UNIVERSITY OF TORONTO
Faculty of Arts and Science

December EXAMINATIONS 2014

CHM 220F

Duration - 2 hours: Non-programmable calculators allowed.

Answer all questions **in ink** in the spaces provided on the test paper.

Supplementary information can be found at the end of the test paper.
Please note that some questions involve multiple parts and not all questions are worth the same number of marks.

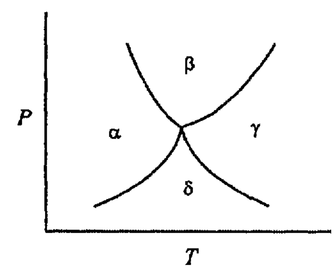
Name: ____
Please print clearly

Student Number: ___________________________________

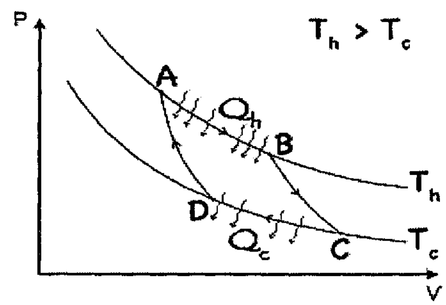
Marks	
1.	
2.	
3.	
4.	
5.	
Total	/100

1. (5 points) Explain why the boiling temperature of a one component liquid always increases with pressure for temperatures below the critical point.

2. (5 points) What is wrong with the phase diagram for a *single* component system in the picture below? Note that α, β, γ and δ denote different phases.



3. (25 marks total) Consider a Carnot cycle heat engine using an *arbitrary* gas as a working substance. Recall that the processes between states $A \to B$ and $C \to D$ are reversible and isothermal, while those between states $B \to C$ and $D \to$A are reversible and adiabatic. Use the first and second laws of thermodynamics to answer the questions below.



(i) (10 points) By computing entropy changes, show that

$$\frac{T_c}{T_h} = \frac{-Q_c}{Q_h},$$

where T_c and T_h are the cold and hot temperatures in the isothermal steps of the cycle and Q_c and Q_h are the heat flow during these steps.

(ii) (10 points) Show that the work done is given by

$$W = -Q_h \left(1 - \frac{T_c}{T_h}\right).$$

(iii) (5 points) Show that the efficiency ϵ of the Carnot cycle is a function only of the ratio of the temperature of the cold reservoir to that of the hot reservoir,

$$\epsilon = 1 - \frac{T_c}{T_h}.$$

4. (20 marks total) Suppose we have one mole of a **pure** system of a volatile substance A with a vapor pressure $P_A^* = 2$ atm at a temperature T.

   (i) (5 marks) Describe the phase composition of the system as the pressure P is gradually increased isothermally from a pressure of $P = 1$ atm to a pressure of $P = 3$ atm. Note the pressures where the system changes composition.

Now suppose that one mole of a volatile substance B with vapor pressure $P_B^* = 1$ atm is added to the system at temperature T.

   (ii) (5 marks) At what pressure does vapor first appear in the mixture and what is the composition of this vapor?

(iii) (10 marks) Suppose the total pressure of the mixture is $P = 1.4$ atm. Compute the composition of the liquid and vapor phases and determine the number of moles of liquid and vapor at this pressure.

5. (45 marks total) Consider a particle of mass m confined by a harmonic potential of the form $V(x) = \frac{1}{2}m\omega^2 x^2$, where ω is the frequency of the oscillator. The energy of the state $\psi_n(x)$ with quantum number n is $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$.

(i) (15 marks) Write down the Hamiltonian operator for the system and **verify** that the ground state wavefunction

$$\psi_0(x) = \left(\frac{\alpha^2}{\pi}\right)^{1/4} e^{-\alpha^2 x^2/2},$$

where $\alpha^2 = m\omega/\hbar$, satisfies the time-independent Schrödinger equation with energy $E_0 = \hbar\omega/2$.

(ii) (5 marks) What is the lowest frequency of light ν at which the system absorbs?

(iii) (10 marks) Using the wave function in part (i) and the integrals provided in the formula sheet, show that the expectation value of the potential energy in the ground state is equal to half the energy of the ground state, i.e $\langle V \rangle = E_0/2$.

