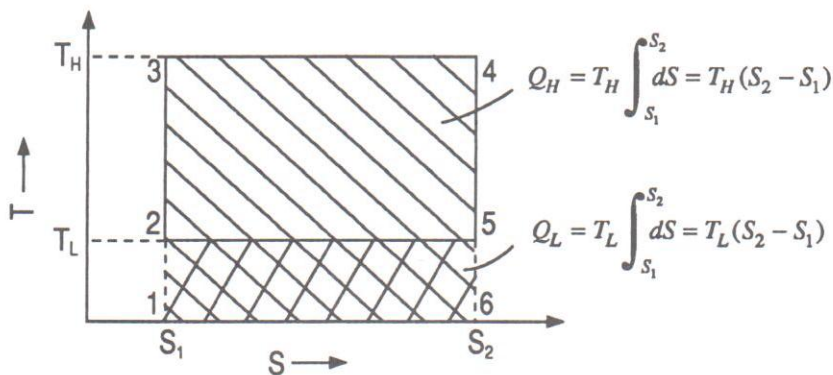
Mathematically, T is an integrating factor since the inexact differential δQ^{Rev} is made exact by dividing by the absolute temperature. Based on the previous discussion, the *Second Law of Thermodynamics* states that entropy, defined by equation [3-5], is a thermodynamic property.

Example Problem 3-1

Plot the Carnot cycle on a temperature-entropy diagram. Using the definition of entropy [3-5], prove [3-2]. The processes in the Carnot cycle involve: (1) *isentropic* (constant entropy) expansion, (2) isothermal transfer of heat from a high temperature (T_H) reservoir, (3) isentropic compression, and (4) isothermal transfer of heat to a low temperature (T_L) reservoir.

Solution

The Carnot cycle processes are plotted on the T - S diagram below and [3-5] is applied.



Substituting for Q_H and Q_L in [3-1],

$$\eta = \frac{T_H(S_2 - S_1) - T_L(S_2 - S_1)}{T_H(S_2 - S_1)} = \frac{(T_H - T_L)/T_H}{1}$$

An alternate solution follows from [3-1]:

$$\eta = \frac{Q_H - Q_L}{Q_H} = \frac{\text{Area 2345} - \text{Area 123456}}{\text{Area 123456}} = \frac{(T_H - T_L)(S_2 - S_1)}{T_H(S_2 - S_1)} = \frac{(T_H - T_L)/T_H}{1}$$

Now, substituting [1-10] and [3-5] into [2-2],

$$dU = TdS - PdV \quad [3-6]$$

Writing [2-4] in differential form,

$$dH = dU + PdV + VdP,$$

and substituting [3-6] into this expression,

$$dH = TdS + VdP \quad [3-7]$$

At constant pressure, [3-7] reduces to

$$dS = \frac{dH_p}{T} \quad [3-8]$$

Integrating [3-8] at constant temperature,

$$\int_{S_1}^{S_2} dS = (1/T) \int_{H_1}^{H_2} dH_p$$

or

$$\Delta S = \frac{\Delta H_p}{T} \quad [3-9]$$

Substituting [2-12] into [3-8] and integrating with respect to temperature,

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p dT}{T} \quad [3-10]$$

At constant volume, [3-6] reduces to

$$dS = \frac{dU_v}{T} \quad [3-11]$$

Integrating [3-11] at constant temperature,

$$\int_{S_1}^{S_2} dS = (1/T) \int_{U_1}^{U_2} dU_v$$

or

$$\Delta S = \frac{\Delta U_v}{T} \quad [3-12]$$

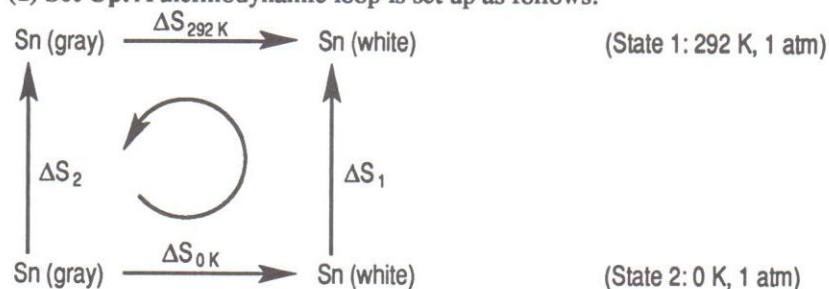
Substituting [2-9] into [3-11] and integrating with respect to temperature,

$$\Delta S = \int_{T_1}^{T_2} \frac{C_v dT}{T} \quad [3-13]$$

3.2 ENTROPY OF REACTION AND THE THIRD LAW

Consider the *allotropic** transformation of tin (Darken and Gurry, 1953, p. 197) at 1 atm pressure. Using TL analysis,

(1) Set Up. A thermodynamic loop is set up as follows:



* Allotropes are polymorphic elements.

