CHM2132 Test 1: Wednesday October 5th, 2011

Name: ______________________________

Student #: ______________________________

This is a closed book exam with no notes allowed.
Calculators are permitted.
Show all your work.
Remember to include units in all your calculations**.**
Marks will be deducted if units are not shown in your final answer.

Constants and Data:
R = 8.314 J K^{-1} mol^{-1} = 0.08206 L atm mol^{-1} K^{-1} = 0.08314 L bar mol^{-1} K^{-1}
1 L = 10^{-3} m^3 1 kJ = 1000 J 1 atm = 101325 Pa
1 bar = 10^5 Pa 1 L atm = 101.325 J 1 J = 1 kg m^2 s^{-2} 1 Pa = 1 kg m^{-1} s^{-2}

$\Delta_f H^o(C_3H_8O(l))$ = -303 kJ/mol
$\Delta_f H^o(CO_2(g))$ = -354 kJ/mol
$\Delta_f H^o(H_2O\ (g))$ = -242 kJ/mol
$\Delta_{vap} H^o(H_2O)$ = 44.0 kJ/mol at 298 K

$$\boxed{pV = nRT} \qquad \boxed{z = \frac{pV}{nRT}} \qquad \boxed{p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2}$$

$$\boxed{w = -\int pdV} \qquad \boxed{\Delta U = w + q} \qquad \boxed{H = U + pV}$$

$$\boxed{\left(\frac{\partial U}{\partial T}\right)_V = C_V} \qquad \boxed{\left(\frac{\partial H}{\partial T}\right)_P = C_P} \qquad \boxed{\pi_T = \left(\frac{\partial U}{\partial V}\right)_T}$$

$$\boxed{C_p - C_V = nR} \qquad \boxed{p_1V_1^\gamma = p_2V_2^\gamma \quad \gamma = \frac{C_p}{C_V}} \qquad \boxed{\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}}$$

$$\boxed{\Delta_r H_m^\circ = \sum_{\text{Products}} \nu \Delta_f H_m^\circ - \sum_{\text{Reactants}} \nu \Delta_f H_m^\circ} \qquad \boxed{\Delta\left(\Delta_r H^o\right) = \Delta C_p \Delta T}$$

Q1: __________/8 Q2: __________/12 Q3: __________/15 Q4: __________/4

Total = __________/39

Name:________________________________

1. The following statements are **FALSE**. **Choose 4 of the 5 statements below** and:

(i) Change the sentence so that it becomes a correct statement.
(ii) In one sentence explain why the statement was incorrect. In some cases you might use a *p*-*V* graph to help your explanation. (8 marks)
NOTE; There are many ways to alter the sentences to make them correct.

a) The surroundings does work on the system when a balloon is taken from a cold room to a warm room.

The system does work on the surroundings when a balloon is taken from a cold room to a warm room.

As gas heat up it will expand, hence $dV > 0$.

Put this into $w = -\int p\,dV$ to get $w < 0$. Since work is negative the system is doing the work.

Also, because the gas is doing the pushing, we know that gas is doing the work.

b) It is possible to do an adiabatic expansion at constant pressure.

It is not possible to do an adiabatic expansion at constant pressure.

The gas needs energy to carry out this expansion and do work. If it can not get this energy by thermal transfer from the surroundings then there is no energy available for this to occur.
Or, since $q=0$, $\Delta U = w$. Since the temperature of the gas must increase for the expansion to occur ΔU must be greater than zero. However, we know that work is less than zero for an expansion (see a for reasoning) and so this process is not possible. (You cannot get positive ΔU with a negative work.

c) The work of a constant pressure expansion is larger when it is done irreversibly instead of reversibly.

The work of a constant pressure expansion is the same when it is done irreversibly instead of reversibly.
The gas pushes against the same external pressure to do the expansion, regardless of whether it is done quickly or slowly, so the path is the same in both cases.
Note that this was not an isothermal expansion. (You can not assume it is isothermal – this is something you must be told.)

d) If q<0 then the temperature of the system must decrease.

