CCHE 4273
FIRST PUBLIC EXAMINATION
Preliminary Examination in Chemistry

## SUBJECT 3 : PHYSICAL CHEMISTRY

TRINITY TERM 2010
Wednesday, 9th June 2010, 9.30 a.m. - noon
Time allowed $2 \frac{1}{2}$ hours

Candidates should attempt ALL questions in section A and TWO questions in section B.
Use SEPARATE booklets for your answers to Section A and Section B.
The numbers in square brackets indicate the approximate weight given to each part of the question.

Do not turn over until instructed to do so by an invigilator

## Fundamental Constants

| Speed of light in a vacuum | $c$ | $2.997 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$ |
| :---: | :---: | :---: |
| Planck constant | $h$ | $6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}$ |
|  | $\hbar=h / 2 \pi$ | $1.055 \times 10^{-34} \mathrm{~J} \mathrm{~s}$ |
| Boltzmann constant | $k_{\text {B }}$ | $1.381 \times 10^{-23} \mathrm{~J} \mathrm{~K}^{-1}$ |
| Gas constant | $R$ | $8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ |
| Faraday constant | $F$ | $9.649 \times 10^{4} \mathrm{C} \mathrm{mol}^{-1}$ |
| Elementary charge | $e$ | $1.602 \times 10^{-19} \mathrm{C}$ |
| Electron mass | $m_{\text {e }}$ | $9.109 \times 10^{-31} \mathrm{~kg}$ |
| Proton mass | $m_{\text {p }}$ | $1.673 \times 10^{-27} \mathrm{~kg}$ |
| Neutron mass | $m_{\mathrm{n}}$ | $1.675 \times 10^{-27} \mathrm{~kg}$ |
| Vacuum permittivity | $\epsilon_{0}$ | $8.854 \times 10^{-12} \mathrm{~F} \mathrm{~m}^{-1}$ |
| Avogadro constant | $N_{\text {A }}$ | $6.022 \times 10^{23} \mathrm{~mol}^{-1}$ |
| Atomic mass unit | u | $1.661 \times 10^{-27} \mathrm{~kg}$ |
| Gravitational constant | $G$ | $6.673 \times 10^{-11} \mathrm{~N} \mathrm{~m}^{2} \mathrm{~kg}^{-2}$ |
| Gravitational acceleration | $g$ | $9.807 \mathrm{~m} \mathrm{~s}^{-2}$ |

Other conventions

$$
\begin{array}{ll}
p^{\curvearrowright} & =1 \mathrm{bar}=1 \times 10^{5} \mathrm{~Pa} \\
1 \mathrm{~atm} & =101.3 \mathrm{kPa}=760 \mathrm{Torr} \\
1 \mathrm{D} \text { (Debye) } & =3.336 \times 10^{-30} \mathrm{C} \mathrm{~m}
\end{array}
$$

## SECTION A <br> Attempt ALL six questions

1. (a) State the First and Second Laws of Thermodynamics.
(b) Show from basic thermodynamic considerations that the reversible change in entropy for a closed system at constant pressure is given by,

$$
\begin{equation*}
T \mathrm{~d} S=C_{p} \mathrm{~d} T \tag{4}
\end{equation*}
$$

where $C_{p}$ is the heat capacity at constant pressure.
(c) Two quantities of water (RMM 18) each of mass 216 g are mixed together in a vessel. The temperatures of the two quantities before mixing are 303 K and 333 K . The entire system is perfectly insulated and the vessel has a negligible heat capacity. Calculate the change in entropy after equilibrium has been established, and comment on your result in the light of the Second Law of Thermodynamics. Note that $C_{p}=75.5 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ for liquid water in this temperature range. [4]
2. (a) Explain the physical significance of the electronic radial distribution function in an atom.
(b) The normalized wavefunction for the $1 s$ electron of the hydrogen atom (assuming an infinitely heavy nucleus) is,

$$
\psi(r)=\left(\frac{1}{\pi a_{0}^{3}}\right)^{1 / 2} \exp \left(-r / a_{0}\right)
$$

where $a_{0}$ is the Bohr radius.
(i) Sketch the radial distribution function for the $1 s$ orbital.
(ii) Derive an expression for the expectation value of the potential energy of an electron in the $1 s$ orbital of a hydrogen atom.