(2) **Sum.** Summing in the counterclockwise direction,

$$\sum \Delta S_{TL} = 0 = \Delta S_{0K} + \Delta S_1 - \Delta S_{292K} - \Delta S_2.$$

(3) **Substitute.**[†]

$$\Delta S_1 = \int_0^{292} C_p(\text{white Sn}) dT / T = -38.12 \text{ J}/(\text{mol} \cdot \text{K})$$

$$\Delta S_2 = \int_0^{292} C_p(\text{gray Sn}) dT / T = -46.19 \text{ J}/(\text{mol} \cdot \text{K})$$

$$\Delta S_{292} = \Delta H_{292} / T^{\text{Tr}} = 2263.5 / 292 = 7.75 \text{ J}/(\text{mol} \cdot \text{K}).$$

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

$$0 = \Delta S_{0K} - 38.12 - 7.75 + 46.19.$$

(4) **Solve.**

$$\Delta S_{0K} = -0.32 \text{ J}/(\text{mol} \cdot \text{K}).$$

Assuming that the calculated value of ΔS_{0K} is within experimental error, it has been shown that ΔS_{0K} is zero. Consequently, it is concluded that the entropies of gray and white tin are the same at 0 K. It follows from the analysis above that the entropies of all substances are the same at 0 K and therefore assumed to be zero at 0 K. This conclusion is stated as the *Third Law of Thermodynamics*: "the entropy of any homogeneous substance which is in complete internal equilibrium may be taken as zero at 0 K" (Darken and Gurry, 1953, p. 193). As will be discussed in Section 3.5, complete order implies the same conclusion. For additional reading concerning the third law, refer to Swalin (1964, p. 51–58), Gaskell (1981, p. 134–145), and DeHoff (1993, p. 32–34). In the context of the previous discussion, standard state entropy values are absolute within the limits of experimental error and are denoted by a superscript 0 in Table 3.1. Since S_{0K}^0 of any homogeneous substance in complete internal equilibrium is zero, the *absolute standard entropy* of any such substance at temperature T can be calculated from [3-10]:

$$\Delta S_T^0 = S_T^0 = \int_0^T \frac{C_p dT}{T}.$$

[†] Below 80 K, C_p was obtained from a combination of Debye's formula and an expression for $C_p - C_v$ given in Exercise Problem [4.12]. Above 80 K, C_p was obtained experimentally.

Table 3.1: Standard State Entropy

<i>State of Aggregation</i>	<i>Pure Elements</i> $P^0 = 1 \text{ atm}, T \text{ (K)}$	<i>Pure Compounds</i> $P^0 = 1 \text{ atm}, T \text{ (K)}$
Solid (internal equilibrium)	$S_{0K}^0 = 0$	$S_{0K}^0 = 0$

Values of S_{298K}^0 for selected pure solids are found in Table A.1.

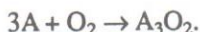
The *standard entropy of reaction* is

$$\int_{\text{Reactants}}^{\text{Products}} dS = \Delta S_T^0$$

or

$$\Delta S_T^0 = \sum n S_T^0 (\text{Products}) - \sum n S_T^0 (\text{Reactants}) \quad [3-14]$$

Consider the standard state oxidation of element A at a temperature $T = 298$ K as given by



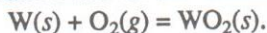
The entropy of the reaction is

$$\Delta S_{298}^0 = (1) S_{298, A_3O_2}^0 - (3) S_{298, A}^0 - (1) S_{298, O_2}^0$$

where $S_{298, A}^0 \neq 0$, $S_{298, O_2}^0 \neq 0$.

Example Problem 3-2

Calculate ΔS^0 at 298 K and 1 atm for the reaction



Solution

Applying [3-14],

$$\Delta S_{298}^0 = (1) S_{298, WO_2}^0 - (1) S_{298, W}^0 - (1) S_{298, O_2}^0$$

$$= 66.95 - 33.48 - 205.10$$

$$= -171.63 \text{ J/(mol} \cdot \text{K)}.$$

In this example WO_2 is formed from its component elements, all in the most stable form at 298 K and 1 atm. Therefore, $\Delta S_{298}^0 = \Delta S_{298}^{0,f}$ where $\Delta S_{298}^{0,f}$ is the *standard entropy of formation* of WO_2 .

3.3 TL ANALYSIS: TEMPERATURE DEPENDENCE

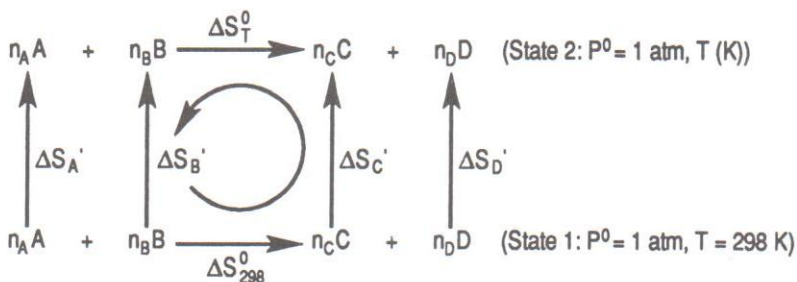
To determine an expression for the entropy change of a reaction as a function of temperature, the procedure described in Example Problem 2-4, Section 2.7 is followed.

