

EXAM 1  
2 October 1991

**IMPORTANT:** Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a few words of explanation.

(1) 34 points ONLY A FEW LINES ARE NEEDED FOR FULL CREDIT IN EACH PART

- Interpret the Van der Waals  $a$  and  $b$  in terms of assumptions about ideal gases.
- Explain the difference between *reversible* and *irreversible* processes.
- Outline the *Joule experiment* and what it was designed to test.
- Define the *compression factor*,  $Z$ , for a gas. Sketch a plot of  $Z$  versus pressure  $p$  for a typical gas, and explain how  $Z$  is qualitatively related to intermolecular forces.
- Outline one important difference between a parameter which is a *function of state* and one which is not. Give one physical example of each kind.
- What is an *adiabatic* process?
- Define the *average bond dissociation enthalpy* of  $\text{CF}_4$  as clearly as you can.
- Solid zinc reacts with hydrochloric acid:  
$$\text{Zn}(s) + 2 \text{HCl}(aq) \rightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)$$
Explain *qualitatively* whether you expect  $\Delta H$  at 1 atm and 298 K to be more positive than, equal to or less than  $\Delta U$ .
- Calculate  $(\partial p/\partial T)_V$  for (i) an ideal gas, and (ii) a Van der Waals gas.
- By consideration of  $U$  as a function of  $V$  and  $T$ , show that  $dU$  is given by  $\pi_T dV + C_V dT$ , where  $\pi_T = (\partial U/\partial V)_T$ , and hence derive an expression for  $(\partial U/\partial T)_p$ .

(2) 12 points

When ice melts at 273 K,  $\Delta H_{\text{fus}} = 100.00 \text{ kJ mol}^{-1}$ . Use the information that  $C_p(\text{ice}) = 8 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $C_p(\text{water}) = 32 \text{ J K}^{-1} \text{ mol}^{-1}$  (both assumed to be temperature-independent) to estimate  $\Delta H$  for melting ice at 253 K.

(3) 14 points

1 mol of ideal gas at 300 K is heated at constant pressure until its volume has increased by 20%.  $C_V$  for the gas is  $20 \text{ J K}^{-1}$  and  $C_p = C_V + R$ .

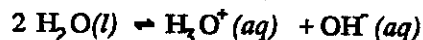
- What is the final temperature of the gas?
- What is  $\Delta H$  for the gas?
- How much heat  $q$  was absorbed by the gas?
- What is  $\Delta U$  for the gas?
- What is the work  $w$  done on the gas?
- Sketch an indicator diagram for the process (label the axes) and use it to illustrate the answer to (c) graphically.

EXAM 2  
1 November 1991

*IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a few words of explanation.*

(1) 12 points

The pH of pure water at 298 K is 7, and at 380 K the pH is 6. By a qualitative argument only, does the observation that the neutral pH decreases with increasing temperature tell you that  $\Delta H$  for the autoprotolysis of water



is positive or negative?

On the assumption that  $\Delta H$  is independent of T, now calculate  $\Delta H$  in  $\text{kJ mol}^{-1}$ .

(2) 16 points

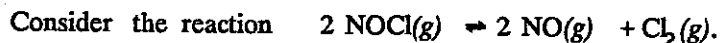
a) Given that  $dG = Vdp - SdT$ , and by considering  $G$  as a function of  $p$  and  $T$ , show that

$$(\partial G / \partial p)_T = V \quad \text{and that} \quad (\partial G / \partial T)_p = -S.$$

b) Thus derive one of the Maxwell relations,  $(\partial V / \partial T)_p = -(\partial S / \partial p)_T$ .

c) Use this result to find an expression for  $(\partial S / \partial p)_T$  for 1 mol of an ideal gas.

(3) 18 points



$\Delta G_f^\circ(\text{NO})$  and  $\Delta G_f^\circ(\text{NOCl})$  are 87 and 10  $\text{kJ mol}^{-1}$ , respectively. The standard pressure is  $10^5$  Pa and the temperature is 400 K. Assume ideal gas behavior.

