PHYSICAL CHEMISTRY EXAM

21 September 1988

CONSTANTS: $g=9.81 \text{ ms}^{-2}$ R=8.314 J K⁻¹ mol⁻¹ N_A = L = 6.022 x 10^{23} mol⁻¹

(1) 10 points.

By considering momentum changes for an individual molecule inside a rectangular box, derive an expression for PV in terms of the molecular mass, the number of molecules and the mean square speed.

Compare this to the ideal gas equation to show that the mean kinetic energy of a molecule is $1.5 \, \frac{R}{L} \, T_{\bullet}$

(2) 10 points.

A balloon contains 1 kg He (molar mass $0.004 \, \mathrm{kg}$) at 2 x $10^5 \, \mathrm{Pa}$ and 298 K. Assume ideal gas behavior.

- a) What is the volume of the gas?
- b) How many He atoms are there?
- c) What is the root mean square velocity?
- d) What is the mean kinetic energy of the He atoms?
- e) What is the total kinetic energy of the gas?
- (3) 2 points.

What is Graham's law of effusion?

- (4) 10 points.
- a) Give 3 postulates or assumptions of the kinetic-molecular model for ideal gases.
- b) The van der Waals equation $(P + \underline{a} \underline{n}^2) (V n b) = n R T$ better describes the behavior of real gases. Explain the physical significance of a and b in the light of your answer to part (a).
- c) Sketch a P versus V diagram for a real gas and label the axes.

 Show i) The 4 areas corresponding to the liquid, gas, liquid + vapor, and supercritical fluid phases.
 - ii) The critical point.
 - iii) An isotherm corresponding to gas liquefaction by pressure.

- (5) 8 points.
- a) Barometric pressure varies as $P = P_0 \exp(-Mgh)$. Assume that $P_0 = 10^5$ Pa, T is constant at 298 K and M = 0.029 kg mol⁻¹. Estimate P at the height of a space shuttle orbit, h = 100 km.
- b) The mean free path is given by $\lambda = \frac{V}{\sqrt{2} \pi d^2 N}$.

In a few lines explain the physical significance of ?.

- c) Assuming ideal gas behavior, substitute for V to express λ as a function of P and T.
- d) Hence calculate λ for the conditions of part (a). Use d = 3 x 10⁻¹⁰ m.

ANSWERS Exam of 9-21-88

1) See notes and text book for PV= Nm u2. m is the molecular mass

2) (a) $V = \frac{nRT}{P}$. $n = \frac{1}{0.004 \text{ Jymol}^{-1}} = 250 \text{ mol}$.

.. V= 3.10 m3.

(f) 250 mol x 6.022 x 102 mol = 1.51 x 1026 atom = N.

(c) PV = \frac{1}{3} Nm \overline{U^2} : \overline{U^2} = \frac{3PV}{Nm} m is the nudecular mass (see (1)) = Hence $\overline{uz} = 1.85 \times 10^6 \text{ m/s}^{-2}$: $\sqrt{uz} = 1360 \text{ m/s}^{-1}$.

(d) KE = \frac{1}{2}mu = 6.16x10^{21} J.

times answer to (d) i.e. 9:30 × 10 J.

3) The rate of affision: inversely proportional to the square root of the indecular mass or the square root of the density.

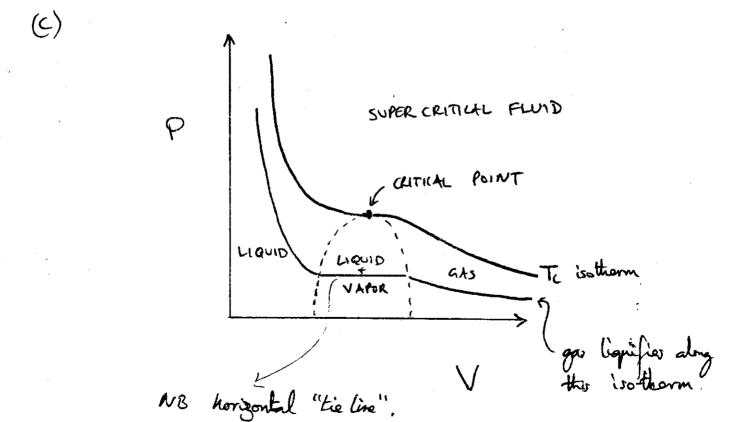
rate, = \frac{m_2}{m_1} = \frac{e_2}{e_1}

- 4) (a) The undecides are in content unbion.