Example Problem 3-3

Derive an expression for the standard entropy change of the general reaction $n_A A + n_B B \rightarrow n_C C + n_D D$ as a function of temperature at $P^0 = 1$ atm.

Solution

(1) Set Up.



(2) **Sum.** Summing in the counterclockwise direction,

$$\sum \Delta S_{TL} = 0 = \Delta S_{298}^0 + \Delta S_{C'} + \Delta S_{D'} - \Delta S_T^0 - \Delta S_{A'} - \Delta S_{B'}$$

(3) **Substitute.** Applying [3-10] to each reaction component and rearranging,

$$\begin{aligned} \Delta S_T^0 &= \Delta S_{298}^0 + n_C \int_{298}^T \frac{C_p^C dT}{T} + n_D \int_{298}^T \frac{C_p^D dT}{T} - n_A \int_{298}^T \frac{C_p^A dT}{T} - n_B \int_{298}^T \frac{C_p^B dT}{T} \\ &= \Delta S_{298}^0 + \int_{298}^T \frac{\Delta C_p dT}{T} \end{aligned}$$

where ΔC_p is defined by [2-17].

(4) **Solve.**

$$\Delta S_T^0 = \Delta S_{298}^0 + \int_{298}^T \frac{\Delta C_p dT}{T} \quad [3-15]$$

or in general,

$$\Delta S_T^0 = \Delta S_{T_1}^0 + \int_{T_1}^T \frac{\Delta C_p dT}{T} \quad [3-16]$$

Approximations similar to [2-19] and [2-20] are

Case I: $\Delta C_p = 0$, hence

$$\Delta S_T^0 = \Delta S_{T_1}^0 \quad [3-17]$$

Case II: $\Delta C_p = a$ (constant), hence

$$\Delta S_T^0 = \Delta S_{T_1}^0 + a \ln(T/T_1) \quad [3-18]$$

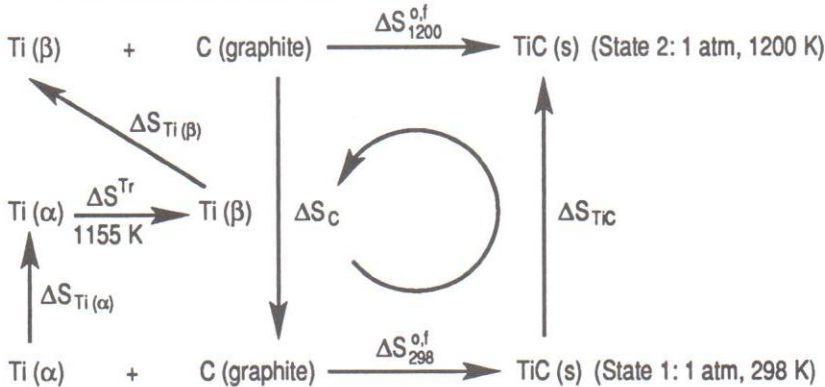
Example Problem 3-4

Calculate the entropy of formation of $\text{TiC}(s)$, $\Delta S_{\text{TiC}}^{0,f}$, at 1200 K.

Solution

TL analysis is applied in a manner analogous to that of Example Problem 2-5.

(1) **Set Up.** A TL is set up to include the $\text{Ti}(\alpha) \rightarrow \text{Ti}(\beta)$ phase transformation at 1155 K.



(2) **Sum.** Summing in the counterclockwise direction,

$$\sum \Delta S_{\text{TL}} = 0 = \Delta S_{298}^{0,f} + \Delta S_{\text{TiC}} - \Delta S_{1200}^{0,f} + \Delta S_C - \Delta S_{\text{Ti}(\beta)} - \Delta S^{\text{Tr}} - \Delta S_{\text{Ti}(\alpha)}$$

Rearranging and solving for $\Delta S_{1200}^{0,f}$,

$$\Delta S_{1200}^{0,f} = \Delta S_{298}^{0,f} + \Delta S_{\text{TiC}} + \Delta S_C - \Delta S_{\text{Ti}(\beta)} - \Delta S^{\text{Tr}} - \Delta S_{\text{Ti}(\alpha)}$$

(3) **Substitute.** $\Delta S_{298}^{0,f}$ is calculated using [3-14] and substituted along with the heat capacity and transformation enthalpy data given below into the expression for $\Delta S_{1200}^{0,f}$.

$$\Delta S_{298}^{0,f} = S_{298, \text{TiC}}^0 - S_{298, \text{Ti}(\alpha)}^0 - S_{298, \text{C}}^0 = -11.96 \text{ J}/(\text{mol} \cdot \text{K}).$$

