Chemistry 553

Problem set 3

Due: 11 February 2011

From your text,

1. 8.3
2. 8.5
3. 8.7
4. 8.9
5. 8.14
6. 8.18
7. 9.9
8. 9.14

Problem set 3

1. 8.3

a) $P_A = 0.42\,\text{atm}, \quad V_A = 100\,L$

$P_B = 0.15\,\text{atm}$

$PV = \text{const} \Rightarrow \quad V_B = \frac{P_A V_A}{P_B} = \frac{(0.42)}{(0.15)} 100\,L$

$V_B = 280\,L$

b), 1c) isothermal $\Rightarrow \Delta T = 0$ so $\Delta U = \Delta H = 0$.

$\Delta U = 0 = q_{by} - \int P dV \Rightarrow \quad q_{by} = RT \ln(V_2/V_1) = (8.315\frac{J}{K})(500\,K) \ln\left(\frac{280}{100}\right)$

$q_{by} = 2.9\,kJ$

2. 8.5

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

but $dA = -SdT - PdV$

so $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

and $dS(T,V) = C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV$

For an isothermal expansion of an ideal gas

$dS = \frac{N k_B}{V} dV \Rightarrow \Delta S = N k_B \ln(V_2/V_1)$

a) $\Delta S = 2R \ln(300/100) = 2R \ln(3) = 18.3\,J/K$

b) $\Delta G = +\Delta H - T\Delta S = -T\Delta S = -300\,K\,(18.3\,\frac{J}{K})$

$\Delta G = -5.5\,kJ$

3. 8.7

$$\oint dU = \oint dG = 0, \quad \oint dq, \oint dw, \oint PdV \text{ do not.}$$

4. 8.9

$$\begin{tikzcd}
L(373) \arrow[rr, "b"] & & G(373) \arrow[d, "c"] \\
L(473) \arrow[u, "a"] \arrow[rr, Rightarrow, "\text{desired path}"'] & & G(473)
\end{tikzcd}$$

$$\Delta H_{\substack{\text{desired}\\ \text{path}}} = \Delta H_a + \Delta H_b + \Delta H_c$$

$$\Delta H_a = 75 \frac{J}{K \cdot mol} (373 - 473)$$

$$\Delta H_b = 40.7 \text{ kJ/mole}$$

$$\Delta H_c = 3.5 \frac{J}{K \cdot mol} * (473 - 373)$$

$$\Delta H = 40{,}700 + 350 - 7500 = 33.6 \text{ kJ/mole}$$

5. 8.14

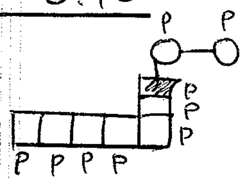
$$dA = -SdT - PdV$$

$$dA = -\frac{N k_B T}{V} dV \Rightarrow \Delta A = -N k_B T \ln(V_2/V_1)$$

$$G(V) = A + PV = A + N k_B T$$

$$G(V) = -N k_B T \ln V + N k_B T = -N k_B T \ln(V/e)$$

6. 8.18



The flexible bit can have 9 configurations while attached to the top or side of the darkened block.

a) $\therefore W = k_B \ln W = k_B \ln 9$

b) $A_{Bound} = 5\epsilon - k_B T \ln \underbrace{W_{bound}}_{=1} = 5\epsilon$

$A_{unbound} = -k_B T \ln W = -k_B T \ln 9$

$\Delta A = 5\epsilon + k_B T \ln 9$

c) $\Delta A = -5 \times 1\text{ kcal} + \left(8.315 \frac{J}{K \cdot mole}\right)(300K) \ln 9 = -15.4\text{ kJ}$

$\left(1.98 \frac{cal}{K}\right)$ $= -3.7\text{ kcal}$

d) $5\epsilon + k_B T \ln 9 = 0 \Rightarrow T = \frac{-5\epsilon}{k_B \ln 9} = \frac{5\text{ kcal}}{1.98 \frac{cal}{K} \cdot \ln 9}$

$T_{dis} \cong 1150\text{ K}$

e) If the flexible bit were rigid, then

$\Delta A = \epsilon = -5\text{ kcal} = -20.9\text{ kJ}$

f) rigid loop favors binding.

7. 9.9

For the rubber band,

$$dU = TdS + fdL$$

where $f = aT(L-L_o)$ $\therefore$ as L increases beyond L_o, the internal energy increases

a) $dA = dG = d[U-TS] = -SdT + fdL$

$\Rightarrow$ maxwell $\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L = -a(L-L_o)$

and $dS = -\left(\frac{\partial f}{\partial T}\right)_L dL = -a(L-L_o)dL$

$$\Delta S = -a\int_{L_o}^{L} dL\,(L-L_o) = -a\int_0^{\Delta L} d(\Delta L)\,\Delta L$$

$$\Delta S = -(a/2)(\Delta L)^2$$

As for ΔH

$$dG = d[H-TS] = dH - TdS = dA = fdL$$

$$dH = fdL + TdS = \left[f - T\left(\frac{\partial f}{\partial T}\right)_L\right]dL = 0$$

$$\Delta H = 0$$

b) Adiabatic stretching $dU = \underbrace{dq}_{=0} + fdL$

$$CdT = fdL = aT(L-L_o)\,dL$$

$$\frac{dT}{T} = \frac{a}{C}\,\Delta L\,d(\Delta L) \Rightarrow \ln\left(\frac{T_2}{T_1}\right) = \frac{a}{2C}(\Delta L)^2$$

and $T_2 = T_1 \exp\left(\frac{a}{2C}(\Delta L)^2\right)$

As $\Delta L \uparrow$, so does T.

8. 9.14

a) $dU = TdS + fdx$ $\qquad f = (aT+b)x$

$dA = dG$ (can ignore PV changes)

$dA = -SdT + fdx = dG$

At const T, $dG = fdx, \quad \Delta G = \int_{x_0}^{x} dx\, f$

$$\Delta G = \int_{x_0}^{x} dx\, x\,(aT+b) = \tfrac{1}{2}(x^2 - x_0^2)(aT+b)$$

b) maxwell $\Rightarrow \left(\frac{\partial f}{\partial T}\right)_x = \cancel{-}\left(\frac{\partial S}{\partial x}\right)_T = aX$

c) $\left(\frac{\partial S}{\partial x}\right)_T = -aX \Rightarrow \Delta S = -\frac{a}{2}(x^2 - x_0^2)$

d) $dG = fdx, \quad dS = -\left(\frac{\partial f}{\partial T}\right)_x dx$

$dG = d(H - TS) = dH - TdS$ so

$dH = dG + TdS = fdx - T\left(\frac{\partial f}{\partial T}\right)_x dx$

or $dH = \left[f - T\left(\frac{\partial f}{\partial T}\right)_x\right] dx$

$= bx, \qquad \Delta H = \frac{1}{2}b(x^2 - x_0^2)$

e) $\Delta G = \Delta H - T\Delta S = (\underbrace{\tfrac{1}{2}b}_{\Delta H} + \underbrace{\tfrac{1}{2}aT}_{T\Delta S})(x^2 - x_0^2)$

when $aT > b$ entropy rules.