 They have negligible volume.

 There are no intermolecular forces.
 - (b) a reflects the influence of intermolecular forces. The alteraction between a molecule close to the wall of a vessel and the bulk of the gas slightly reduces the effective pressure below the ideal value.

 It is a correction for the non-zono volume of the nuclecules and account for the volume free to be excupied being less than in the ideal case.



()
$$V = \frac{nRT}{P}$$
 : $\lambda = \frac{nRT}{\sqrt{2}\pi d^2 NP}$

but
$$\frac{n}{N} = \frac{1}{L}$$

PHYSICAL CHEMISTRY EXAM 2

7 October 1988

DATA: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. $C_{p} - C_{v} = R$. $C_{p} / C_{v} = X$.

(1) 10 Points.

Consider the reversible adiabatic expansion of 1 mol of an ideal gas, from V_1 at T_1 to V_2 at T_2 . Show, using the 1st Law of Thermodynamics, that $C_{V} \ln(T_{Z}/T_{1}) + R \ln(V_{Z}/V_{1}) = \emptyset$. Hence find the relation between P, V and X for an adiabat. On a P-V diagram sketch and label the isotherm and the adiabat which both pass through the point V_1 , P_1 at temperature T_1 .

(2) 10 Points.

- i) What is the difference between a process that is carried out reversibly or irreversibly ?
- ii) What is an exact differential and what is special about it ?
- iii) What is the distinction between C_{P} and C_{V} ?
- iv) What is the standard heat of formation of a substance ?
- v) What are endothermic reactions ? Are they permitted by the 1st Law of Thermodynamics ?

(3) 10 Points.

 $\Delta_{\tau} H^{\phi}(298 \text{ K}) C_{2}H_{4}(g) = 52.3 \text{ kJ mol}^{-1}.\Delta_{\tau} H^{\phi}(298 \text{ K}) CO_{2}(g) = -393.5 \text{ kJ mol}^{-1}.$ $\Delta_{+}H^{-}(298 \text{ K}) H_{2}U(1) = -237.2 \text{ kJ mol}^{-1}$. $C_{p} C_{2}H_{4}(g) = 43.6$, $C_{p} O_{2}(g) = 29.4$, $C_p H_2O(1) = 75.5$ and $C_p CO_2(g) = 37.1 J K^{-1} mol^{-1}$.

- i) What is △H°(298 K) for the combustion of C₂H₄ ?
- ii) What is $\Delta H^{o}(3700 \text{ K})$ for this combustion ?
- iii) If 0.01 mol C_2H_4 is burnt in the open, at 298 K and 10^{-5} Pa pressure, what is the work done against the atmosphere ?
- iv) What is ΔU for the situation in (iii) ?
- v) If the combustion of 0.01 mol occurred in a sealed rigid vessel at 298 K, what would be the work done in this case ?

(4) 8 Points.

 $\Delta_{+}H^{\circ}(H_{2}O(g)) = -241.8 \text{ kJ mol}^{-1}. \Delta_{+}H^{\circ}(OH(g)) = 249.2 \text{ kJ mol}^{-1}. \Delta_{+}H^{\circ}(O(g)) =$ 246.8 kJ mol⁻¹. $\Delta_{+}H^{\circ}(H(g)) = 218.0 \text{ kJ mol}^{-1}$. Calculate

- i) The heat of atomization of $H_{\geq}D(g)$.
- ii) The average bond dissociation energy of $H_{2}O(g)$.
- iii) The H-OH bond strength.
- iv) Would you expect your answers to (ii) and (iii) to be equal ? Why ?

