This examination consists of 8 consecutively numbered pages. Please check that your paper is complete before starting work. All work must be shown in this booklet.

Name: ________________________ Student number: ________________________
(print, surname first)

Signature: ________________________

University of British Columbia

Sample Midterm Examination Solutions
25 October 2099

CHEMISTRY 304
Fundamentals of Thermodynamics and Statistical Mechanics

Time: 1 hour 20 minutes

NON-PROGRAMMABLE NON-GRAPHING CALCULATORS ARE PERMITTED

READ AND OBSERVE THE FOLLOWING EXAM RULES

1. Each candidate must be prepared to produce, upon request, a UBCcard for identification.
2. Candidates are not permitted to ask questions of the invigilators, except in cases of supposed errors or ambiguities in examination questions.
3. No candidate shall be permitted to enter the examination room after the expiration of one-half hour from the scheduled starting time, or to leave during the first half hour of the examination.
4. Candidates suspected of any of the following, or similar, dishonest practices shall be immediately dismissed from the examination and shall be liable to disciplinary action.

   Having at the place of writing any books, papers or memoranda, calculators, computers, sound or image players/recorders/transmitters (including telephones), or other memory aid devices, other than as authorized by the examiners.

   Speaking or communicating with other candidates.

   Purposely exposing written papers to the view of other candidates or imaging devices.
   The Plea of accident or forgetfulness shall not be received.
5. Candidates must not destroy or mutilate any examination material; must hand in all examination papers; and must not take any examination material from the examination room without permission of the invigilator.
6. Candidates must follow any additional examination rules or directions communicated by the instructor or invigilator.

Part	Max	Mark
I	8	
II	7	
III	10	
IV	10	
V	10	
VI	5	
Total	50	

Part I [8 marks]

1. Consider a closed system in which only $P - V$ work acts. This system undergoes an isobaric process, so $Q = \Delta H$. For such a process, if $\Delta H > 0$, then $\Delta S > 0$ as well.

[✓ 1) True]   2) False   3) Can't answer

From the Clausius inequality, $TdS \geq dq$, so if $\Delta H > 0$ then $q > 0$ so $\Delta S > 0$ as well (since T is always positive). This argument applies whether the process is reversible or irreversible.

2. The thermodynamic entropy of 1 mol of neon gas at $T = 298\,\mathrm{K}$ and $P = 1\,\mathrm{atm}$ is $232\,\mathrm{J\,K^{-1}}$. Thus, a system consisting of 5 neon atoms will have, under the same conditions, an entropy of $5(232/N_A)\,\mathrm{J\,K^{-1}}$ (N_A is Avogadro's number).

1) True   [✓ 2) False]   3) Can't answer

Thermodynamics applies to macroscopic objects, that is systems in the thermodynamic limit. A system composed of 5 atoms is too small to be in this limit, so fluctuations are strong and the "entropy" is not single-valued (in other words, not defined in the thermodynamic sense).

3. Mixing together 100 mL of water with 100 mL of methanol produces a solution with a volume of 200 mL.

1) True   [✓ 2) False]   3) Can't answer

Partial molar volumes are required to calculate the final volume, and due to molecular interactions between water and methanol, depend upon the mole fractions in the final solution. In general, partial molar volumes differ from the molar volumes of the pure substances. Thus, the volumes are not additive so the final volume will not be 200 mL.

4. The "Principle of Equal a Priori Probabilities" states that the probability a system has energy E_ℓ is the same for all energies.

1) True   [✓ 2) False]   3) Can't answer

The "Principle of Equal a Priori Probabilities" states that the probability a system occupies a microstate is proportional to that microstate's energy. The probability a system has energy E_ℓ also depends upon the degeneracies of the microstates, with the result that the probability for occupying different energy levels is not the same for all energies, in general.

5. Any macroscopic object at a finite temperature must have a non-zero absolute entropy.

[✓ 1) True]   2) False   3) Can't answer

A finite temperature is any non-zero, non-infinite temperature, so using the Third Law gives the absolute entropy as $S(T) = \int_0^T dq_{rev}/T$. Since some amount of heat, $dq_{rev} > 0$, is required to move system from $T = 0$ to T, $S(T)$ must be a non-zero, positive number.

6. A process is spontaneous if $\Delta G < 0$.

1) True 2) False 3) Can't answer

The condition $\Delta G < 0$ is a predictor for spontaneity only for processes at constant T and P, in which $P - V$ work alone is present. The general condition for spontaneity is $\Delta S_{universe} > 0$.

---

7. Changing the volume of a real gas always changes its internal energy.

1) True 2) False 3) Can't answer

It is possible to change the volume of a real gas but have $dU = 0$, for example in a Joule-Thompson experiment where a gas expands into a vacuum under adiabatic conditions, or by using heat to compensate for the work done by a volume change, that is by making $q + w = 0$.