If q<0 then the temperature of the system can decrease.
Or If q<0 then the temperature of the system must decrease if no work can be done on the system.

If more work energy is given to the system than heat energy is lost during the process then the temperature could increase. Also, during a phase transition heat can be lost but the temperature of the system does not change during the transition.

e) The formation enthalpy of graphite at 300 K can be calculated using $\Delta H_m^o = C_{p,m}^o \Delta T$.

The formation enthalpy of graphite at 300 K is zero.
The formation enthalpy for any element in its most stable state under those conditions is zero at any temperature.
or
The formation enthalpy of graphite at 300 K can be calculated using Kirchoff's equation.
It is possible to use $\Delta\left(\Delta H_m^o\right) = \Delta C_{p,m}^o \Delta T$ to calculate the formation enthalpy at the new temperature. It won't make much sense though, since the reaction would be C(s) -> C(s). But it will give $\Delta C_{p,m}^o = 0$, and hence formation enthalpy at 300 K = formation enthalpy at 298 K = 0…

Name:________________________________

2. Liquid propanol (C_3H_8O) undergoes a combustion reaction at 298 K

a) Write the balanced chemical equation for this process. Be sure to indicate the phases for this reaction. (3 marks)

$$C_3H_8O(l) + 9/2 O_2(g) \rightarrow 3\ CO_2(g) + 4H_2O(l)$$

1 mark for correct stoichiometry and phase for carbon dioxide, water and oxygen.

b) Use the data on the first page to calculate the standard enthalpy for the complete combustion of **1.25 mol** of propanol at 298 K. Your final answer should be in units of kJ. (5 marks)

$$\Delta_r H_m^\circ = \sum_{\text{Products}} \nu\Delta_f H_m^\circ - \sum_{\text{Reactants}} \nu\Delta_f H_m^\circ \qquad \text{1 mark}$$

$$= 4\Delta_f H_m^\circ(\mathrm{H_2O(l)}) + 3\Delta_f H_m^\circ(\mathrm{CO_2(g)}) - \tfrac{9}{2}\Delta_f H_m^\circ(\mathrm{O_2(g)}) - \Delta_f H_m^\circ(\mathrm{C_3H_8O(g)}) \quad \text{1 mark}$$

$\Delta_f H_m^\circ(\mathrm{O_2(g)}) = 0$ since oxygen gas is a reference element. 0.5 marks

We have been given $\Delta_f H_m^\circ(\mathrm{H_2O(g)})$ instead of the liquid-state value required. We can add the heat of condensation to this formation enthalpy to get the formation enthalpy of liquid water. The enthalpy of condensation is just the negative of the enthalpy of vaporization (the reverse process).

$$\Delta_f H_m^\circ(\mathrm{H_2O(l)}) = \Delta_f H_m^\circ(\mathrm{H_2O(g)}) - \Delta_{vap} H_m^\circ(\mathrm{H_2O}) \quad \text{1 mark}$$

$$\Delta_c H_m^\circ = 4\left[\Delta_f H_m^\circ(\mathrm{H_2O(g)}) - \Delta_{vap} H_m^\circ(\mathrm{H_2O})\right] + 3\Delta_f H_m^\circ(\mathrm{CO_2(g)}) - \Delta_f H_m^\circ(\mathrm{C_3H_8O(g)})$$

$$\Delta_c H_m^\circ = \left[4\left[-242-44\right] + 3(-354) - (-303)\right] \text{ kJ mol}^{-1} \quad \text{1 mark}$$

$$= -1903 \text{ kJ mol}^{-1}$$

Now calculate the total enthalpy change:

$$\Delta_c H^\circ = n \times \Delta_c H_m^\circ$$

$$= (1.25 \text{ mol}) - 1903 \text{ kJ mol}^{-1} = 2380 \text{ kJ} \quad \text{0.5 marks}$$

c) What is ΔU_m^o for this reaction at 298K? Your final answer should be in units of kJ mol^{-1} (4 marks)