(5) 12 Points.

Helium may be treated as an ideal gas. $C_p = 20.79 \, \mathrm{J} \, \mathrm{mol}^{-1}$.

- A. 1 mol, initially at 298 K and 1.013 x 100 Pa, is heated by 10 K within a sealed rigid vessel.
- i) How much heat is required ?
- ii) How much work is done ?
- iii) What is the change in internal energy of the gas ?
- B. 1 mol, initially at 298 K and 1.013 x 100 Pa, is heated by 10 K within a vessel with a movable piston, at a constant pressure of 1.013 x 100 Pa. iv) How much heat is required ?
- v) How much work is done ?
- vi) What is the change in internal energy of the gas ?

PHYSICAL CHEMISTRY EXAM 3

28 October 1988

Data: $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

(1) 10 Points.

Illustrate the Carnot cycle on a P-V diagram and label each of the four parts. Derive an expression for the efficiency of a reversible Carnot engine in terms of the temperatures between which it works, T_h and T_c . You may assume these results for changes from 1 to 2: $q = RT \ln(V_2/V_1)$ and w = -q for the reversible isothermal expansion of an ideal gas, and $w = C_v(T_2-T_1)$ for the reversible adiabatic expansion of an ideal gas.

Suppose $T_h = 800 \text{ K}$, $T_c = 200 \text{ K}$ and $q_h = 150 \text{ J}$.

- a) What is the thermodynamic efficiency of the engine?
- b) How much heat is rejected at the lower temperature?
- c) What is the entropy increase of the working fluid during the isothermal expansion at 800 K?
- (2) 10 Points.

1 mol of an ideal gas is expanded isothermally from 2 to 20 dm³ at 400 K. Calculate (a) ΔU (b) ΔH (c) ΔS (d) ΔA (e) ΔG .

(3) 12 Points.

Initially at 500 K and 10^5 Pa pressure, 1 mol of an ideal gas undergoes an irreversible isothermal expansion in which its volume is doubled, and the work it performs is 500 J. What are the values of q, ΔU , ΔH , ΔS and ΔG ? What would be the work performed if the expansion had been carried out reversibly?

(4) 8 Points.

Prove that for 1 mol of a van der Waals gas, $(\partial U/\partial V)_{\tau} = a/V^2$, where V is the molar volume. The equation of state for 1 mol of a van der Waals gas is $(P + a/V^2)(V - b) = RT$. Show your reasoning and any results you assume.

(5) 1 Point. Bonus question: part of an arithmetic survey!

Suppose a car sells for \$10,000 when tax at 7% is included in the price. What is the price of the car before tax is added?

ANSWERS for EXAM 3 1988 , Fall

$$E = \frac{T_{h} - T_{c}}{T_{h}} = \frac{800 - 200}{800} = 75\%$$

6)
$$25\%$$
 of the heat is therefore rejected = 37.5 J.
c) $\Delta S = \int \frac{dq}{T} \frac{rev}{800 \text{ K}} = 0.1875$ J.K.1.

2 a) b)
$$\Delta U = \Delta H = 0$$
 because U and H are function of T only.
c) $\Delta S = R \ln \frac{20}{2} = 19.14 \text{ JK-1}.$
d) $\Delta A = \Delta U - T\Delta S = -7657 \text{ J}.$
e) $\Delta G = \Delta H - T\Delta S = -7657 \text{ J}.$

3)
$$w = -500 \text{ J}$$
 : $q = 500 \text{ J}$ fecause $\Delta U = 0$ (see 2a). $\Delta H = 0$ for some reason.