Initially,  $p(\text{NO}) = 10^4$  Pa,  $p(\text{Cl}_2) = 2 \times 10^4$  Pa and  $p(\text{NOCl}) = 10^3$  Pa.

a) Calculate  $\Delta G^\circ$  for the reaction.

b) Calculate the reaction Gibbs function, and hence predict whether the spontaneous direction of reaction under these conditions favors formation of more NOCl or not.

c) Sketch a graph of the Gibbs function for the reacting system,  $G$ , as a function of the extent of reaction ( $\xi$ ). On this plot mark (i) the approximate conditions outlined above with an "X", and (ii) the equilibrium position with an "O".

(4) 10 points

Imagine you are cooling the interior of a house at 295 K while the outside temperature is 315 K, with an air conditioner that may be considered to function as a reversible Carnot engine.

a) How much work is required to move 1 kJ of heat from 295 to 315 K, and how much heat is rejected at the higher temperature?

b) If this is done reversibly, what is  $\Delta S$  for the surroundings? What is  $\Delta S$  for the universe?

1) Higher T → lower pH → larger  $a(\text{H}_3\text{O}^+)$  → larger  $K_w$

∴ by Le Chatelier's principle  $\Delta H > 0$ .  
 $T_1 = 298 \text{ K}$ ,  $a(\text{H}_3\text{O}^+) = 10^{-\text{pH}} = 10^{-7}$  ∴  $K_w = a(\text{H}_3\text{O}^+) a(\text{OH}^-)$  but here  $a(\text{OH}^-) = a(\text{H}_3\text{O}^+)$

∴  $K_w = 10^{-14}$  Similarly, at 380 K,  $K_w = 10^{-12}$ .

$$\frac{\Delta H}{R} = \frac{\ln 0.01}{\frac{1}{380} - \frac{1}{298}} = \frac{-4.605}{-7.241 \times 10^{-4}} = 6360 \quad \therefore \Delta H = +52.9 \text{ kJ mol}^{-1}$$

2a)  $dG = Vdp - SdT$  and also  $(\frac{\partial G}{\partial T})_p dT + (\frac{\partial G}{\partial p})_T dp$   
 ∴ by comparing terms,  $V = (\frac{\partial G}{\partial p})_T$  and  $-S = (\frac{\partial G}{\partial T})_p$ .

b)  $(\frac{\partial V}{\partial T})_p = \left( \frac{\partial (\frac{\partial G}{\partial p})_T}{\partial T} \right)_p = \left( \frac{\partial (\frac{\partial G}{\partial T})_p}{\partial p} \right)_T = \left( \frac{\partial -S}{\partial p} \right)_T = -\left( \frac{\partial S}{\partial p} \right)_T$

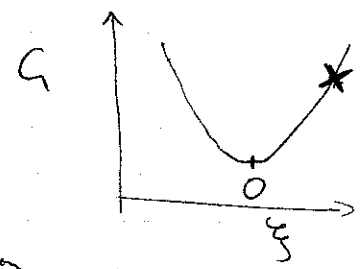
c)  $(\frac{\partial S}{\partial p})_T = -\left( \frac{\partial V}{\partial T} \right)_p = -\left( \frac{\partial}{\partial T} \right)_p \left( \frac{RT}{p} \right) = -R/p$

3a)  $\Delta G_f(\text{Cl}_2) = 0$  because it is an element.  $\Delta G^\circ = 2\Delta G_f(\text{NO}) + \Delta G_f(\text{Cl}_2) - 2\Delta G_f(\text{NOCl}) = +154 \text{ kJ mol}^{-1}$

b)  $a = p/p^\ominus$  ∴  $a_{\text{Cl}_2} = 0.2$ ,  $a_{\text{NO}} = 0.1$ ,  $a_{\text{NOCl}} = 0.01$ .

$$Q = \frac{0.2 \times 0.1^2}{0.01^2} = 20, \quad \Delta G_r = \Delta G^\circ - RT \ln Q = 154 - 10 \text{ kJ mol}^{-1} = +144 \text{ kJ mol}^{-1}$$

Positive ∴ reactants favored ∴ more NOCl formed



f)  $T_h = 315 \text{ K}$ ,  $T_c = 295 \text{ K}$ .  $\epsilon = \frac{T_h - T_c}{T_h} = 0.0635$ .