(iv) (15 marks) Suppose two identical non-interacting particles of mass m are positioned in the harmonic potential. Write down

- The Hamiltonian for the two particle system.
- The wavefunctions $\psi_{n_1,n_2}(x_1, x_2)$ in terms of the single particle wavefunctions $\psi_n(x)$ **and** the allowed energies $E_{n_1 n_2}$ assuming that the overall wavefunction must be anti-symmetric with respect to how we label particles so that

$$\psi_{n_1,n_2}(x_1, x_2) = -\psi_{n_1,n_2}(x_2, x_1).$$

- The ground state energy of the system.

Equation sheet

$$T^o = 298\ K = 25^o\ C \qquad P^o = 1\text{ bar} = 1\times 10^5\text{ Pa} = 1\times 10^5 \frac{\text{Kg}}{\text{m}-\text{s}^2}$$

$$R = 8.3145\ J/(K-\text{mol}) = 0.082\text{ L}-\text{atm}/(\text{K}-\text{mol})$$

$$\hbar = 1.055\times 10^{-34} J-s \qquad h = 6.626\times 10^{-34} J-s \qquad c = 3.0\times 10^8 m/s$$

$$dU = TdS - pdV \qquad H = U + PV \qquad G = H - TS \qquad A = U - TS$$

$$TdS = dq_{\text{rev}} \qquad dS \geq dq/T \qquad \epsilon = -w/q_a \qquad \left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \qquad \left(\frac{\partial H}{\partial P}\right)_S = V \qquad \left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V \qquad \left(\frac{\partial \mu}{\partial T}\right)_P = -\overline{S} \qquad \left(\frac{\partial \mu}{\partial P}\right)_T = \overline{V}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j\neq n_i} \qquad G = \sum_i n_i\mu_i \qquad \Delta G^o_{\text{rxn}} = \sum_i \nu_i \Delta G^o_{f,i} = -RT\ln K$$

$$K = \prod_i a_i^{\nu_i} \qquad \frac{d\ln K_P}{dT} = \frac{\Delta H^o_{\text{rxn}}}{RT^2} \qquad f = c - p + 2$$

$$\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{\Delta\overline{S}_{\text{tr}}}{\Delta\overline{V}_{\text{tr}}} = \frac{\Delta\overline{H}_{\text{tr}}}{T\Delta\overline{V}_{\text{tr}}} \qquad \ln\frac{P_f}{P_i} = -\frac{\Delta\overline{H}_{\text{vap}}}{R}\left(\frac{1}{T_f} - \frac{1}{T_i}\right)$$

$$\frac{1}{T} = \frac{1}{T_{\text{fus}}} - \frac{R\ln\chi_{\text{solvent}}}{\Delta\overline{H}_{\text{fus}}}$$

$$\mu_i^{\text{soln}} = \mu_i^* + RT\ln P_i/P_i^* \qquad \mu_i^{\text{soln}} = \mu_i^* + RT\ln a_i$$

$$P = P_2^* + (P_1^* - P_2^*)\chi_1 = \frac{P_1^* P_2^*}{P_1^* + (P_2^* - P_1^*)y_1} \qquad \chi_1 = \frac{y_1 P_2^*}{P_1^* + (P_2^* - P_1^*)y_1}$$

$$y_1 = \chi_1^v = \frac{P_1^*}{P}\frac{P - P_2^*}{P_1^* - P_2^*} = \chi_1\frac{P_1^*}{P} \qquad Z_1 = \frac{n_1}{n_T} \qquad \frac{n_{\text{tot}}^{\text{liq}}}{n_{\text{tot}}^{\text{vap}}} = \frac{y_1 - Z_1}{Z_1 - \chi_1}$$

$$\Pi = c_{\text{solute}}RT \qquad \mu_i = \mu_i^o + RT\ln c_i/c_i^o$$

Identities:

$$\frac{d}{dx}e^{-\alpha^2x^2/2} = -\alpha^2 x e^{-\alpha^2x^2/2} \qquad \frac{d^2}{dx^2}e^{-\alpha^2x^2/2} = -\alpha^2\left(1 - \alpha^2x^2\right)$$

Integrals:

$$\int_{-\infty}^{\infty} dx\ e^{-\alpha^2x^2} = \frac{\sqrt{\pi}}{\alpha}, \quad \int_{-\infty}^{\infty} dx\ x^2 e^{-\alpha^2x^2} = \frac{\sqrt{\pi}}{\alpha}\frac{1}{2\alpha^2}$$

$$e^{ix} = \cos x + i\sin x, \quad \left(e^{ix}\right)^* = e^{-ix}$$