From: $H = U + pV$ 1 mark

$$dH = dU + d(pV)$$

Since we don't know how volume changes, but we do know that the process is isothermal:

$$dH = dU + d(nRT) \quad \text{0.5 marks}$$

$$= dU + RTdn$$

Integrate on both sides and divide by the total number of moles in the system:

$\Delta H_m^o = \Delta U_m^o + \Delta\nu RT$ (for a standard pressure process) 0.5 marks

Now we use $\Delta_c H_m^o$ calculated in last question, and the stoichiometric coefficients from the balanced chemical equation to get:

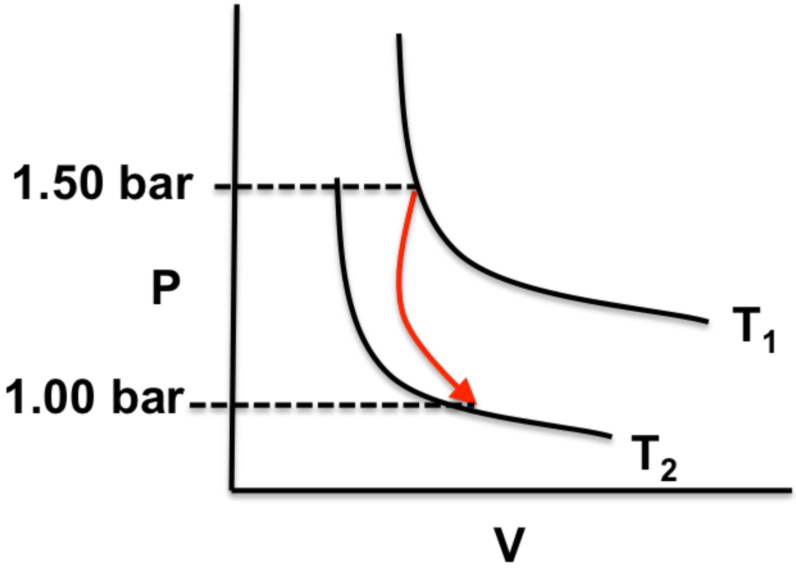
$$\Delta U_m^o = \Delta H_m^o - \Delta\nu RT$$

$$= -1903 \text{ kJ mol}^{-1} - \left(3 - \tfrac{9}{2}\right)\left(8.314 \text{ J K}^{-1} \text{ mol}^{-1}\right)\left(10^{-3} \text{ kJ J}^{-1}\right)(298 \text{ K}) \quad \text{1 mark}$$

$$= -1900 \text{ kJ mol}^{-1}$$

3. A sample consisting of 0.50 mol of an ideal monoatomic gas ($C_p = 5/2\ R$) is confined in a 2.00 L container at 1.50 bar is allowed to expand adiabatically and reversibly to a final volume of 1.00 bar.

a) Draw the path for this process in a p-V diagram. Be sure to label the axes with *p* and *V*, show isotherm(s) and indicate pressure values for the initial and final states in the graph. Indicate the direction of the process with an arrow. (5 marks)



2 isotherms (1 mark)
axes labeled with p and V (2 marks)
path links 2 isotherms (1 mark)
Process shown is an expansion (0.5 mark)
Pressures of initial and final state labeled (0.5 marks)

b) What is the heat of this process? (1 mark)

Adiabatic, so $q=0$

c) What is the final volume of the gas? (3 marks)

