Quiz 7 – Core Course 2002 Name: ______________________________

Please show your work, and your thinking, in the space provided. Be brief, but complete. Long, wandering answers typically demonstrate a lack of understanding…

$\hbar = 1.054x10^{-34} J\,s$ $m_e = 9.109x10^{-31} kg$
$h = 6.626x10^{-34} J\,s$ $e = 1.602x10^{-19} C$
$c = 2.998x10^{8} m\,s^{-1}$ $N_0 = 6.022x10^{23} mol^{-1}$
$k = 1.381x10^{-23} J\,K^{-1}$ $\pi = 3.14159$

$$W = \frac{N!}{n_1!n_2!\dots n_t!} \qquad S = k\ln W$$
$$W_{total} = W_A W_B \qquad S_{total} = S_A + S_B$$

$$U = \sum_{i=1}^{t} N_i\varepsilon_i \qquad \partial U = \partial q + \partial w \qquad \partial w = -P\partial V$$

$$x! \approx \left(\frac{x}{e}\right)^x \qquad \ln(x!) \approx x\ln\left(\frac{x}{e}\right) = x\ln(x) - x$$

$$H = U + PV \qquad G = H - TS$$

$$E = h\upsilon = \frac{hc}{\lambda}$$

$$\partial S = \left(\frac{\partial S}{\partial U}\right)_{V,N}\partial U + \left(\frac{\partial S}{\partial V}\right)_{U,N}\partial V + \sum_{j=1}^{M}\left(\frac{\partial S}{\partial N_j}\right)_{U,V,N_{i\neq j}}\partial N_j$$

$$\frac{n_B}{n_A} = e^{-\frac{\varepsilon_B - \varepsilon_A}{kT}}$$

$$\partial U = \left(\frac{\partial U}{\partial S}\right)_{V,N}\partial S + \left(\frac{\partial U}{\partial V}\right)_{S,N}\partial V + \sum_{j=1}^{M}\left(\frac{\partial U}{\partial N_j}\right)_{S,V,N_{i\neq j}}\partial N_j$$

$$C_p = \left(\frac{\partial q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\partial U = T\partial S - p\partial V + \sum_{j=1}^{M}\mu_j\partial N_j$$

$$\mu_j = \left(\frac{\partial U}{\partial n_j}\right)_{V,S,n_{i\neq j}} = \left(\frac{\partial G}{\partial n_j}\right)_{T,P,n_{i\neq j}} = \left(\frac{\partial H}{\partial n_j}\right)_{S,P,n_{i\neq j}}$$

$$\partial S = \frac{1}{T}\partial U + \frac{p}{T}\partial V - \sum_{j=1}^{M}\frac{\mu_j}{T}\partial N_j$$

1. (15 points) Using what you know about chemistry, which of the following equations are true and which are false? You need not do any deriving here. Simply use common sense.

$T = \left(\frac{\partial S}{\partial U}\right)_{V,N}$	**True**	**False**
$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$	**True**	**False**
$\mu_j = \left(\frac{\partial U}{\partial N_j}\right)_{S,V,N_{i\neq j}}$	**True**	**False**

Answer: False, True, True

2. a) (20 points) Consider an NMR experiment in a field for which protons resonate (transitions from ground to excited state occur when subjected to radiowaves) at a frequency of 800 MHz. What is the ratio of excited to ground state population at room temperature (25° C)?

Use the Boltzmann equation:

$$\Delta\varepsilon = h\upsilon = \left(6.626x10^{-34}\,J\,s\right)\left(800x10^{6}\,s^{-1}\right) = 5.30x10^{-25}\,J$$

$$\frac{n_{excited}}{n_{ground}} = e^{-\frac{\Delta\varepsilon}{kT}} = e^{-\frac{5.30x10^{-25}\,J}{\left(1.381x10^{-23}\,J\,K^{-1}\right)(25+273)K}} = e^{-\left(1.29x10^{-4}\right)} = 0.99987$$

Just for fun:

$$\Delta E = N_0\Delta\varepsilon = 5.30x10^{-25}\,J\left(6.022x10^{23}\,mol^{-1}\right) = 0.32J\,mol^{-1} = 0.00032kJ\,mol^{-1}$$ Tiny!!

b) (15 points) What is the ratio for that same transition at at 1.0 K?

at 1 K: $$\frac{n_{excited}}{n_{ground}} = e^{-\frac{\Delta\varepsilon}{kT}} = e^{-\frac{5.30x10^{-25}\,J}{\left(1.381x10^{-23}\,J\,K^{-1}\right)1K}} = e^{-\left(3.84x10^{-2}\right)} = 0.962$$

Even at 1 K, the levels are *nearly* equally populated!