Note that

$$
\int_{0}^{\infty} x^{n} \exp (-\alpha x) \mathrm{d} x=\frac{n!}{\alpha^{n+1}}, \quad n \geq 0
$$

3. A cell potential of -0.111 V is obtained for the following voltaic cell at 298 K ,

$$
\mathrm{Pb}(\mathrm{~s})\left|\mathrm{Pb}^{2+}(1 \cdot \mathrm{M})\right| \operatorname{HCl}(0.3 \mathrm{M})\left|\mathrm{PbCl}_{2}(\mathrm{~s})\right| \mathrm{Pb}(\mathrm{~s})
$$

(a) Write down the cell reaction.
(b) What is the standard reduction potential for the cathode reaction at 298 K ? [3]
(c) Calculate the solubility product, $K_{s p}$, for $\mathrm{PbCl}_{2}$ at 298 K .

You may use the following standard reduction potential measured at 298 K :

$$
\mathrm{Pb}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Pb}(\mathrm{~s}) ; \quad E^{\ominus}=-0.13 \mathrm{~V}
$$

4. The gas phase reaction of fluorine atoms with bromine follows the equation,

$$
\mathrm{F}+\mathrm{Br}_{2} \rightarrow \mathrm{FBr}+\mathrm{Br}
$$

The gas concentrations as a function of time are determined by

$$
k_{2} t=\left(\frac{1}{\left[\mathrm{Br}_{2}\right]_{0}-[\mathrm{F}]_{0}}\right) \ln \left(\frac{\left[\mathrm{Br}_{2}\right][\mathrm{F}]_{0}}{[\mathrm{~F}]\left[\mathrm{Br}_{2}\right]_{0}}\right),
$$

where $k_{2}$ is the overall second order rate constant and $[\mathrm{X}]_{0}$ represents the initial concentration of species X.
The following concentrations of $\mathrm{Br}_{2}$ were observed as a function of time at 298 K when the initial fluorine concentration was $[\mathrm{F}]_{0}=4.00 \times 10^{-9} \mathrm{~mol} \mathrm{dm}^{-3}$.

$$
\begin{array}{c|ccccc}
\text { Time } / \mathrm{ms} & 0.0 & 0.7 & 1.3 & 2.7 & 3.9 \\
\hline\left[\mathrm{Br}_{2}\right] / 10^{-9} \mathrm{~mol} \mathrm{dm} & \\
\hline-3 & 0.100 & 0.066 & 0.048 & 0.022 & 0.011
\end{array}
$$

(a) Explain why for these particular initial conditions the reaction is expected to be pseudo first order with respect to $\mathrm{Br}_{2}$.
(b) Demonstrate that the reaction is indeed pseudo first order with respect to $\mathrm{Br}_{2}$ and determine $k_{2}$.
5. The Maxwell-Boltzmann distribution for the probability density of the $x$-component of velocity of a molecule of mass $m$ is

$$
f\left(v_{x}\right)=\left(\frac{m}{2 \pi k_{B} T}\right)^{1 / 2} \exp \left(-\frac{m v_{x}^{2}}{2 k_{B} T}\right)
$$

(a) Use this expression to demonstrate that the kinetic energy of an ideal gas satisfies the principle of the equipartition of energy.
(b) Calculate the root-mean-square speed for ${ }^{14} \mathrm{~N}_{2}$ molecules at 298 K .

Note that

$$
\int_{-\infty}^{\infty} x^{2} \exp \left(-\alpha x^{2}\right) \mathrm{d} x=\frac{1}{2 \alpha} \sqrt{\frac{\pi}{\alpha}}
$$

6. The partial charges on the hydrogen and chlorine atoms of HCl are +0.177 e and -0.177 e , respectively (where e is the elementary charge). The bond length of HCl is 127 pm .
(a) Calculate the permanent dipole moment of HCl (expressed in Debyes).
(b) State the expression for the energy of a dipole, $\mathbf{p}$, in an electric field, $\mathbf{E}$.
(c) An HCl molecule is subject to an electric field of strength $1 \mathrm{~V} \mathrm{~m}^{-1}$. Determine the interaction energy of the molecule with the field when,
(i) the field is parallel to the molecular axis (in your answer state the orientation of the molecule);
(ii) the field is perpendicular to the molecular axis.

