UNIVERSITY OF TORONTO
Faculty of Arts and Science
December EXAMINATIONS 2012
CHM 220
duration: 2 hours – no aids allowed
total marks: 50 marks

Answer all questions in ink in the spaces provided on the test paper.
Supplementary information is at the end of the test.

Name ( surname first, followed by given names): ______________________________________
please print clearly

Student number: ______________________________________

Tutorial group code: T_____________________________________

| MARKS | |
|---|---|
| 1. | |
| 2. | |
| 3. | |
| 4. | |
| 5. | |
| total | |

1. (10 marks) A reversible Carnot cycle engine operates between the temperatures $T_1$ and $T_2$, $(T_1 > T_2)$. The working substance is one mole of a gas with equation of state $PV = RT(1+\frac{c}{V^2})$, where $c$ is a constant. The steps in the cycle are:

$$1 = (T_1, V_1) \xrightarrow{(a)} 1' = (T_1, V_{1'}) \xrightarrow{(b)} 2 = (T_2, V_2) \xrightarrow{(c)} 2' = (T_2, V_{2'}) \xrightarrow{(d)} 1 = (T_1, V_1).$$

(i) Compute the heat absorbed by the system in the steps (a) and (c).

(ii) Compute the entropy changes for each step in the cycle.

(iii) Draw a sketch of this Carnot cycle in the internal energy-volume $(U, V)$ plane. Label the points and lines in this diagram and discuss why the lines have the forms that you have drawn.

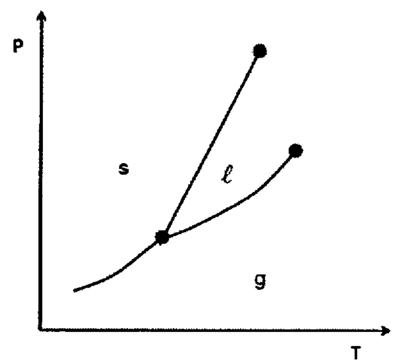
(iv) For a heat engine operating between the temperatures $T_1$ and $T_2$, (positive) work is done on the system and a certain amount of (positive) heat is transferred from the cold $(T_2)$ reservoir to the hot $(T_1)$ reservoir. What is Clausius' statement of the Second Law of Thermodynamics and is it violated by this process?

2. (8 marks) This question concerns conditions for equilibrium.

(i) Salt ($B$) is dissolved in water ($A$) to form a solution with mole fraction $x_A$. The solution is in equilibrium with its vapor and the vapor pressure of $A$ above the solution satisfies Raoult's law. Starting from the condition for equilibrium between the liquid and vapor phases, obtain an expression for the mole fraction of $A$ in solution, $x_A$, in terms of the Gibbs free energy per mole of vaporization, $\Delta\overline{G}_{vap}$.

(ii) The reaction $B + 2A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 3A$ occurs in the gas phase at a fixed temperature $T$ and total pressure $P$. The gas may be assumed to be ideal. What is the condition for *chemical* equilibrium?

3. (8 marks) This question concerns one-component phase equilibria.
(i) A pressure-temperature $(P, T)$ phase diagram for a one-component substance is shown below. It may or may not have a correct form.




Label the lines and points in this diagram. If any aspects of the diagram violate physical principles, discuss them.

(ii) In the diagram above, two of the lines are depicted as being more highly curved than the other line. Using the Clapeyron equation, discuss this feature of the diagram.

4. (12 marks) A one-dimensional quantum harmonic oscillator with potential energy operator $\hat{V}(x) = \frac{1}{2}m\omega^2\hat{x}^2$ is in its first excited state described by the wave function $\psi_1(x)$ (see supplementary material).

(i) What is the expectation value of the potential energy operator $\hat{V}(x)$ when the oscillator in this first excited state?

Next, suppose the oscillator is described by the wave function $\psi(x) = \frac{1}{2}(\psi_0(x) + \sqrt{3}\psi_1(x))$, where $\psi_0(x)$ and $\psi_1(x)$ are the ground and first excited states of the oscillator given in the supplementary material. Parts (ii)-(iv) pertain to a system with this wave function.

(ii) Determine if this wave function is normalized. If it is not, construct a wave function that is normalized.