From heat capacity data,

$$\Delta S_{\text{TiC}} = \int_{298}^{1200} \left(\frac{49.50 + 3.35 \times 10^{-3} T - 14.98 \times 10^{-5} T^{-2}}{T} \right) dT$$

$$\Delta S_C = \int_{1200}^{298} \left(\frac{17.15 + 4.27 \times 10^{-3} T - 8.79 \times 10^5 T^{-2}}{T} \right) dT$$

$$\Delta S_{Ti(\beta)} = \int_{1155}^{1200} \left(\frac{28.91}{T} \right) dT$$

$$\Delta S_{Ti(\alpha)} = \int_{298}^{1155} \left(\frac{22.09 + 10.04 \times 10^{-3} T}{T} \right) dT.$$

Substituting ΔH_{Ti}^{Tr} from Example Problem 2-5 into [3-9],

$$\begin{aligned} \Delta S^{Tr} &= \Delta H^{Tr}/T \\ &= 3473/1155 = 3.01 \text{ J/(mol}\cdot\text{K)}. \end{aligned}$$

- (4) **Solve.** The desired unknown is obtained by integrating and completing calculations. Integration, left to the reader, gives

$$\Delta S_{1200}^{0,f} = -13.64 \text{ J/(mol}\cdot\text{K)}$$

Note that substitution of $\Delta H_{1200}^{0,f} = -186.7 \text{ kJ/mol}$ (Example Problem 2-5) and $T = 1200 \text{ K}$ into [3-9] *cannot* be used to calculate $\Delta S_{1200}^{0,f}$ since the carbide forming reaction is *irreversible*.

3.4 STABILITY CRITERIA: ENTROPY

The *net entropy* change associated with a reaction or process, ΔS_{Net}^* , is defined by

$$\Delta S_{\text{Net}} = \Delta S_{\text{Sys}} + \Delta S_{\text{Surr}}^{\text{Rev}} \quad [3-19]$$

where ΔS_{Sys} denotes the entropy change of the system and $\Delta S_{\text{Surr}}^{\text{Rev}}$ denotes the *reversible* entropy change of the surroundings (see Swalin, 1964, p. 17-20 for additional information regarding ΔS_{Net}). Equation [3-19] can be used to assess whether or not a reaction or process will proceed. Consequently, it assesses the stability of the products under the conditions for which ΔS_{Net} is calculated.

Three *stability criteria* are defined:

- (1) If $\Delta S_{\text{Net}} = 0$, the reaction or process is at equilibrium;
- (2) If $\Delta S_{\text{Net}} > 0$, the reaction or process as described is spontaneous;
- (3) If $\Delta S_{\text{Net}} < 0$, the reaction or process as described is nonspontaneous.

* ΔS_{Net} is also referred to as ΔS_{Total} or as $\Delta S_{\text{Universe}}$.

The above criteria are applicable under the following conditions:

- (a) The system and surroundings are at constant pressure, hence from [2-6], $dH = \delta Q_p$.
- (b) The *surroundings* behave reversibly and isothermally even though the reaction is proceeding irreversibly. Thus $\delta Q_{\text{Surr}}^{\text{Rev}} = -\delta Q_{\text{Sys}}$ and from [2-6], $dH_{\text{Surr}}^{\text{Rev}} = -dH_{\text{Sys}}$.

Combining [2-6] and [3-5] with $T = T_{\text{Surr}}$,

$$dS_{\text{Surr}}^{\text{Rev}} = \frac{\delta Q_{\text{Surr}}^{\text{Rev}}}{T_{\text{Surr}}} = \frac{-\delta Q_{\text{Sys}}}{T_{\text{Surr}}} = \frac{-dH_{\text{Sys}}}{T_{\text{Surr}}} \quad [3-20]$$

and upon integration as in [3-9],

$$\Delta S_{\text{Surr}}^{\text{Rev}} = \frac{\Delta H_{\text{Surr}}^{\text{Rev}}}{T_{\text{Surr}}} = \frac{-\Delta H_{\text{Sys}}}{T_{\text{Surr}}} \quad [3-21]$$

- (c) The temperature of the system and surroundings are not necessarily the same.

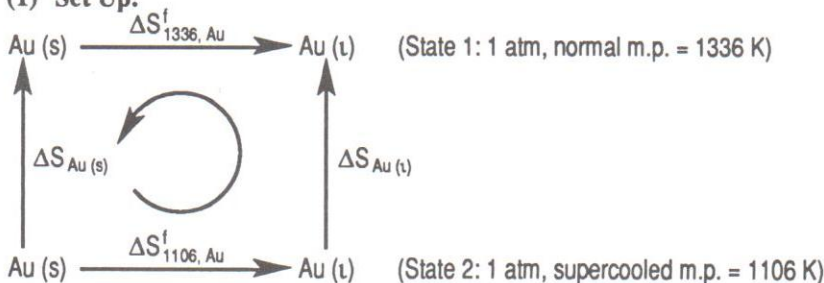
Example Problem 3-5

Referring to Example Problem 2-6, calculate the entropy change for the isothermal fusion of 1 gram atom of gold supercooled 230°C below the freezing point at atmospheric pressure (Upadhyaya and Dube, 1977, p. 39). What is the entropy change of the surroundings if the surroundings are at the supercooled temperature? Is fusion spontaneous?