---

8. Modelled as van der Waals gases, the parameter 'b' for $C_4H_{10}(g)$ is greater than that for $H_2(g)$.

1) True 2) False 3) Can't answer

The parameter 'b' in the van der Waals equation is proportional to the volume occupied by the particles, and since butane is much larger than dihydrogen, its value is expected to be larger.

Part II [7 marks]

1. For an ideal gas, write an expression giving the change of volume in terms of the change of pressure as the system undergoes isothermal compression.

For a closed system, the total differential of volume can be written as

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

Since this is an isothermal process, dT is zero and dV becomes

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP$$

For an ideal gas,

$$V = \frac{nRT}{P}$$

and therefore

$$(\frac{\partial V}{\partial P})_T = \frac{-nRT}{P^2}$$

From this, dV can be rewritten as

$$dV = \frac{-nRT}{P^2}\, dP$$

Integrating this equation gives the change of volume in terms of the change of pressure, the resulting equation is

$$(V_2 - V_1) = \frac{nRT}{P_2} - \frac{nRT}{P_1}$$

2. Sketch a physical apparatus that can perform an isothermal compression of a gas. Clearly describe the procedure for performing the compression: i) reversibly, and ii) irreversibly.

One possible apparatus includes a gas in a cylinder with a piston .

i. For a reversible compression, slowly increase the pressure above the piston to compress the gas.

ii. For an irreversible compression, lock the piston in place with pins, set the air pump to increase the pressure substantially above the piston, then release the pins, causing the piston to rapidly compress the gas. Alternatively, use a piston with friction, for example by making the inside of the cylinder rough instead of smooth.

Part III [10 marks]

At 1 atm, dry ice, $CO_2(s)$, sublimes at $-78.5\,°C$ to carbon dioxide gas with $\Delta H^0_{sub} = 25.2\,\mathrm{kJ\,mol^{-1}}$. At $-150\,°C$, converting $CO_2(s)$ to $CO_2(g)$ at 1 atm involves an entropy change of $\Delta S^0 = 136.4\,\mathrm{J\,K^{-1}\,mol^{-1}}$. If $C_{P,m}(CO_2(g)) = 36.94\,\mathrm{J\,K^{-1}\,mol^{-1}}$, calculate $C_{P,m}$ for dry ice (assume constant heat capacities).

Since data is provided for the process at two different temperatures, a cycle like the one pictured is suggested.

$$\begin{tikzcd}
CO_2(s) \arrow[r, "T = -78.5\ \mathrm{C}", "\Delta S^0_a"'] \arrow[d, "\Delta S^0_1"'] & CO_2(g) \\
CO_2(s) \arrow[r, "\Delta S^0_b", "T = -150\ \mathrm{C}"'] & CO_2(g) \arrow[u, "\Delta S^0_2"']
\end{tikzcd}$$

At the sublimation temperature $T_{sub} = -78.5\,°C = 194.65\,\mathrm{K}$, the conversion from solid to gas is a reversible process $\Delta G^0 = 0$ so

$$\Delta S^0_a = \frac{\Delta H^0_{sub}}{T_{sub}} = \frac{25200\,\mathrm{J\,mol^{-1}}}{194.65\,\mathrm{K}} = 129.46\,\mathrm{J\,K^{-1}\,mol^{-1}}\ .$$

We are given $\Delta S^0_b = \Delta S^0 = 136.4\,\mathrm{J\,K^{-1}\,mol^{-1}}$, and for the parts of the cycle involving cooling and heating the reactants and products, a reversible, isobaric process is used, giving $dS^0 = C_{P,m}dT/T$, that is (note that $T = -150\,°C = 123.15\,\mathrm{K}$ and that the stoichiometric coefficients for both the reactants and products is 1)

$$\Delta S^0_1 = C_{P,m}(CO_2(s)) \ln\left(\frac{123.15\,\mathrm{K}}{194.65\,\mathrm{K}}\right) = -0.45780 \times C_{P,m}(CO_2(s))\ ,$$

$$\Delta S^0_2 = C_{P,m}(CO_2(g)) \ln\left(\frac{194.65\,\mathrm{K}}{123.15\,\mathrm{K}}\right) = 36.94\,\mathrm{J\,K^{-1}\,mol^{-1}} \times \ln\left(\frac{194.65\,\mathrm{K}}{123.15\,\mathrm{K}}\right) = 16.911\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