AG= OH-TOS= -2881 J.
Romamber AG = max work, the nevertible work:

max work that cold be done is 2881 J.

$$\frac{25}{7} \text{ Tr} = \frac{25}{\sqrt{60}} \text{ Tr} = \frac{27 + A = 0}{\sqrt{60}} \text{$$

It would also be acceptable to write down this segnation of state without proof.

$$\frac{1}{2} \left(\frac{\partial R}{\partial T} \right)_{V} = \frac{R}{V + b} \Rightarrow \left(\frac{\partial U}{\partial V} \right)_{T} = -P + \frac{RT}{V - b} = -P + \left(P + \frac{q}{V^{2}} \right) = \frac{q}{V^{2}}.$$

EXAM **14 November 1988**

 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ Data:

1 atm = 101325 Pa

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) 10 points.

A gas reaction A = B + C is exothermic and has $K_p = 1$ atm at 298 K. With reference to a standard state of 1 atm.

a) What is ΔG° at 298 K?

b) What is the sign of ΔS° ? Why?

Will K₀ at 310 K be greater or less than 1 atm? Why? c)

What will be the sign of ΔG° at 310 K? Why? d)

Calculate K_c (standard state 1 mol dm⁻³) at 298 K.

(2) 10 points.

In the gas phase, n-pentane ("A") can isomerize to neopentane ("B"). Thermodynamic data for A and B, for 298 K and a standard state of I atm, are:

 $\Delta_{r}H^{o} = -146.44 \text{ kJ mol}^{-1}$ В

 $S^{\circ} = 349.0 \text{ J K}^{-1} \text{ mol}^{-1}$

 $\Delta_{\rm f} H^{\circ} = -165.98 \text{ kJ mol}^{-1}$

 $S^{\circ} = 306.4 \text{ J K}^{-1} \text{ mol}^{-1}$

For the reaction A = B at 298 K.

Calculate ΔH° and ΔS° . a)

- Calculate ΔG° and K_n . If the temperature is raised, does the shift in b) equilibrium favor A or B? Why?
- Pure A is in a vessel at 1 atm and 298 K, and the reaction to form B is allowed c) to proceed to equilibrium. Calculate the final partial pressures of A and B.
- If the reaction had been written as 2A = 2B instead, how would your calculated d) ΔG^{o} , K_{p} and final partial pressures have changed, if at all?
- 12 points.

The temperature dependence of K_p is given by $d(\ln K_p)/d(1/T) = -\Delta H^0/R$.

Assuming ΔH° is independent of T, derive an expression for $\ln(K_{p,1}/K_{p,2})$, the

natural logarithm of the ratio of K_p at two temperatures T_1 and T_2 . Consider the process $N_2O_4 = 2 NO_2$. The following experimental data were obtained b) for an equilibrium mixture:

T $p(N_2O_4)$ $p(NO_2)$ 298 K 0.0605 atm 0.0303 atm 305 K 0.0895 atm 0.0395 atm.

Calculate K, at each temperature.

- Calculate ΔH° for the interval 298 to 305 K, standard state 1 atm, assuming it c) to be independent of T.
- Calculate ΔG° at 298 K and hence ΔS° (standard state 1 atm). d)

What is the degree of dissociation α of N_2O_4 at 298 K? e)

- Calculate K_c at 298 K (standard state 1 mol dm⁻³). f)
- (4) 8 points.

Consider the partial dissolving of a slightly soluble salt AgCl in water: $AgCl(s) = Ag^{\dagger}(aq) + Cl^{\dagger}(aq)$.

- The conventional equilibrium constant for this reaction is called solubility product K_s . What is K_s in terms of the concentrations of the species involved?
- The molar mass of Ag is 0.108 kg; that of Cl is 0.035 kg. A saturated aqueous solution of AgCl contains 1.9 x 10^{-6} kg dm⁻³. What is K_s ? **b**)

To 1 dm³ of the above solution Cl⁻ is added until [Cl⁻(aq)] = 1 mol dm⁻³. What is c)

the new equilibrium [Ag+(aq)]?

Is this new [Ag⁺(aq)] greater or less than the [Ag⁺(aq)] in part (b)? How did the d) system change physically as Cl was added to adjust to the new [Ag+(aq)]?