Solution

Since the problem statement involves fusion, not solidification as in Example Problem 2-6, the direction of the reactions in the TL loop below are reversed so that ΔS_{Au}^f can be determined directly.

(1) Set Up.



(2) Sum. Summing in the counterclockwise direction,

$$\Sigma \Delta S_{\text{TL}} = 0 = \Delta S_{1106, \text{Au}}^f + \Delta S_{\text{Au(l)}} - \Delta S_{1336, \text{Au}}^f - \Delta S_{\text{Au(s)}}$$

Rearranging,

$$\Delta S_{1106, \text{Au}}^f = -\Delta S_{\text{Au}(l)} + \Delta S_{1336, \text{Au}}^f + \Delta S_{\text{Au}(s)}$$

(3) **Substitute.** Inserting heat capacity and transformation enthalpy data,

$$\Delta S_{1106, \text{Au}}^f = - \int_{1106}^{1336} \frac{29.29 dT}{T} + \frac{\Delta H_{1336, \text{Au}}^f}{T^f} + \int_{1106}^{1336} \left(\frac{23.68 + 5.19 \times 10^{-3} T}{T} \right) dT.$$

(4) **Solve.** Integrating,

$$\begin{aligned} \Delta S_{1106, \text{Au}}^f [\text{J}/(\text{mol} \cdot \text{K})] &= -29.29 \ln(1336/1106) + 9.55 + 23.68 \times \ln(1336/1106) \\ &\quad + 5.19 \times 10^{-3} \times (1336 - 1106) \\ &= -5.53 + 9.55 + 5.67 \end{aligned}$$

which reduces to

$$\Delta S_{1106, \text{Au}}^f = \underline{9.69 \text{ J}/(\text{mol} \cdot \text{K})}.$$

The TL analysis above refers to the system. From [3-21] and Example Problem 2-6, the entropy of the surroundings is

$$\begin{aligned} \Delta S_{\text{Surr}}^{\text{Rev}} &= \frac{-\Delta H_{1106, \text{Au}}^f \text{ Sys}}{T_{\text{Surr}}} = \frac{-12,930}{1106} \text{ J}/(\text{mol} \cdot \text{K}) \\ &= \underline{-11.69 \text{ J}/(\text{mol} \cdot \text{K})}. \end{aligned}$$

From [3-19], $\Delta S_{\text{Net}} = (9.69 - 11.69) = \underline{-2.00 \text{ J}/(\text{mol} \cdot \text{K})}$.

Since $\Delta S_{\text{Net}} < 0$, fusion is *not* spontaneous at 1106 K.

3.5 ALTERNATE DEFINITION OF ENTROPY

An alternate equation defines entropy according to

$$S' = k \ln(W) \quad [3-22]$$

where W = number of microstates/macrosate and k is Boltzmann's constant (R/N_{Av}). S' reflects the degree of *randomness* or *disorder* of a system.

In the context of crystalline materials at constant temperature, W corresponds to a configurational or structural change as reactants combine to form compounds or solution mixtures. Consider a physical model of a substitutional solid solution made up of atoms of A and B. Suppose atoms of the same kind are indistinguishable from one another but that A atoms are distinguishable from B atoms. It can then be shown that,

$$W = \frac{(N_{\text{A}} + N_{\text{B}})!}{N_{\text{A}}! \times N_{\text{B}}!}$$

where N_{A} and N_{B} are numbers of A atoms and B atoms respectively. Substituting this expression into [3-22] and expanding by Stirling's approximation,

$$\begin{aligned} \ln(X!) &= X \ln(X) - X, \\ S^m &= -R[X_{\text{A}} \ln(X_{\text{A}}) + X_{\text{B}} \ln(X_{\text{B}})] \end{aligned} \quad [3-23]$$

where S^m is the molar entropy of mixing, and X_A and X_B are the mole fractions of atoms A and B respectively (see SYMBOLS FOR MOLAR PROPERTIES: CHARACTERIZED BY VOLUME). For an equimolar solution, $X_A = X_B = 0.5$; $S^m = -8.3144 \times [0.5 \ln(0.5) + 0.5 \ln(0.5)] = 5.76 \text{ J}/(\text{mol}\cdot\text{K})$. Equation [3-23] will be derived using the classical approach in Chapter 6, Section 6.4.