a) For the perhaps more familiar "forward" direction ( $q_h > 0$ )

$$\epsilon = \frac{T_h - T_c}{T_h} = \frac{w}{q_h} = \frac{q_h - q_c}{q_h} \quad \therefore \epsilon - 1 = \frac{-q_c}{q_h} = \frac{q_c}{q_h} \quad \therefore q_h = -\frac{q_c T_h}{T_c}$$

In this situation ("running backwards")  $q_h = 1000 \text{ J} \times \frac{315}{295} = \underline{1068 \text{ J}}$

and  $w = 1068 - 1000 = \underline{68 \text{ J}}$ .

b)  $\Delta S_{\text{sur}} = q_h / 315 \text{ K} = \underline{+3.4 \text{ J K}^{-1}}$ .

$\Delta S_{\text{uni}} = 0$  for a reversible process.

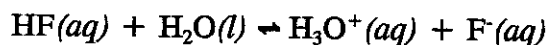
### EXAM 3

11 November 1991

*IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a few words of explanation.*

(1) 16 points

Consider the reaction



and assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature, and that ideal solution behavior applies (standard state = 1 M).

At 298 K the equilibrium constant is  $10^{-8}$ , and it decreases to  $10^{-9}$  at 330 K.

Use this information to

- Calculate  $\Delta G^\circ$  at 298 K. [If you have no answer assume  $100 \text{ kJ mol}^{-1}$ ].
- Calculate  $\text{pK}_a$  for HF at 330 K.
- Derive  $\Delta H^\circ$  for the reaction. [If you have no answer assume  $-20 \text{ kJ mol}^{-1}$ ].
- Summarize Le Chatelier's principle. Explain if it holds here.
- Calculate  $\Delta S^\circ$  for the reaction.

(2) 10 points

Imagine a system consisting of two bodies, at temperatures  $T_1$  and  $T_2$ , where  $T_1 > T_2$ . A small quantity of heat,  $q$ , is transferred from the first body to the second (assume the temperatures are unchanged).

- What is  $\Delta S$  for the system if this change is carried out reversibly? What is its sign?
- Explain how  $\Delta S$  for the same heat transfer, if carried out irreversibly, is related to the answer to (a).
- For the two situations described in (a) and (b), say as much as you can about  $\Delta S$  for the surroundings in each case and justify your statements.

**EXAM 4**  
**25 November 1991**

**IMPORTANT:** Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a few words of explanation.

Arrhenius equation:  $k = A e^{-(E_a/RT)}$ . Ideal gases:  $pV = nRT$ .

For a particle with velocity  $u$  and mass  $m$ , momentum =  $mu$  and kinetic energy =  $0.5 mu^2$ .  
 $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1} = R/N_A$ .  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ .  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ .

(1) 4 points

Briefly summarize (no derivation required) the *steady-state hypothesis*, showing when it is valid.

(2) 12 points

For a sample of an ideal gas, it can be shown that  $pV = (1/3)mN\overline{c^2}$  where  $m$  is the molecular mass,  $N$  is the number of molecules in the sample and  $\overline{c^2}$  is the mean square velocity.

a) Use this result together with the ideal gas law to show that the average kinetic energy  $\epsilon$  of the molecules is given by  $\epsilon = (3/2)k_B T$  where  $k_B$  is Boltzmann's constant.

b) Consider two bulbs, containing  $H_2$  and  $O_2$  respectively, under identical conditions. The molar masses are in the ratio 1:8. For the molecules in the two bulbs, deduce the ratios of (i) the average kinetic energy of the molecules, and (ii) the root mean square velocity.

(3) 16 points

a) Give a general definition of the *half-life* of a reaction,  $t_{1/2}$ .

b) Consider the reaction  $X \rightarrow Y$ , where  $d[X]/dt = -k[X]$  and initially at  $t=0$  there is pure  $X$ , with concentration  $[X]_0$ .

Rearrange and integrate the above rate law to find  $[X]$  as a function of  $k$ ,  $t$  and  $[X]_0$ .

c) Use your answer to (b) to show that for this reaction,  $t_{1/2} = (\ln 2)/k$ .

d)  $t_{1/2}$  for this reaction is measured to be 20 s. What is the rate constant (give units) ?

(4) 10 points

An Arrhenius plot is shown:

a) What is the order of the reaction?

b) Derive the Arrhenius parameters (give units).