Problem 4. (continued)

(iii) What is the probability of finding the oscillator in the region $x > 0$?

(iv) Suppose a single measurement of the energy (Hamiltonian operator) was made and the result $E_1$ was found. What is the probability of finding this result?

5. (12 marks) A quantum particle is confined to a one-dimensional box of length $L$ by the potential energy function $V(x) = 0$ for $0 < x < L$ and $V(x) = \infty$ otherwise, corresponding to the Hamiltonian operator, $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ inside the box. Suppose the particle has the ground state wave function $\psi_1(x)$ (see supplementary material).

(i) Repeated measurements of the energy are made on this system. What is the probability of finding the energy $E_2$?

(ii) For this particle-in-a-box system consider the two operators $\hat{x}\hat{H}$ and $\hat{H}\hat{x}$. By computing how they operate on an arbitrary wave function $\psi(x)$, determine the value of the commutator $[\hat{x}, \hat{H}] = \hat{x}\hat{H} - \hat{H}\hat{x}$. Comment on whether it is possible to measure these two operators simultaneously.

Problem 5. (continued)

(iii) What is the expectation value of the operator $\hat{x}\hat{H}$?

(iv) What is the expectation value of the operator $\hat{H}\hat{x}$?

**Supplementary information**:

A possibly useful identity is $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ and the Clapeyron equation is $\frac{dP}{dT} = \frac{\Delta \overline{S}}{\Delta \overline{V}}$.

Work in a reversible adiabatic process from state $(P_1, V_1, T_1)$ to state $(P_2, V_2, T_2)$ for an ideal gas: $w = \frac{P_1V_1}{(\gamma-1)}\left[\left(\frac{V_2}{V_1}\right)^{1-\gamma} - 1\right] = \frac{P_1V_1}{(\gamma-1)}\left[\left(\frac{T_2}{T_1}\right) - 1\right]$, $\gamma = \frac{R}{C_V} + 1$. The second form follows from the result proven in class that $\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{1-\gamma}$.

For a closed system:

$$dU = TdS - PdV, \quad dH = TdS + VdP, \quad dA = -SdT - PdV, \quad dG = -SdT + VdP.$$

The mole fraction of species $B$ in a binary solution, $x_B$, is related to its mole fraction in the vapor, $x_B^g$, by $x_B = P_A^* x_B^g / [P_B^* - (P_B^* - P_A^*)x_B^g]$.

Integrals:

$$\int_0^L dx\ \sin^2\frac{n\pi x}{L} = \frac{L}{2}, \quad \int_0^L dx\ x\sin^2\frac{n\pi x}{L} = \frac{L^2}{4}, \quad \int_0^L dx\ \sin\frac{n\pi x}{L}\cos\frac{n\pi x}{L} = 0.$$

$$\int_0^L dx\ x^2 \sin^2\frac{n\pi x}{L} = \left(\frac{L}{2\pi n}\right)^3\left(\frac{4\pi^3 n^3}{3} - 2\pi n\right).$$

$$\int_0^\infty dx\ e^{-ax^2} = \frac{1}{2}\sqrt{\frac{\pi}{a}}, \quad \int_0^\infty dx\ xe^{-ax^2} = \frac{1}{2a}, \quad \int_0^\infty dx\ x^2 e^{-ax^2} = \frac{1}{4}\sqrt{\frac{\pi}{a^3}},$$

$$\int_0^\infty dx\ x^3 e^{-ax^2} = \frac{1}{2a^2}, \quad \int_0^\infty dx\ x^4 e^{-ax^2} = \frac{3}{8a^2}\sqrt{\frac{\pi}{a}}.$$

Wave functions and energies for a particle in a one-dimensional box:

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x, \quad E_n = \frac{\pi^2\hbar^2 n^2}{2mL^2}, \quad n = 1, 2, \ldots$$

Wave functions and energies for the first three states of a one-dimensional harmonic oscillator:

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

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$$

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4}(2\alpha x^2 - 1)e^{-\alpha x^2/2}$$

where $\alpha = \frac{m\omega}{\hbar}$. The harmonic oscillator energies are $E_n = (n + \frac{1}{2})\hbar\omega$, $(n = 0, 1, 2, \ldots)$.