

DCHA 2706

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

GENERAL PHYSICAL CHEMISTRY II

Thursday, 3rd June 1999, 2.30 p.m. to 5.30 p.m.

Candidates should answer *five* questions

The marks in square brackets indicate the weight the examiners expect to assign to each part of the question.

Speed of light, c	=	$2.998 \times 10^8 \text{ m s}^{-1}$
Planck constant, h	=	$6.626 \times 10^{-34} \text{ J s}$
Boltzmann constant, k_B	=	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Gas constant, R	=	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Avogadro constant, N_A	=	$6.022 \times 10^{23} \text{ mol}^{-1}$
1 M	=	1 mol dm^{-3}
p^\ominus	=	$1 \text{ bar} = 10^5 \text{ Pa}$
1 atm	=	$101.325 \text{ kPa} = 760 \text{ Torr}$
Elementary charge, e	=	$1.602 \times 10^{-19} \text{ C}$
Atomic mass unit, u	=	$1.661 \times 10^{-27} \text{ kg}$
Faraday constant, F	=	$9.6487 \times 10^4 \text{ C mol}^{-1}$
1 Da	=	1 g mol^{-1}
Vacuum permittivity ϵ_0	=	$8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Electron mass, m_e	=	$9.109 \times 10^{-31} \text{ kg}$
V_m^\ominus	=	$24.79 \text{ dm}^3 \text{ mol}^{-1} \text{ at } 298 \text{ K}$

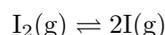
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Turn over

1. At high temperatures molecular iodine, I_2 , confined in a closed container, partially dissociates into atoms, so that measurable deviations from the pressures expected without dissociation are observed. Observed pressures p , and expected pressures without dissociation p_0 are listed below for several absolute temperatures, T .

T/K	973	1073	1173
p_0/bar	0.0576	0.0631	0.0684
p/bar	0.0624	0.0750	0.0918

(a) Use the data above to calculate the equilibrium constant, K_p , for the reaction



at each of the three temperatures listed in the table. [5]

(b) The Van't Hoff equation is

$$\frac{d(\ln K)}{dT} = \frac{\Delta H_m^\circ}{RT^2}$$

where the symbols have their usual meaning. By integration of this equation suggest a suitable straight line plot by which ΔH_m° might be deduced if values of K are known at several temperatures. State any assumptions made.

Use a plot of this form to estimate the enthalpy of dissociation ΔH_m° of iodine at temperatures near 1073 K. [7]

(c) State how the equipartition principle permits estimates of the heat capacities of gaseous atoms and small molecules to be made. Ignoring vibrational contributions, estimate $\Delta C_{p,m}$ for the reaction given above and write down an expression relating the enthalpy of iodine dissociation at a temperature, T , $\Delta H_m^\circ(T)$ to that at 1073 K, $\Delta H_m^\circ(1073)$. [4]

(d) Outline how you would estimate the standard Gibbs energy of dissociation of iodine at 298 K using the results in (b) and (c). Numerical calculations are **not** required. [4]

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2. Answer **all** parts.

A. The internal energy of a gas is related to the molecular partition function q and the number of molecules N by:

$$U - U(0) = Nk_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V$$

where $U(0)$ is the internal energy at absolute zero.

- (i) Show that if q is proportional to T^z , then $U - U(0) = zNk_B T$.
- (ii) Comment on this result in the context of the translational, rotational and vibrational motion of diatomic molecules. [5]

B. The molar entropy of a gas is given by

$$S_m = \frac{U_m - U_m(0)}{T} + R \ln q$$

Making appropriate approximations, which should be clearly stated, account for the following *differences* in molar entropies (in $\text{J K}^{-1} \text{mol}^{-1}$) at 300 K:

- (i) $S(\text{Xe}) - S(\text{Ar}) \cong 15$
- (ii) $S(\text{DI}) - S(\text{HI}) \cong 6$
- (iii) $S(\text{D}_2) - S(\text{H}_2) \cong 14$
- (iv) $S(^{35}\text{Cl}^{37}\text{Cl}) - S(^{35}\text{Cl}_2) \cong 6$

Note the following relative atomic masses: $m(\text{Xe}) = 131$; $m(\text{Ar}) = 40$; $m(\text{I}) = 127$; $m(\text{H}) = 1$; $m(\text{D}) = 2$. [8]

C. Account for the temperature dependence of the molar heat capacity $C_{V,m}$ of HD: [7]

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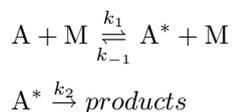
3. Answer **three** of the following (all parts carry equal weight) [20]

A. For the reaction $A + BC \rightarrow AB + C$, show how transition state theory predicts that the pre-exponential factor of the rate constant should either be proportional to $T^{-\frac{1}{2}}$ or temperature *independent* depending on the geometry of the transition state.