(a)	\$9°=0
,	$\Delta S \leq 0$.
<u>c)</u>	
d)	۵٩>٥.
e)	Nc = 0.0409 md dm3
<i>(</i>)	
2a)	
<u> </u>	DG= -6845 Jmol' =-RT hkp
	: Kp = 15.85 atm.
·	txothernic: highert favors A.
c)	$A \longrightarrow B$ $ x_p - \frac{x}{1-x} , x = 0.9406$
	Eq. 1-x x
	2. pA = 0:0594.
7 \	h (K)/K2) = AH (+2-+).
) a)	m (1/h) - R (T2-T).
~ 1	
	Kp (2984) = 0.0152 atm, Kp (305 K) = 0.0174 atm
<u>e)</u>	Kp (2984) = 0:0152 atm, Kp (305 K) = 0.0174 atm. DH = 14.80 kJ ml-1 by (9).
e) d)	Kp (298K) = 0.0152 atm, Kp (305 K) = 0.0174 atm. ΔH = 14.80 kJ ml-1 by (9). Δ9° (298) = 10372 J ml-1: ΔS = ΔH-Δ9 = 14.86 J K-1 mol-1.
e) e)	$K_{p}(298K) = 0.0152 \text{ atm}, K_{p}(305K) = 0.0174 \text{ atm}.$ $\Delta H = 14.80 \text{ kT ml}^{-1} \text{ by (a)},$ $\Delta G^{o}(298) = 10372 \text{ T ml}^{-1} : \Delta S = \Delta H - \Delta G = 14.86 \text{ T K}^{-1} \text{ mol}^{-1}.$ Initial $p(N_{20}) = 0.0605 + 0.0303 \text{ atm} : 20\% \text{ discoulted}.$
e) e)	Kp (298K) = 0.0152 atm, Kp (305 K) = 0.0174 atm. ΔH = 14.80 kJ ml-1 by (9). Δ9° (298) = 10372 J ml-1: ΔS = ΔH-Δ9 = 14.86 J K-1 mol-1.
e) d) e) f)	K_{p} (298K) = 0.0152 dm, K_{p} (305K) = 0.0174 dtm. $\Delta H = 14.80 \text{ kT ml}^{-1}$ by (9). ΔS° (298) = 10372 $T \text{ ml}^{-1}$: $\Delta S = \Delta H - \Delta S = 14.86 T K^{-1} \text{ mol}^{-1}.Initial p(N_{20}) = 0.0605 + 0.0303 \text{ dm}^{-1}; Z_{0} dissociated.K_{c} = K_{p}/RT = 6.22 \times 10^{-4} \text{ mol} \text{ dm}^{-3}.$
e) d) f) 4 a)	K_{p} (2984) = 0:0(52 atm, K_{p} (305 K) = 0:0174 atm. $\Delta H = 14.80 \text{ kT ml}^{-1}$ by (9). ΔG° (293) = 10372 ΔM^{-1} : $\Delta S = \Delta H^{-}\Delta G = 14.86 \Delta M^{-1}.Initial P(N_{20}) = 0:0605 + \frac{0:0303}{2} atm.; \Delta S = \frac{1}{2} disjointed.K_{c} = K_{p}/RT = 6.22 \times (0^{-4} \text{ need dm}^{-3}).$
e) d) f) 4 a)	 Kp (298K) = 0.0152 atm, Kp (305 K) = 0.0174 atm. ΔH = 14.80 kJ ml-1 by (a). ΔG° (293) = 10372 J ml-1 : ΔS = ΔH-ΔΩ = 14.86 J K-1 mol-1. Initial p(N204) = 0.0605 + 0.0303 atm : 20% dissociated. Kc = Kp/RT = 6.22 x (6.4 mol dm³). Ks = [AgT][CT]. Modar mass Ag(L = 0.183h) : CAgT] = [CLT] = 1.33 x 10⁻⁵ mol dm⁻³
e) d) e) f) 4 a) 6)	Kp (298 K) = 0.015 ε atm, Kp (305 K) = 0.017 k atm. ΔH = 14.80 kJ ml-1 by (9). ΔG° (293) = 1037 ε J ml-1 : ΔS = ΔH-ΔG = 14.86 J K-1 mol-1. Initial p(N204) = 0.0605 + 0.0303 atm : 20% dissociated. Kc = Kp/RT = 6.22 x (0-4 mol dm ⁻³). Ks = [Ag ⁻][(1]]. Molar mass Ag (1 = 0.183 h : CAg ⁻) = [(1-] = 1.33 x 10 ⁻⁵ mol dm ⁻³ in Ks = 1-77 x (0 ⁻¹⁰ mol dm ⁻⁶ .
e) d) e) f) 4 a) 6)	Kp (298K) = 0.0152 atm, Kp (305 K) = 0.0174 atm. ΔH = 14.80 kJ ml-1 by (9). ΔG° (298) = 10372 J ml-1: ΔS = ΔH-ΔG = 14.86 J K-1 ml-1. Initial p(N204) = 0.0605 + 0.0303 atm: 20% dissociated. Kc = Kp/RT = 6.22 x (0-4 mol dm-3. Ks = [Ag ⁷][Cl]. Holar mass Ag(l = 0.143h; (Ag ⁷) = [Cl] = 1.33 x 10-5 mol dm-3 ∴ Ks = 1-77 x (0-6 mol dm-6. CAg ⁷] = 1-77 x (0-6 mol dm-3.
e) d) e) f) 4 a) 6)	Kp (298 K) = 0.015 ε atm, Kp (305 K) = 0.017 k atm. ΔH = 14.80 kJ ml-1 by (9). ΔG° (293) = 1037 ε J ml-1 : ΔS = ΔH-ΔG = 14.86 J K-1 mol-1. Initial p(N204) = 0.0605 + 0.0303 atm : 20% dissociated. Kc = Kp/RT = 6.22 x (0-4 mol dm ⁻³). Ks = [Ag ⁻][(1]]. Molar mass Ag (1 = 0.183 h : CAg ⁻) = [(1-] = 1.33 x 10 ⁻⁵ mol dm ⁻³ in Ks = 1-77 x (0 ⁻¹⁰ mol dm ⁻⁶ .

