Chemistry 410B **Exam 4** **Spring 2008**

Solutions

1. Find an expression for $D \equiv N_1 - N_2$ in terms of the Einstein coefficients, the total number of molecules N, and the radiation density $\rho(\nu_{12})$, assuming a two-state system in steady state, with both states non-degenerate. **Solution:** We can start from the stead state condition

$$\frac{dN_1}{dt} = -N_1 B_{12}\rho(\nu_{12}) + N_2 B_{21}\rho(\nu_{12}) + N_2 A_{21} = 0.$$

We can simplify this, because if $g_1 = g_2 = 1$, then $B_{21} = g_1 B_{12}/g_2 = B_{12}$. We then look for D, and rewrite N_2 in terms of D and N:

$$\begin{aligned}
0 &= -N_1 B_{12}\rho(\nu_{12}) + N_2 B_{12}\rho(\nu_{12}) + N_2 A_{21} \\
&= B_{12}\rho(\nu_{12})(N_2 - N_1) + \frac{1}{2}\left[(N_1 + N_2) - (N_1 - N_2)\right] A_{21} \\
&= -B_{12}\rho(\nu_{12})D + \frac{1}{2}(N - D)A_{21} \\
&= D\left[-B_{12}\rho(\nu_{12}) - \frac{A_{21}}{2}\right] + \frac{NA_{21}}{2} \\
D &= \frac{NA_{21}/2}{B_{12}\rho(\nu_{12}) + A_{21}/2} = \frac{N}{(2B_{12}\rho(\nu_{12})/A_{21}) + 1}
\end{aligned}$$

2. A process is carried out such that $\Delta H = -6.2$ kJ mol^{-1}, $\Delta G = +23.7$ kJ mol^{-1}, and $\Delta F = +27.6$ kJ mol^{-1}. Find ΔE. **Solution:**

$$\begin{aligned}
H &= E + PV & G &= H - TS \\
TS &= H - G & F &= E - TS = E - (H - G) \\
E &= F + H - G \\
\Delta E &= \Delta F + \Delta H - \Delta G \\
&= (27.6 - 6.2 - 23.7)\ \text{kJ mol}^{-1} = \boxed{-2.3\ \text{kJ mol}^{-1}.}
\end{aligned}$$

3. Circle the letter for *each* of the following which is equal to the pressure P of the sample:

[✓ a.] $k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{T,n}$ Eq. 17.35

b. $T\left(\frac{\partial S}{\partial E}\right)_{T,n}$ wrong units

[✓ c.] $-\left(\frac{\partial F}{\partial V}\right)_{T,n} = -\left(\frac{-S\partial T - P\partial V - \mu\partial n}{\partial V}\right)_{T,n} = P$

d. $\frac{1}{\kappa_T}\frac{dV}{V} = -V\left(\frac{\partial P}{\partial V}\right)_T \frac{dV}{V} = dP \neq P$

[✓ e.] $\frac{k_B T}{\rho} = \frac{nRT}{V} = P$

[✓ f.] $-\frac{dw_{\text{rev}}}{dV} = -\left(\frac{-PdV}{dV}\right) = P$

4. For the non-linear triatomic molecule FNO, the average vibrational energy per molecule between 280 K and 320 K is given roughly by the equation

$$\langle \epsilon_{\text{vib}} \rangle \approx k_B \left[a + b(T - T_0) + c(T - T_0)^2 \right]$$

where $a = 33.71$ K, $b = 0.630$, $c = 0.00232\ \text{K}^{-1}$, and $T_0 = 222.2$ K. This includes all of the vibrational modes. Find the *total* molar heat capacity C_{Pm} of FNO at 298 K, assuming the sample otherwise behaves like an ideal gas. **Solution:** Divide the heat capacity up into its distinct contributions, keeping in mind that a non-linear molecule has 3 rotational degrees of freedom:

$$\begin{aligned}
C_{Pm} &= C_{Vm} + R = C_{\text{trans}} + C_{\text{rot}} + C_{\text{vib}} + R \\
&= \frac{3}{2}R + \frac{3}{2}R + \mathcal{N}_A \frac{d \langle \epsilon_{\text{vib}} \rangle}{dT} + R \\
&= 4R + (\mathcal{N}_A k_B) \frac{d}{dT} \left[a + b(T - T_0) + c(T - T_0)^2 \right] \\
&= 4R + R\left[b + 2c(T - T_0)\right] = R\left[4 + 0.630 + 2(0.00232)(298 - 222.2)\right] \\
&= \boxed{41.4\ \text{J K}^{-1}\ \text{mol}^{-1}}.
\end{aligned}$$

5. For a monatomic ideal gas, set $\mu = \frac{3}{2}RT$. We add Δn moles of a monatomic ideal gas to a sample at constant pressure P and temperature T. Find an equation for the work w during this process in terms of P, T, and/or Δn. Because adding the gas invloves net motion of the molecular mass, the $\mu\, dn$ term contributes to the work in this problem. **Solution:**

$$\begin{aligned}
w &= \int \left[-PdV + \mu dn \right] = -P\Delta V + \mu \Delta n \\
&= -P\Delta \left(\frac{nRT}{P} \right) + \frac{3}{2}RT\Delta n = -RT\Delta n + \frac{3}{2}RT\Delta n \\
&= \boxed{\tfrac{1}{2}RT\Delta n}.
\end{aligned}$$