

Chemistry 553

Problem set 2

Due: 28 January 2011

1. Provide a clear, but terse statement of the two laws of thermodynamics. Define all terms. The second law is definable in a number of ways. Provide two ways.

From your text,

2. 5.3
3. 7.1
4. 7.3
5. 7.4
6. 7.6
7. 7.9

1. First law

$$\Delta U_{\text{universe}} = 0$$

$$\Delta U_{\text{sys}} = dq + dW_{\text{on by}}$$

energy of the universe is conserved

energy of the system increases if: the system absorbs energy or work is done on the system

Second law:

$$\Delta S_{\text{univ}} \geq 0$$

entropy of the universe increases for all spontaneous processes

$$\Delta S \geq dq/T$$

the change in system

entropy always exceeds q/T unless the process is reversible

5.3

2. a) $W_A = \frac{N!}{(N-n)!n!} \times \frac{M!}{(M-m)!m!}$

b) $W_B = \frac{(M+N)!}{(M+N-n)!n!} \times \frac{(M+N-n)!}{(M+N-m-n)!m!}$

place n particles on the $N+M$ sites

place the m particles in the remaining sites

$$W_B = \frac{(M+N)!}{m!n!(M+N-m-n)!}$$

c) using $\ln x! = x \ln x - x$, and take $M=N$, $m=n$

we find (use Maple) $\frac{W_A}{W_B} = -2 \ln(2) \times n$

$$\Delta S = k_B \ln(W_A/W_B) = -2k_B n \ln(2)$$

3 7.1

$$\begin{aligned} \text{a) } W_{\text{by}} &= \int_{V_1}^{V_2} P dV = RT \int \frac{dV}{V-b} - a^2 \int \frac{dV}{V^2} \\ &= RT \ln\left(\frac{V_2-b}{V_1-b}\right) + a^2 \left\{ \frac{1}{V_2} - \frac{1}{V_1} \right\} \end{aligned}$$

b) more or less work? rewrite as densities

$$W_{\text{by}} = RT \ln\left(\frac{1-b\rho_2}{1-b\rho_1}\right) + RT \ln\left(\frac{\rho_1}{\rho_2}\right) + a^2(\rho_2 - \rho_1)$$

less ideal gas more

If $\rho_1 < \rho_2$,

then whether its more or less depends on both a & b .

4 7.4

$$\begin{aligned} W_{\text{by}} &= \int_{V_1}^{V_2} dV P = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln\left(\frac{2V}{V}\right) \\ &= nRT \ln(2) = \text{work done by the system} \end{aligned}$$

5 7.3

$$W_{\text{by}} = \int P_{\text{ext}} dV = P_{\text{ext}} \Delta V$$

$$V_L = \left[\frac{1.0 \text{ cm}^3}{\cancel{9}} \right] \times 8g = 8 \text{ cm}^3 \text{ of liquid H}_2\text{O}$$

$$\text{vs. } V_S = \left(\frac{1 \text{ cm}^3}{0.915g} \right) \times 8g \Rightarrow \Delta V = V_S - V_L = 0.743 \text{ cm}^3$$

$$\begin{aligned} W_{\text{by}} &= 1 \text{ atm} \times 0.743 \text{ cm}^3 = 1 \text{ atm} \times \frac{1 \text{ L} \times 10^{-3}}{\text{cm}^3} \times 0.743 \text{ cm}^3 \\ &= 0.743 \times 10^{-3} \text{ L} \cdot \text{atm} \\ &= \frac{8.315 \text{ J}}{8.206 \times 10^{-2} \text{ L} \cdot \text{atm}} (0.743 \times 10^{-3} \text{ L} \cdot \text{atm}) = 0.075 \text{ J} \end{aligned}$$

6.7.6

Work for the indicated cycle

$$W_{B \rightarrow C} = P_C \Delta V(B \rightarrow C)$$

$$W_{D \rightarrow A} = P_A \Delta V(D \rightarrow A) = -P_A \Delta V(B \rightarrow C)$$

so

$$\oint dW = (P_C - P_A)(\Delta V(B \rightarrow C))$$

$$= 200 \text{ atm} (1 \text{ cm}^3) \times \frac{1 \text{ L}}{10^3 \text{ cm}^3} \times \frac{8.206 \text{ J}}{0.08206} \times \frac{315}{1000}$$

$$\oint dW = 20.3 \text{ J}$$

7.7.9

a) constant volume \Rightarrow no work

b) $\oint dU = 0$

c) $\oint dW = RT_1 \ln\left(\frac{V_1}{V_4}\right) + RT_2 \ln\left(\frac{V_3}{V_2}\right)$

but $\frac{V_3}{V_2} = \frac{V_4}{V_1}$, $\oint = R(T_1 - T_2) \ln\left(\frac{V_1}{V_4}\right)$

$V_4 = 10$, $V_1 = 0.1$, $V_4/V_1 = 10$, $T_1 = 3000 \text{ K}$
 $T_2 = 2000 \text{ K}$

$$\oint dW = (0.1 \text{ mole}) \left(\frac{8.315 \text{ J}}{\text{K} \cdot \text{mole}} \right) (1700 \text{ K}) \ln\left(\frac{1}{100}\right)$$

work done by the gas = ~~2154 J~~
6.5 kJ