Answers to EXAM 4.

TAKE HOME QUESTIONS Due on Monday 21 November, 10 am

Data:

 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

1 atm = 101325 Pa

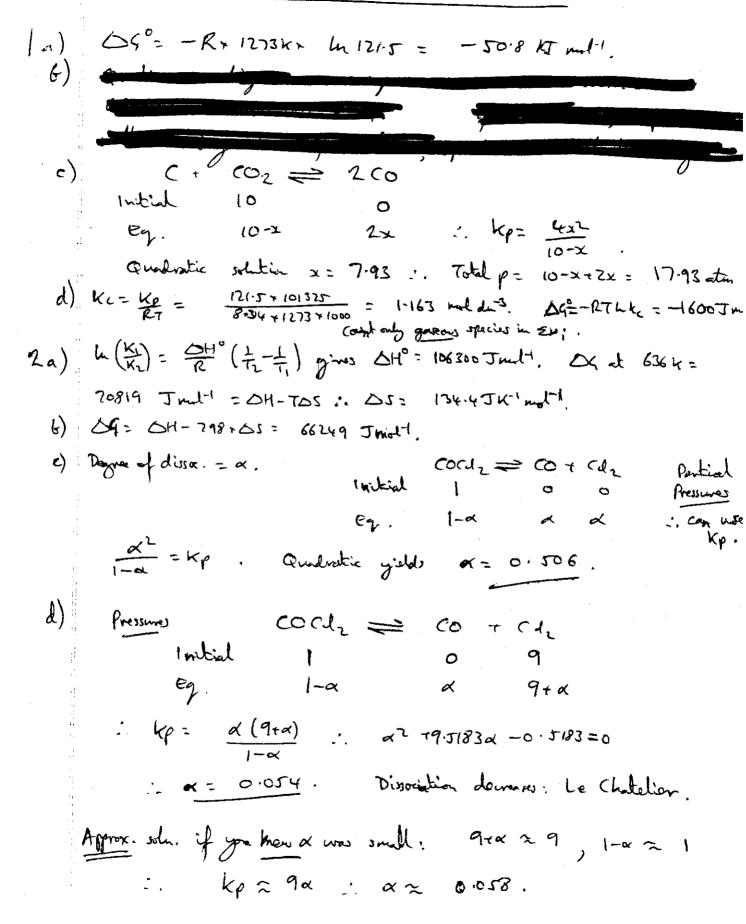
IT IS ESSENTIAL that you show working or give brief explanations. You will not get full credit otherwise.