B. Lindemann theory predicts an expression of the following form for the dependence of the rate of the unimolecular decomposition of substance A on concentration of an inert diluent [M].

$$\frac{-d[A]}{dt} = k_{uni}[A] = \frac{k_1 k_2 [M]}{k_2 + k_{-1} [M]} [A]$$

based on applying the steady state approximation to the reaction scheme



Show that on the basis of this model k_{uni} falls to one-half of its limiting high-pressure value (k_∞) when $[M] = k_\infty/k_1$. Explain why values of k_1 determined from this equation are generally much larger than predicted from simple collision theory. (Note: you are **not** required to derive the above rate expression, and will not obtain credit for doing so).

C. Explain why the rates of many radical-radical recombination reactions in the gas-phase at low pressure show third-order kinetics, and why the rates decrease with increasing temperature.

D. Explain why the gas-phase reaction $\text{Li} + \text{F}_2 \rightarrow \text{LiF} + \text{F}$ has a reaction cross section, (approximately 100 \AA^2) that is much larger than the hard-sphere collision cross section for these species based on Van der Waals radii, and why the LiF product is scattered predominantly in the forward direction with respect to the initial Li atom direction.

E. In the reaction of HCl with K, ($\Delta H = 4 \text{ kJ mol}^{-1}$) laser excitation of HCl to $v = 1$ (requiring 34.5 kJ mol^{-1}) increases the reaction rate by a factor of 100, whereas increasing the average thermal energy of the reactants by the same amount through heating of the gases only increases the reaction rate by a factor of 10. The majority of the excess energy of this reaction is partitioned directly into translational energy of the products. Discuss what can be inferred from this data about the potential energy surface for the reaction.

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4.

(a) The lowest three electronic states of the N_2^+ ion have the symmetries $^2\Sigma_g^+$, $^2\Pi_u$, and $^2\Sigma_u^+$, and each can be accessed by removal of one electron from the ground electronic configuration of N_2 .

Identify the electronic configurations giving rise to each, and discuss the meaning of the term symbols employed. [7]

(b) The vibrational wavenumbers and rotational constants for these states are listed below.

	Vibrational wavenumber ω_e/cm^{-1}	Rotational constant B_e/cm^{-1}
$^2\Sigma_g^+$	2207.0	1.9317
$^2\Pi_u$	1903.7	1.7444
$^2\Sigma_u^+$	2419.8	2.0746

For the ground state of N_2 , $\omega_e = 2358.6 \text{ cm}^{-1}$ and $B_e = 1.998 \text{ cm}^{-1}$. Discuss these values in terms of the molecular orbital diagram for N_2 and N_2^+ . [8]

(c) The electronic emission spectrum of N_2^+ involving the states listed above shows one band with an origin at 9015.5 cm^{-1} with a band head in the R branch, while another band occurs at $25\,566 \text{ cm}^{-1}$ with a band head in the P branch.

Identify the electronic states involved, giving reasons for your assignment.

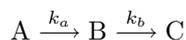
[The wavenumbers of transitions in the R branch are given by the formula

$$\tilde{\nu}_J = \tilde{\nu}_0 + (B' + B'')(J + 1) + (B' - B'')(J + 1)^2$$

where B' and B'' are the rotational constants for the upper and lower states and $\tilde{\nu}_0$ is the band origin.] [5]

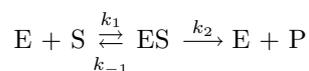
5.

(a) What is the steady state approximation in chemical kinetics and why is it useful? State without derivation the conditions under which it is valid for the following reaction?



[5]

(b) Some enzyme catalysed reactions are well-described by the simple reaction scheme



where E, S, ES and P represent respectively enzyme, substrate, enzyme-substrate complex and product.