3. a) (15 points) Assuming ΔH° and ΔS° independent of temperature, derive, in terms of only ΔH° and/or ΔS° (and appropriate fundamental constants), an expression for:

$$\frac{\partial \ln(K_{eq})}{\partial\left(\frac{1}{T}\right)} =$$

Answer:

$$\ln K_{eq} = -\frac{\Delta G^o}{RT} = -\frac{\Delta H^o}{RT} + \frac{T\Delta S^o}{RT} = -\frac{\Delta H^o}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^o}{R}$$

$$\frac{\partial \ln K_{eq}}{\partial\left(\frac{1}{T}\right)} = \frac{\partial}{\partial\left(\frac{1}{T}\right)}\left[-\frac{\Delta H^o}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^o}{R}\right]$$

$$\frac{\partial \ln K_{eq}}{\partial\left(\frac{1}{T}\right)} = -\frac{\Delta H^o}{R}$$

b) (10 points) From simple extensions of the Boltzmann equation as we've seen it, we can derive for any reaction:

$$K_{eq} = e^{-\frac{\Delta G^o}{RT}}$$

Use the answer to part (a) to derive an expression for the temperature dependence of the equilibrium constant. In other words, derive K_{T_2} in terms of T_1, T_2, K_{T_1}, ΔH°, and/or ΔS° (and appropriate fundamental constants).

Answer:

$$\partial \ln K_{eq} = -\frac{\Delta H^o}{R}\partial\left(\frac{1}{T}\right)$$

$$\int_{T_1}^{T_2} \partial \ln K_{eq} = \int_{T_1}^{T_2}\left[-\frac{\Delta H^o}{R}\partial\left(\frac{1}{T}\right)\right] = -\frac{\Delta H^o}{R}\int_{T_1}^{T_2}\partial\left(\frac{1}{T}\right)$$

$$\ln K_{T_2} - \ln K_{T_1} = -\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln K_{T_2} = \ln K_{T_1} - \frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$K_{T_2} = K_{T_1} e^{-\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

4. For the mixing of a two component system, n_A molecules of A and n_B molecules of B, the multiplicity of states is given by:

$$W = \frac{N!}{n_A! n_B!} \qquad N = n_A + n_B$$

Remember also that the mole fraction for each is defined as: $\chi_i = \frac{n_i}{N}$

a) (15 points) Consider the mixing of two solutions. Derive the entropy of mixing in terms of χ_A and χ_B - Remembering that there are a *large* number of molecules in a real system, show that $\Delta S_{mix} = -k[n_A \ln \chi_A + n_B \ln \chi_B]$

Answer:

$$W = \frac{N!}{n_A! n_B!}$$

$$\Delta S_{mix} = k \ln W = k \ln\left(\frac{N!}{n_A! n_B!}\right)$$

$$\Delta S_{mix} = k[\ln(N!) - \ln(n_A!) - \ln(n_B!)]$$

$$\Delta S_{mix} = k[N \ln(N) - N - (n_A \ln(n_A) - n_A) - (n_B \ln(n_B) - n_B)]$$

$$\Delta S_{mix} = k[N \ln(N) - n_A \ln(n_A) - n_B \ln(n_B) - N + n_A + n_B]$$

$$\Delta S_{mix} = k[(n_A + n_B)\ln(N) - n_A \ln(n_A) - n_B \ln(n_B) + 0]$$

$$\Delta S_{mix} = k[n_A \ln(N) + n_B \ln(N) - n_A \ln(n_A) - n_B \ln(n_B)]$$

$$\Delta S_{mix} = k\left[-n_A \ln\left(\frac{n_A}{N}\right) - n_B \ln\left(\frac{n_B}{N}\right)\right]$$

$$\Delta S_{mix} = -k[n_A \ln \chi_A + n_B \ln \chi_B]$$

b) (10 points) Finally, express ΔS_{mix} in terms of N and χ_A only (you can use the result from part (a) that is already given to you)

Answer:

$$1 = \frac{N}{N} = \frac{n_A + n_B}{N} = \frac{n_A}{N} + \frac{n_B}{N} = \chi_A + \chi_B = 1$$

$$\chi_B = 1 - \chi_A$$

$$\Delta S_{mix} = -k[n_A \ln \chi_A + n_B \ln \chi_B]$$

$$\Delta S_{mix} = -kN\left[\frac{n_A}{N} \ln \chi_A + \frac{n_B}{N} \ln \chi_B\right] = -kN[\chi_A \ln \chi_A + \chi_B \ln \chi_B]$$

$$\Delta S_{mix} = -kN[\chi_A \ln \chi_A + (1 - \chi_A)\ln(1 - \chi_A)]$$