If A and B atoms are indistinguishable from one another, it can be shown that

$$W = \frac{(N_A + N_B)!}{N_A! \times N_B!} = 1.0 \text{ and } S^m = 0.$$

In such a case, the mixture of A and B atoms is completely ordered.

In general, entropy increases as the degree of randomness increases. This behavior is noted, for example, in the transition from solid to liquid (melting), liquid to gas (vaporization), and solid to gas (sublimation). At 0 K, complete order implies that entropy of a homogeneous substance is zero.

3.6 DISCUSSION QUESTIONS

- (3.1) Entropy is related to the degree of randomness or disorder in a system (Section 3.5). Give three examples that illustrate a change in randomness and state how each change effects entropy.
- (3.2) Consider the chemical reaction $n_A A + n_B B \rightarrow A n_A B n_B$. If $\Delta S^0 > 0$ for this reaction, can it be concluded that the reaction is spontaneous?
- (3.3) Assuming the reaction in (3.2) is spontaneous, does

$$\Delta S_T^0 = \Delta H_T^0 (\text{reaction})/T (\text{reaction})?$$

- (3.4) Is S_{298}^0 of an internally equilibrated homogeneous element or compound zero?
- (3.5) Two phase transformations occur at a temperature T and pressure P . The phases involved are A and A', and the corresponding entropy changes are as follows:
- (1) $A \rightarrow A' \quad \Delta S_1$
 (2) $A \rightarrow A' \quad \Delta S_2$
- How is ΔS_1 related to ΔS_2 ?

- (3.6) For which mineral reaction below is $\Delta S_T^0 = \Delta S_{T, \text{Anorthite}}^{0,f}$?
- (a) $\text{SiO}_2(s) + 2\text{Al}_2\text{SiO}_5(s) + \text{Ca}_3\text{Al}_2(\text{SiO}_4)_3(s) \rightarrow 3\text{CaAl}_2\text{Si}_2\text{O}_8(s)$
 Quartz Kyanite Grossular Anorthite
- (b) $3\text{Ca}(s) + 6\text{Al}(s) + 6\text{Si}(s) + 12\text{O}_2(g) \rightarrow 3\text{CaAl}_2\text{Si}_2\text{O}_8(s)$

3.7 EXERCISE PROBLEMS

- [3.1] Prove that PV^γ is constant for an ideal gas. The process is adiabatic. Let $\gamma = C_p/C_v$.
- [3.2] Compute the standard entropy of formation for the reaction $2\text{H}_2(g) + \text{S}_2(g) \rightarrow 2\text{H}_2\text{S}(g)$ from 300 to 800 K in 100 K increments. Plot the

entropy as a function of temperature. What is the significance of the plot?

Ans: ΔS^{of} (J/K) = -78.07 at 300 K, -84.42 at 400 K, -89.00 at 500 K, -92.36 at 600 K, -94.83 at 700 K, and -96.62 at 800 K. The plot shows that ΔS^{of} (reaction) decreases as the temperature increases (since $V_{\text{Product}} < V_{\text{Reactants}}$) and that the volume effect on ΔS^{of} 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?

Ans: ΔV^0 (cm³/mol) = -24,617 at 300 K, -32,823 at 400 K, -41,029 at 500 K, -49,234 at 600 K, -57,440 at 700 K, and -65,646 at 800 K. The plot shows that ΔS^{of} decreases as ΔV^0 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.

Ans: $\Delta S_{\text{Net}} = 76.36 \text{ J}/(\text{mol}\cdot\text{K}) > 0$, 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 $C_p^{\text{Fe}(\alpha)}$ and assume that the reservoir is sufficiently large to maintain constant temperature.

Ans: $\Delta S_{\text{Steel}} = -9.36 \text{ J}/(\text{mol}\cdot\text{K})$, $\Delta S_{\text{Res}} = 10.67 \text{ J}/(\text{mol}\cdot\text{K})$, and $\Delta S_{\text{Net}} = 1.32 \text{ J}/(\text{mol}\cdot\text{K})$.

(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.

Ans: $\Delta S_{\text{Net}} = 0.63 \text{ J}/(\text{mol}\cdot\text{K})$.

(c) Explain how "equilibrium quenching" could be approached.

Ans: $\Delta S_{\text{Net}} = 0$.

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

Ans: $\Delta S_{\text{Sys}} = -6.47 \text{ J}/(\text{mol}\cdot\text{K})$, $\Delta S_{\text{Surr}} = 6.47 \text{ J}/(\text{mol}\cdot\text{K})$, and $\Delta S_{\text{Net}} = 0$.

- [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?

THE SECOND AND THIRD LAWS OF THERMODYNAMICS

Ans: $\Delta S_{\text{Sys}} = -11.21 \text{ J}/(\text{mol}\cdot\text{K})$, $\Delta S_{\text{Surr}} = 13.03 \text{ J}/(\text{mol}\cdot\text{K})$, $\Delta S_{\text{Net}} = 1.82 \text{ J}/(\text{mol}\cdot\text{K}) > 0 \Rightarrow$ 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 $\Delta C_p = 0$?

