

CHEMISTRY 440/540

PHYSICAL CHEMISTRY: FALL, 2006.

Name: _____ Social Security No. _____

Examination No. 1

October 23, 2006

Answer all questions on this exam in the space provided using a non-erasable pen. In order to receive full credit for any question you must state all assumptions, show all equations, show all your work and supply the proper sign and units for your answer. If I cannot follow your logic, then I will not assign any partial credit. PLEASE BE NEAT. **[Note that the universal gas constant, R, varies according to the units one wishes to use]**

NB: This exam totals 110 points. Full credit, however, can be received from a score of 100.

Question 1 [40 points; 20 points each]

- (a) Suppose that 10.0 mol of $C_2H_6(g)$ is confined to 4.860 dm^3 at 27°C . Predict the pressure exerted by this gas from the (a) perfect gas and (b) van der Waals equation of state. Calculate the compression factors in both a and b.
For ethane: $a = 5.562 \text{ L}^2 \text{ atm mol}^{-2}$; $b = 6.380 \times 10^{-2} \text{ L mol}^{-1}$.

- (b) 2 moles of Helium were expanded isothermally at $22\text{ }^{\circ}\text{C}$ from 22.4 dm^3 to 44.8 dm^3 (a) reversibly (b) against a constant external pressure, P_{ext} , equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes, calculate q , w , ΔU and ΔH .

(f) work

(g) van der Waals loops

(h) Maxwell construction

(i) mathematical representation of Kirchoff's law

(j) internal pressure

Question 3 **[30 points; 10 points each]**

(a) If $c = C_{v,m}/R$, prove that in an adiabatic expansion

$$T_f = T_i \left(\frac{v_i}{v_f} \right)^{\frac{1}{c}}$$

where subscripts i and f denote initial and final states respectively.

- (b) Prove that for an irreversible expansion of a gas, the work done by the gas is given by $w = -P\Delta V$ Joules where P is the external pressure and ΔV is the increase in volume in m^3 . (Use the simple example of a frictionless cylinder lying on its side)

- (c) The enthalpy change for the following reaction is difficult to experimentally determine from calorimetric techniques:



It can be determined, however, indirectly, by using the enthalpies of combustion of $\text{C}(\textit{graphite})$, $\text{H}_2(\text{g})$ and $\text{CH}_4(\text{g})$ whose values are respectively (in kJ mol^{-1}): -393.51, -285.84 and -890.35. Using these data, determine $\Delta\text{H}^0_{\text{rxn}}$.

For Bonus points only. **[10 points; 5 points each]**

- (a) Using the standard heat capacities at constant volume and constant pressure, prove that $C_p - C_v = nR$ (or $C_{p,m} - C_{v,m} = R$). **[5 points]**

- (b) The derivation in (a), above, applies to ideal gases. For real gases, the correct relationship is

$$C_p - C_v = \left[P + \left(\frac{\delta U}{\delta V} \right)_T \right] \left(\frac{\delta V}{\delta T} \right)_P$$

Prove that this relationship gives you the simple relationship you derived in (a) when applied to ideal gases. **[5 points]**

[you can use the back of this page to complete your solution]