Using the steady state approximation derive an expression of the following form for ν , the rate of the reaction ($[E]_0$ is the *total* amount of enzyme present):

$$\nu = \frac{k_2[E]_0[S]}{K_M + [S]}$$

and obtain an equation relating K_M to k_1 , k_{-1} , and k_2 .

[7]

(c) The following initial rates of reaction were measured for 1.0×10^{-9} g of an enzyme ($M_r = 29\,600$) dissolved in 0.01 dm^3 of water.

$[S]/10^{-5} \text{ M}$	0.1	0.3	0.5	1.0	3.0	5.0
$\nu/10^{-9} \text{ M s}^{-1}$	0.183	0.417	0.567	0.750	0.967	1.017

Verify that these data are consistent with the above reaction scheme and determine K_M and k_2 .

[5]

(d) What fraction of the enzyme is complexed to substrate when $[S] = 5 \times 10^{-5} \text{ M}$?

[3]

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6. (a) The Debye-Hückel limiting law for an aqueous solution of electrolyte at 298 K is

$$\log_{10} \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I}$$

where γ_{\pm} is the mean ionic activity coefficient, z_+ and z_- the ionic charges, and I the ionic strength. Summarize the physical model used in establishing the Debye-Hückel limiting law. [6]

(b) Write down the cell reaction for the Harned cell



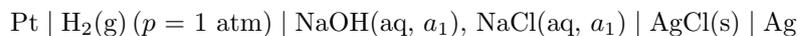
and obtain an expression for the EMF, E , assuming that the gas-phase species behaves ideally. [2]

(c) The data given below show the EMF for the Harned cell at 298 K as a function of the molality, m , of the Cl^- ion. Using the Debye-Hückel limiting law, determine the standard potential of the silver/silver chloride electrode.

$m/\text{mol kg}^{-1}$	0.003215	0.005619	0.009138
E/mV	520.63	492.57	468.60

$[RT/F = 25.69 \text{ mV at } 298 \text{ K}]$ [8]

(d) At 298K the cell



has an EMF of 1.05080 V. Estimate the autoprotolysis constant (ionic product), K_w , of water at 298 K. [4]

7. Comment on **four** of the following aspects of liquid-phase reactions. [5 each]

(a) The rate constants for recombination of methyl radicals in hexane and water are *ca* 2×10^{10} and *ca* 7×10^9 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ respectively. The rate constants for recombination of solvated electrons and molecular cations in hexane and water are *ca* 1.0×10^{14} and *ca* 1.0×10^{10} $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ respectively.

(b) For a number of ion-ion reactions in solution there exists a correlation between the entropy of activation, the volume of activation and the dependence of the reaction rate on pressure.

(c) For a series of similar electron transfer reactions it is sometimes possible to measure rate constants that *decrease* as the Gibbs energy of the reaction becomes more negative.

(d) Addition of an inert electrolyte accelerates some ion-ion reactions and decelerates others.

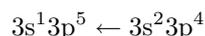
(e) Photolysis of compound A (below) produces a mixture of isomers B and C. A greater proportion of B is formed if the reaction proceeds via an excited singlet state of A than if an excited triplet state is involved.

8. (a) The Ar^{2+} ion in the gas phase has the configuration $1s^2 2s^2 2p^6 3s^2 3p^4$ in its ground state. Predict the following, explaining your reasoning.

- (i) The *terms* arising from that configuration and their energy ordering
- (ii) The J quantum number for the lowest energy level.

[6]

(b) The lowest energy *fully-allowed* electric-dipole transition in the *absorption* spectrum of Ar^{2+} is of the type

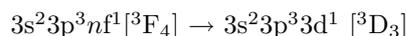


and occurs at a wavenumber of approximately $115\,000\text{ cm}^{-1}$.

Deduce the term symbols for the two states involved in this transition and draw a diagram showing the allowed transitions between all the levels of the two terms.

[6]

(c) A series of transitions are observed in the emission spectrum of Ar^{2+} of the type



n	$\tilde{\nu}/\text{cm}^{-1}$
4	111 290
5	133 527
6	145 605
7	152 887

The quantum defect for the upper 3F_4 levels may be assumed to be zero and the ionization energy of Ar^{2+} is $329\,966\text{ cm}^{-1}$.

Use a graphical procedure with the data given above to determine the energy required to ionize the Ar^{2+} ion from the $3s^2 3p^3 3d^1 [^3D_3]$ level and hence determine the excitation energy from the ground state to this level.

[8]