Ans: $\Delta S_{\text{Sys}} = -11.53 \text{ J}/(\text{mol}\cdot\text{K})$, $\Delta S_{\text{Surr}} = 15.11 \text{ J}/(\text{mol}\cdot\text{K})$, $\Delta S_{\text{Net}} = 3.58 \text{ J}/(\text{mol}\cdot\text{K}) > 0 \Rightarrow$ spontaneous. Error $\approx 100\%$.

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

Ans: $\Delta S^{l \rightarrow v} \approx 2.08 \text{ kJ}/(\text{kg}\cdot\text{K})$.

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

Ans: $\Delta S_{\text{Net}} \approx 0$.

- [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 $P^0 = 1 \text{ atm}$.

(a) Calculate the temperature shift associated with the volume change.

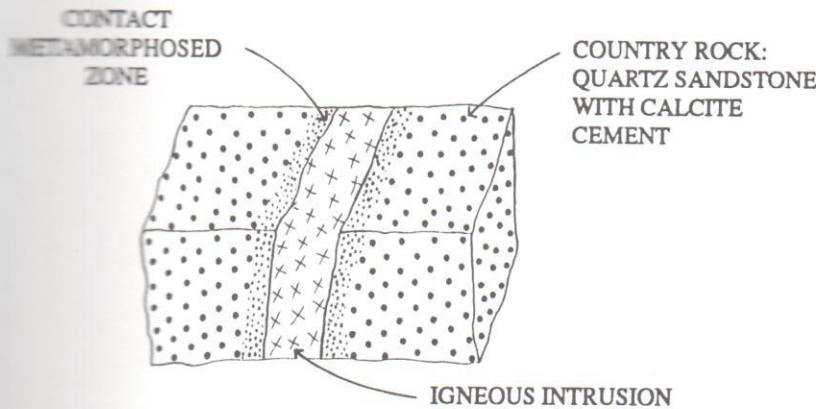
Assume $\alpha V_{1\text{atm}, 298 \text{ K}}$ is constant over the temperature interval.

Ans: $\Delta T = 12.49 \text{ K}$.

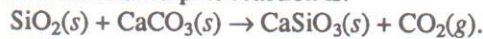
(b) Use the result from (a) to calculate the corresponding change in entropy.

Ans: $\Delta S = 2.73 \times 10^{-2} \text{ kJ}/(\text{mol}\cdot\text{K})$.

- [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:



α -Quartz Calcite Wollastonite

Calculate ΔS^0 for this reaction at 565°C .

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Ans: $\Delta S_{\text{Sys}} = -11.21 \text{ J}/(\text{mol}\cdot\text{K})$, $\Delta S_{\text{Surr}} = 13.03 \text{ J}/(\text{mol}\cdot\text{K})$, $\Delta S_{\text{Net}} = 1.82 \text{ J}/(\text{mol}\cdot\text{K}) > 0 \Rightarrow$ 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 $\Delta C_p = 0$?

Ans: $\Delta S_{\text{Sys}} = -11.53 \text{ J}/(\text{mol}\cdot\text{K})$, $\Delta S_{\text{Surr}} = 15.11 \text{ J}/(\text{mol}\cdot\text{K})$, $\Delta S_{\text{Net}} = 3.58 \text{ J}/(\text{mol}\cdot\text{K}) > 0 \Rightarrow$ spontaneous. Error $\approx 100\%$.

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

Ans: $\Delta S^{l \rightarrow v} \approx 2.08 \text{ kJ}/(\text{kg}\cdot\text{K})$.

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

Ans: $\Delta S_{\text{Net}} \approx 0$.

- [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 $P^0 = 1 \text{ atm}$. (a) Calculate the temperature shift associated with the volume change.

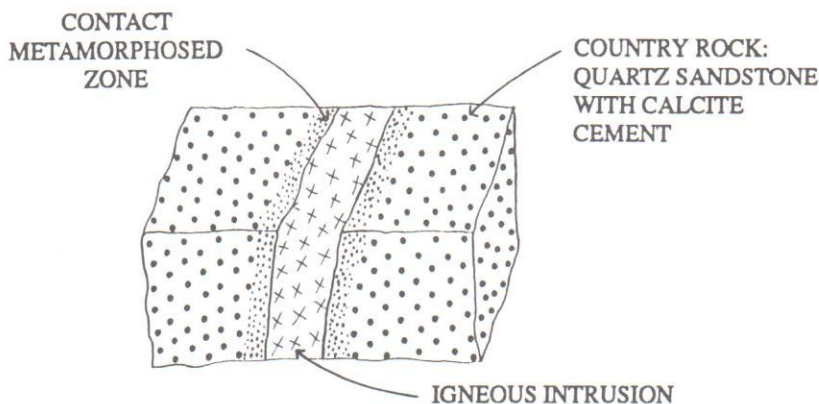
Assume $\alpha V_{1\text{atm}, 298 \text{ K}}$ is constant over the temperature interval.