Using the entropy changes for the whole cycle, substituting in the calculated values, and then solving for the unknown heat capacity, gives

$$\Delta S^0_a = \Delta S^0_1 + \Delta S^0_b + \Delta S^0_2\ ,$$

$$129.46\,\mathrm{J\,K^{-1}\,mol^{-1}} = -0.45780 \times C_{P,m}(CO_2(s)) + 136.4\,\mathrm{J\,K^{-1}\,mol^{-1}} + 16.911\,\mathrm{J\,K^{-1}\,mol^{-1}}\ ,$$

$$C_{P,m}(CO_2(s)) = \frac{136.4 + 16.911 - 129.46}{0.45780}\,\mathrm{J\,K^{-1}\,mol^{-1}} = 52.10\,\mathrm{J\,K^{-1}\,mol^{-1}}\ .$$

Part IV [10 marks]

The pressure on an insulated iron block, initially at 300 K, is slowly increased from 1 atm to 10,000 atm. For this question, please use the following data for iron (assumed constant): $\alpha = 33.3 \times 10^{-6}\,\mathrm{K}^{-1}$, $\kappa = 6.02 \times 10^{-7}\,\mathrm{atm}^{-1}$, $C_{p,m} = 25.09\,\mathrm{J\,K^{-1}\,mol^{-1}}$, and $V_m = 7.114 \times 10^{-3}\,\mathrm{L\,mol^{-1}}$.

a) Do you expect the temperature of the iron block to be higher, lower, or the same after the pressure increase? Please justify your response.

The increase in pressure does $P - V$ work on the system ($w > 0$), and since the system is insulated, this energy increases the internal energy of the iron block, which is expected to manifest itself by an increase in temperature.

b) Estimate the temperature, in K, of the block at the final pressure, being sure to state and justify any approximations. *Hint: for a reversible process in a closed system involving only $P - V$ work, $dH = \delta Q_{rev} + VdP$.*

The pressure is slowly increased on the iron block, so treat the process as reversible. The block is also insulated so the process is adiabatic, that is $dq_{rev} = 0$. Use this information to develop the "Hint" as

$$dH = VdP\ ,$$

$$C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = VdP\ ,$$

$$C_P dT + V(1 - \alpha T)dP = VdP\ ,$$

$$C_P dT = \alpha V T dP\ ,$$

$$\frac{dT}{T} = \alpha \frac{V}{C_P} dP\ , \quad \text{integrate both sides treating } V \text{ as constant}$$

$$\ln\left(\frac{T_2}{T_1}\right) = \alpha \frac{V_m}{C_{P.m}}(P_2 - P_1)\ ,$$

$$T_2 = T_1 \exp\left[\alpha \frac{V_m}{C_{P,m}}(P_2 - P_1)\right]\ ,$$

$$T_2 = 300\,\mathrm{K} \times \exp\left[33.3 \times 10^{-6}\,\mathrm{K}^{-1} \times \frac{7.144 \times 10^{-3}\,\mathrm{L\,mol^{-1}}}{25.09\,\mathrm{J\,K^{-1}\,mol^{-1}}}(10000 - 1)\,\mathrm{atm}\right]$$

$$T_2 = 302.9\,\mathrm{K}\ ,$$

in which $(\partial H/\partial P)_T = V(1 - \alpha T)$ was used in the second line, $V/C_P = V_m/C_{P,m}$ was used in the fifth line, and V_m was treated as a constant during the integration over pressure in the sixth line (this is reasonable because solids are very incompressible so the volume change is very small after the pressure increase). Note that in the last line, a unit conversion $1\,\mathrm{L\,atm} = 101.325\,\mathrm{J}$ was needed to get the final numerical result.

Part V [10 marks]

Consider one mole of atoms sealed in a container at a constant temperature $T = 1000$ K. Each of the atoms can be either in one of the two energy states: the ground state and an excited state. The energy of the excited state is 10^{-20} J above the energy of the ground state.

a) Find the probability to observe an atom in the ground state.

The probability of finding the atom in state i is given by

$$P_i = \frac{e^{-\beta E_i}}{Z}$$

where

$$Z = \sum_i e^{-\beta E_i}$$

We can write the energy levels of the system as E_0 Joules for the ground state, and $E_0 + \Delta$ J for the excited state, where $\Delta = 10^{-20}$ J.

At temperature T, $\beta = \frac{1}{k_B T}\ J^{-1}$.

The probability of observing an atom in the ground state can therefore be written as

$$P_0 = \frac{e^{-\beta E_0}}{e^{-\beta E_0} + e^{-\beta(E_0+\Delta)}}$$

This can be rewritten as

$$P_0 = \frac{1}{1 + e^{-\beta\Delta}}$$

For $T = 1000$ K and $\Delta = 10^{-20}$ J, we have

$$\beta\Delta = 1/1.38065 = 0.724$$

and

$$e^{-\beta\Delta} = 0.485$$

so

$$P_0 = 0.673$$

b) Find the probability to observe an atom in the excited state.