## SECTION B

Attempt any TWO questions
7. (a) Given that $S=-\left(\frac{\partial G}{\partial T}\right)_{p}$, use the definition of the Gibbs free energy to show that

$$
\left(\frac{\partial(G / T)}{\partial T}\right)_{p}=-\frac{H}{T^{2}}
$$

(b) State the relationship between the equilibrium constant, $K_{p}$, and the standard Gibbs free energy.
(c) Hence, derive the Van 't Hoff equation

$$
\ln \left(\frac{K_{2}}{K_{1}}\right)=\frac{\Delta_{r} H^{\ominus}}{R}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right)
$$

where $K_{2}=K_{p}\left(T_{2}\right)$ and $K_{1}=K_{p}\left(T_{1}\right)$, stating the condition for which it is valid.

Methanol is produced commercially by passing a mixture of carbon monoxide and hydrogen over a zinc oxide/copper oxide catalyst.

$$
\mathrm{CO}(\mathrm{~g})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})
$$

The table below shows the standard enthalpies and Gibbs free energies of formation of the species at 298 K .

|  | $\Delta_{f} H^{\ominus} / \mathrm{kJ} \mathrm{mol}^{-1}$ | $\Delta_{f} G^{\ominus} / \mathrm{kJ} \mathrm{mol}^{-1}$ |
| :---: | :---: | :---: |
| $\mathrm{CO}(\mathrm{g})$ | -110.5 | -137.2 |
| $\mathrm{H}_{2}(\mathrm{~g})$ | 0 | 0 |
| $\mathrm{CH}_{3} \mathrm{OH}(\mathrm{g})$ | -200.7 | -162.0 |

(d) Calculate the equilibrium constant $K_{p}$ for this reaction at 298 K .
(e) A commercial reactor is operated at a temperature of 600 K . Calculate the equilibrium constant $K_{p}$ at this temperature, assuming that $\Delta_{r} H^{*}$ is independent of temperature.
(f) The gas flowing into the reactor comprises two moles of $\mathrm{H}_{2}$ for each mole of CO. If the mole fraction of methanol in the exhaust gas from the reactor is 0.25 , what is the total pressure in the reactor at 600 K ? You may assume that equilibrium is established in the reactor.
8. The motion of a particle on the surface of a sphere may be described by the Hamiltonian

$$
\hat{H}=\frac{\hat{L}^{2}}{2 I}
$$

where $I$ is the moment of inertia of the particle, $\hat{L}$ is the angular momentum operator, which is quantized as

$$
L^{2}=\hbar^{2} J(J+1)
$$

and $J$ is the angular momentum quantum number.
(a) (i) Write down the expression for the energy of a particle on a sphere with an angular momentum quantum number $J$.
(ii) For a given value of $J$ what are the allowed values of the projection of the angular momentum onto an arbitrary axis of quantization? State the degeneracy of the energy level corresponding to the quantum number $J$.
(b) ${ }^{14} \mathrm{~N}_{2}$ has an equilibrium bond length of 110 pm . Calculate:
(i) the energy required to excite ${ }^{14} \mathrm{~N}_{2}$ from its rotational ground state to its first excited state;
(ii) the temperature to which this excitation corresponds.
(c) As a simple approximation, the $72 \pi$-electrons of a $\mathrm{C}_{72}$ molecule may be regarded as being free to move on the surface of a sphere of radius 1.0 nm .
(i) What are the $J$-values of the occupied $\pi$-electron levels for the electronic ground state of $\mathrm{C}_{72}$ ?
(ii) Determine the wavelength of light required to excite a $\pi$-electron from the highest occupied energy level to the lowest unoccupied energy level.
(iii) Is an optical excitation possible from the highest occupied level to the second lowest unoccupied level? Explain your answer in terms of the relevant selection rules.

Note that

$$
\sum_{n=0}^{N}(2 n+1)=(N+1)^{2}
$$

9. The Arrhenius equation $k=A \exp (-E / R T)$ describes the variation of a rate constant $k$ with temperature $T$.
(a) Discuss the physical significance of the constants $A$ and $E$ with reference to the bimolecular reaction of two gaseous reactants X and Y .