Since this is a reversible, adiabatic process:

$$p_1 V_1^\gamma = p_2 V_2^\gamma$$

$$V_2^\gamma = \frac{p_1}{p_2} V_1^\gamma \qquad \text{1 mark}$$

To get rid of the exponent on V_2, we take the log of each side:

$$\log V_2^\gamma = \log \frac{p_1}{p_2} + \log V_1^\gamma$$

$$\gamma \log V_2 = \log \frac{p_1}{p_2} + \gamma \log V_1$$

Divide through by gamma and put it back into exponential form:

$$\log V_2 = \frac{1}{\gamma} \log \frac{p_1}{p_2} + \log V_1$$

$$V_2 = V_1 \left(\frac{p_1}{p_2}\right)^{\frac{1}{\gamma}} = 2.00\ \text{L} \left(\frac{1.50\ \text{bar}}{1.00\ \text{bar}}\right)^{\frac{5}{3}} = 2.55\ \text{L} \qquad \text{1 mark}$$

(Note that $\frac{1}{\gamma} = \frac{C_{V,m}}{C_{p,m}} = \frac{\frac{3}{2}R}{\frac{5}{2}R} = \frac{3}{5}$.) 1 mark

c) How much work was done in this process? (4 marks)

Since q=0, $\Delta U = w = C_V \Delta T$ 1 mark

We don't have temperatures, so we will use the ideal gas law to put equation into terms we can work with:

$$T = \frac{pV}{nR}$$ 1 mark

$$w = nC_{V,m}\left(\frac{p_2V_2}{nR} - \frac{p_1V_1}{nR}\right) = \frac{n}{nR}\left(C_{p,m} - R\right)\left(p_2V_2 - p_1V_1\right)$$ 1 mark

$$= \frac{1}{R}\left(\frac{3}{2}R\right)\left(p_2V_2 - p_1V_1\right)$$

$$= \frac{3}{2}\left[\left(1.00\text{ bar}\right)\left(10^5\text{ Pa bar}^{-1}\right)\left(2.55\text{ L}\right)\left(10^{-3}\text{m}^3\text{ L}^{-1}\right) - \left(1.50\text{ bar}\right)\left(10^5\text{ Pa bar}^{-1}\right)\left(2.00\text{ L}\right)\left(10^{-3}\text{m}^3\text{ L}^{-1}\right)\right]$$ 1 mark

$$= -68\text{ J}$$

d) Suppose the gas was taken back to the initial state by constant volume heating back to the initial temperature, followed by isothermal compression back to the initial volume. What would ΔU be for this process? (2 marks)

We have already calculated ΔU for going from the same two states in part c. We are just being asked what ΔU is for the reverse process. Therefore ΔU = 68 J.

(Or ΔU over the whole cycle is 0.)

4. In Joule's experiment, a gas in one metal container is allowed to expand into a connected container that initially has no gas in it, and changes in the temperature of the surrounding water bath are monitored.

a) Is work greater than, less than, or equal to zero in this experiment? (1 mark)

$$w = 0$$

b) Suppose the temperature of the water bath surrounding the two chambers goes up for a real gas with a negative internal pressure ($\pi_T < 0$). Explain why the temperature increases in this experiment in terms of energy and molecular interactions. (2 marks)

The gas expands, so d$V > 0$. Since internal pressure is negative then dU < 0. (For $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$ to be negative, is dV is positive then dU must be in opposite direction.) 0.5 marks

If the energy is going down then unfavorable interactions must be reduced by expanding into a larger volume – these must be repulsive interactions. 1 mark

The energy that is released will go into the water bath to raise its temperature. 0.5 marks

c) What is the partial derivative that describes how the volume of an ideal gas changes with the temperature for a fixed amount of gas at a constant pressure? (1 mark + 1 bonus mark)

$$\left(\frac{\partial V}{\partial T}\right)_{p,n}$$ 1 mark

$$= \left(\frac{\partial \frac{nRT}{p}}{\partial T}\right)_{p,n} = \frac{nR}{p}\left(\frac{\partial T}{\partial T}\right)_{p,n} = \frac{nR}{p}$$ 1 bonus mark