Since there are only two states possible, the probability to observe an atom in the excited state is $P_1 = 1 - P_0 = 0.327$.

c) Calculate the average energy of the atomic ensemble.

The average energy per atom is given by

$$\bar{\epsilon} = \sum_i E_i P_i$$

Since the choice of zero of energy is arbitrary, we can set $E_0 = 0$ and obtain

$$\bar{\epsilon} = P_1 \Delta = 0.327 \times 10^{-20} \text{ J}$$

There are $N = N_A$ atoms in the atomic ensemble, and so to obtain the average energy of the ensemble, the average energy per atom atom must be multiplied by N.

The average energy of the atomic ensemble $\bar{E} = 0.327 \times 10^{-20} \times 6.022 \times 10^{23} = 1969$ J.

The temperature of the gas has been raised to $10,000$ K.

d) Calculate the change of the average energy of the gas.

For $T = 10000$ K and $\Delta = 10^{-20}$ J, we have

$$\beta \Delta = 0.1/1.38065 = 0.0724$$

and

$$e^{-\beta \Delta} = 0.93$$

so

$$P_0 = 0.518$$

For the excited state:

$$P_1 = 1 - P_0 = 0.482$$

The average energy at $T = 10,000$ K is

$$\bar{E} = N_A \times P_1 = 2902 \text{ J}$$

The change of energy is $2902 - 1969 = 933$ J.

e) Calculate the change of entropy of the gas.

The entropy can be calculated by

$$S = -N k_B \sum_i P_i \ln(P_i)$$

For 1000 K,

$$S = -k_B \times 6.022 \times 10^{23} \times (0.673 \times \ln 0.673 + 0.327 \times \ln 0.327) = k_B \times 6.022 \times 10^{23} \times 0.632 \text{ J}^{-1}$$

For 10000 K,

$$S = -k_B \times 6.022 \times 10^{23} \times (0.518 \times \ln 0.518 + 0.482 \times \ln 0.482) = k_B \times 6.022 \times 10^{23} \times 0.692 \text{ J}^{-1}$$

The change is

$$k_B \times 6.022 \times 10^{23} \times (0.692 - 0.632) = 0.499 \text{ J}^{-1}$$

Part VI [5 marks]

Prove that no engine can be more efficient than the Carnot engine.

There are several ways to prove this.

For example, you could assume there is an engine with efficiency higher than Carnot's and then use the work produced by this engine to run the Carnot engine in reverse. Try this and see where this would lead you.

Alternatively, you could argue as follows.

For a heat engine to be spontaneous, the engine must obey

$$\Delta S = \frac{|Q_c|}{T_c} - \frac{|Q_h|}{T_h}$$

and

$$\Delta S \geq 0$$

Therefore, for any heat engine,

$$\frac{|Q_c|}{T_c} - \frac{|Q_h|}{T_h} \geq 0$$

and

$$|Q_c| \geq |Q_h| \frac{T_c}{T_h}.$$

The work done by the engine is given by

$$|W| = |Q_h| - |Q_c|.$$

The work is maximized when $|Q_c|$ is minimized, which is when $|Q_c| = |Q_h| \frac{T_c}{T_h}$.

Therefore,

$$|W_{max}| = |Q_h| - |Q_{c,min}|$$

$$|W_{max}| = |Q_h| - |Q_h| \frac{T_c}{T_h}$$

$$|W_{max}| = |Q_h|(1 - \frac{T_c}{T_h})$$

The efficiency of a heat engine is given by

$$\eta = \frac{|W|}{|Q_h|}.$$

The maximum efficiency is given by the same equation with W_{max}. The maximum efficiency of a heat engine in general is therefore

$$\eta_{max} = \frac{|Q_h|(1 - \frac{T_c}{T_h})}{|Q_h|}$$

and

$$\eta_{max} = 1 - \frac{T_c}{T_h}.$$

We can now calculate the efficiency of a Carnot engine.
For the steps labelled in lecture as 1, 2, 3, 4, the work done by a Carnot cycle is given by

$$W = -nRT_H \ln \frac{V_2}{V_1} - nRT_c \ln \frac{V_4}{V_3}$$

The energy supplied as heat is given by

$$|Q_h| = nRT_h \ln \frac{V_2}{V_1}$$

For a reversible, adiabatic process the equation $\eta = \frac{|W|}{|Q_h|}$ for the work and heat given above reduces to

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

Alternatively, we know from the lecture notes that the efficiency of the Carnot engine is $\eta = 1 - \frac{T_c}{T_h}$, which is the same as the maximum efficiency possible for a heat engine. Therefore, no heat engine can be more efficient than the Carnot engine.