- (1) At 1000° C, K_p for CO_2 (g) + C (graphite) = 2 CO (g) is 121.5 atm.
- (a) Calculate ΔG^{0} (standard state 1 atm).



- (c) If a vessel at 1000°C initially contains solid carbon and 10 atm of CO₂, what will be the total pressure in the vessel at equilibrium?
- (d) Calculate K_c (standard state I mol dm⁻³) at 1000°C. What is ΔG^o (standard state I mol dm⁻³)?
- (2) K_p for the reaction $COCl_2$ (g) = CO (g) + Cl_2 (g) is measured to be 0.0195 atm at 636 K and 0.5183 atm at 760 K.
- (a) Calculate ΔH^0 and ΔS^0 (standard state 1 atm), on the assumption that they are independent of temperature.
- (b) What is ΔG^0 at 298 K?
- (c) What is the degree of dissociation of 1 atm of pure COCl₂ at 760 K?
- (d) If 1 atm of COCl₂ and 9 atm of Cl₂ are allowed to come to equilibrium at 760 K, what then is the degree of dissociation of the COCl₂?

ANDWERS TO TAKE-HOME QUESTIONS



EXAM 5

Take-home questions on Chapter 9 Due on Wednesday 30 November 1988 at 10 am

Data:

 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

(1) 9 points.

Some results for the rate of a reaction between A and B are:

	and the distriction octation in and is and,		
[A]/mol dm ⁻³	$[B]/mol\ dm^{-3}$	rate/mol dm ⁻³ s ⁻¹	
2	1	5	
2	2	10	
4	4	80	

Deduce the order of the reaction with respect to A and B. What is the overall order of the reaction? What is the rate constant? What are its units?

(2) 15 points.

The composition of a solution initially containing pure A was measured as a function of time. A reacted with stoichiometry A \longrightarrow B in a reaction that was first-order with respect to A and which did not depend on [B]. The following data were obtained:

t/min 0 10 20 30 40
$$\approx$$
 [B]/mol dm⁻³ 0 0.089 0.153 0.200 0.230 0.312

What is a_0 , the initial value of [A]? Find the rate constant by plotting a graph of $\ln \{a_0/(a_0-[B])\}$ against t as discussed in the notes. Fit a straight line to the points by eye: least-squares fitting is not required. Give the units of the rate constant.

ATTENTION: 5 of the points are for graphing style i.e. adherence to the following five essential rules for ANY scientific graph:

- i) Use only graph or squared paper.
- ii) Use a ruler for all straight lines: no freehand sketching.
- iii) Label both axes, and show the units.
- iv) Each axis must be at least 4" (10 cm) long: no micro drawings.
- v) No silly scales like 17.3 squares per unit.

PENCIL IS PERFECTLY ACCEPTABLE AND LETS YOU CORRECT MISTAKES: I recommend it.

(3) 15 points.

The rate constant k of a second-order reaction has been measured as a function of temperature:

Plot a graph of ln k against 1/T. Fit a straight line to the scattered points by eye: a regression analysis is not required. Find the two Arrhenius parameters. Give their units. Again, there are 5 easy points for following the graph rules of Q.2.