Ans: $\Delta T = 12.49 \text{ K}$.

- (b) Use the result from (a) to calculate the corresponding change in entropy.

Ans: $\Delta S = 2.73 \times 10^{-2} \text{ kJ}/(\text{mol}\cdot\text{K})$.

- [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:



α -Quartz Calcite Wollastonite

Calculate ΔS^0 for this reaction at 565°C.

$$\text{Ans: } \Delta S_{565^\circ\text{C}}^0 = 154 \text{ J}/(\text{mol}\cdot\text{K}).$$

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

$$\text{Ans: } \Delta S_{1356}^{0,f} = 122.2 \text{ J}/(\text{mol}\cdot\text{K}).$$

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

$$\text{Ans: } \Delta S_T^0 [\text{J}/(\text{mol}\cdot\text{K})] = -771.17 + 4672.2 \ln(T) - 5.17T - 10.41 \times 10^{-7}T^2 + 131.26 \times 10^3T^{-0.5} - 389.32 \times 10^3T^{-2}.$$

- [3.15] Calculate the standard entropy change for the reaction in Exercise Problem [2.12] at temperature T where $298 \text{ K} < T < 844 \text{ K}$.

$$\text{Ans: } \Delta S_T^0 [\text{J}/(\text{mol}\cdot\text{K})] = 1762.2 - 238.21 \ln(T) + 140.75 \times 10^{-3}T - 113.61 \times 10^{-7}T^2 - 87.38 \times 10^2T^{-0.5} + 24.60 \times 10^5T^{-2}.$$

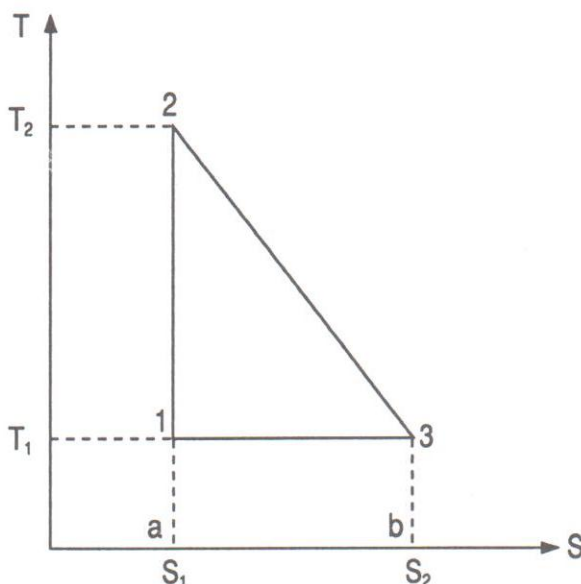
- [3.16] Consider the hypothetical power cycle represented below.

- (a) Calculate actual and Carnot efficiencies for the process if $T_2 = 600 \text{ K}$ and $T_1 = 300 \text{ K}$.

$$\text{Ans: } \eta = 33\%, \eta_{\text{Car}} = 50\%.$$

- (b) If a new alloy permits raising the maximum operating temperature to 750 K, calculate the resulting efficiencies.

$$\text{Ans: } \eta = 43\%, \eta_{\text{Car}} = 60\%.$$



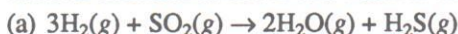
- [3.17] The Carnot cycle efficiency is often used as a basis for estimating the effect of increasing operating input temperature and lowering rejection temperature on the efficiency of a power generating process. Curzon and Ahlborn (1975, p. 22-24) have shown that to achieve theoretical Carnot efficiency, 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:

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

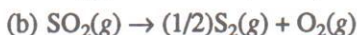
Using the data given in Exercise Problem [3.16], calculate $\eta_{C.A.}$ and compare with η and η_{Car} obtained in the same problem.

Ans: (a) $\eta_{C.A.} = 29.3\%$, (b) $\eta_{C.A.} = 36.8\%$. The predicted efficiencies are closer to the actual values in [3.16]. On a comparative basis, the $\eta_{C.A.}$ equation provides a stronger case for actual modification.

- [3.18] A small amount of $H_2S(g)$ in volcanic gases promotes intense chemical weathering of rocks in the vicinity of a volcanic vent. Calculate the standard entropy of formation associated with the production of $H_2S(g)$ from its elements at 600 K and 1 atm in $kJ/(mol \cdot K)$ and $cal/(mol \cdot K)$.



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



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



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

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

- [3.19] Show that $H_2S(g)$ spontaneously forms at 600 K. Refer to Exercise Problem [3.18]. Assume the surroundings are at 600 K. Use the heat capacity for $S_2(g)$ in Appendix A, Table A.3B.

$$\text{Ans: } \Delta S_{Net} = 100.5 J/(mol \cdot K) > 0 \Rightarrow \text{spontaneous.}$$