Cl atoms react with $\mathrm{H}_{2}$ as follows:

$$
\begin{equation*}
\mathrm{Cl}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{HCl}(\mathrm{~g})+\mathrm{H}(\mathrm{~g}) \tag{1}
\end{equation*}
$$

The following initial reaction rates have been measured for varying temperatures and reactant concentrations:

| Reaction number | 1 | 2 | 3 | 4 |
| :--- | :---: | :---: | :---: | :---: |
| $\mathrm{~d}[\mathrm{HCl}] / \mathrm{d} t / 10^{-2} \mathrm{~mol} \mathrm{~m}^{-3} \mathrm{~s}^{-1}$ | 1.04 | 2.09 | 4.17 | 16.5 |
| $\left[\mathrm{H}_{2}\right] / 10^{-2} \mathrm{~mol} \mathrm{~m}^{-3}$ | 1.0 | 1.0 | 2.0 | 2.0 |
| $[\mathrm{Cl}] / 10^{-4} \mathrm{~mol} \mathrm{~m}^{-3}$ | 1.4 | 2.8 | 2.8 | 2.8 |
| $T / \mathrm{K}$ | 298 | 298 | 298 | 350 |

(b) What is the reaction order with respect to Cl and $\mathrm{H}_{2}$ ?
(c) Calculate the rate constant at 298 K and the Arrhenius parameters $A$ and $E .[8]$
(d) The rate constant is found to change when $\mathrm{H}_{2}$ is replaced by $\mathrm{D}_{2}$. Discuss possible reasons for this.
(e) (i) Given that $\Delta_{r} H^{\ominus}=5 \mathrm{~kJ} \mathrm{~mol}^{-1}$ for reaction (1) given above, calculate the activation energy for the reverse reaction.
(ii) The activation energy for the reaction

$$
\begin{equation*}
\mathrm{H}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g}) \rightarrow \mathrm{HCl}(\mathrm{~g})+\mathrm{Cl}(\mathrm{~g}) \tag{2}
\end{equation*}
$$

is $13 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Comment on the relative importance of the reverse of reaction (1) and reaction (2) in the $\mathrm{H}_{2}+\mathrm{Cl}_{2}$ chain reaction.
10. The Clapeyron equation for the gradient of a phase boundary in the $p-T$ plane is,

$$
\frac{\mathrm{d} p}{\mathrm{~d} T}=\frac{\Delta H_{m}}{T \Delta V_{m}},
$$

while the Clausius-Clapeyron equation for the gradient of the solid-vapour or liquidvapour phase boundary is,

$$
\begin{equation*}
\frac{\mathrm{d} p}{\mathrm{~d} T}=\frac{p \Delta H_{m}}{R T^{2}} \tag{1}
\end{equation*}
$$

(a) (i) Explain the approximations required to derive eqn (1).
(ii) Using eqn (1), derive the integrated form of the Clausius-Clapeyron equation,

$$
\ln p=-\frac{\Delta H_{m}}{R T}+\text { constant }
$$

stating any further approximations made.
(b) The vapour pressure of $\mathrm{CO}_{2}$ (RMM 44) is given in the table below for different temperatures:

$$
\begin{array}{c|cccccc}
T / \mathrm{K} & 196 & 206 & 211 & 221 & 226 & 236 \\
\hline p / 10^{5} \mathrm{~Pa} & 1.146 & 2.479 & 3.558 & 6.296 & 7.704 & 11.212
\end{array}
$$

Using this data, determine graphically for one mole of $\mathrm{CO}_{2}$ in this temperature range,
(i) the latent heat of sublimation;
(ii) the latent heat of vapourization;
(iii) the latent heat of fusion.
(iv) Also, determine the pressure and temperature at the triple point.
(c) At its triple point the densities of solid and liquid $\mathrm{CO}_{2}$ are $1.56 \mathrm{~g} \mathrm{~cm}^{-3}$ and $1.18 \mathrm{~g} \mathrm{~cm}^{-3}$, respectively.
(i) Use this data, in addition to your results from (b), to estimate the gradients of the phase boundaries at the triple point.
(ii) Hence, also using the data, plot the phase diagram of $\mathrm{CO}_{2}$ in the vicinity of the triple point, indicating the different phases.

