22/08(a) The University of Sydney

CHEMISTRY 1A (ADVANCED) - CHEM1901

CHEMISTRY 1A (SPECIAL STUDIES PROGRAM) - CHEM1903

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 2000 <u>TIME ALLOWED: THREE HOURS</u>

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

| SURNAME | | OTHER NAMES | | |
|---------------|---------|----------------|-----------------|--|
| SID NUMBER | FACULTY | | TABLE NUMBER | |

INSTRUCTIONS TO CANDIDATES

All questions are to be attempted. There are 14 pages of examinable material.

Complete the written section of the examination paper in **INK**.

Read each question carefully. Report the appropriate answer and show all relevant working in the space provided.

The total score for this paper is 100. The possible score per page is shown in the adjacent tables.

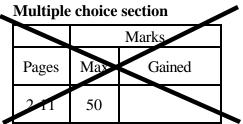
Each new question begins with a •.

Electronic calculators, including programmable calculators, may be used. Students are warned, however, that credit may not be given, even for a correct answer, where there is insufficient evidence of the working required to obtain the solution.

Numerical values required for any question and a Periodic Table may be found on a separate data sheet.

Pages 4, 10, 12, 15 & 20 are for rough working only.

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Short answer section

| | Marks | | | |
|-------------|-------|-------|---|--------|
| Page | Max | Gaine | d | Marker |
| 13 | 9 | | | |
| 14 | 7 | | | |
| 16 | 9 | | | |
| 17 | 8 | | | |
| 18 | 9 | | | |
| 19 | 8 | | | |
| Total | 50 | | | |
| Check Total | | | | |

• Using the information below concerning bond enthalpies, estimate the heat of reaction ΔH° of the following reaction:

Mark s 2

$$C_2 H_2(g) \ + \ ^5/2 O_2(g) \ \to \ 2 C O_2(g) \ + \ H_2 O(g)$$

Bond enthalpies in kJ mol⁻¹

| C–C | 346 | О–Н | 463 | O=O | 498 |
|-----|-----|-----|-----|-----|-----|
| С–Н | 414 | C–O | 358 | C=C | 614 |
| Н–Н | 436 | C≡C | 839 | C=O | 799 |

ANSWER:

• The reaction $H + H \rightarrow H_2$ is exothermic. Briefly describe where the energy released in this reaction came from, *i.e.* in what form was this energy prior to the reaction taking place.

2

5

• The boiling points of the binary hydrides of Group 16 are as follows:

| H ₂ O | H_2S | H ₂ Se | H ₂ Te |
|------------------|--------|-------------------|-------------------|
| 100 °C | −60 °C | −41 °C | −2 °C |

Pure water can be kept indefinitely as a liquid at -5 °C. Which liquid , H_2O or H_2Te , would you expect to exhibit the larger heat of solvation for ionic species at -5 °C? Provide a brief explanation of your answer.

Identify one difference between the atoms oxygen (O) and tellurium (Te) directly associated with the difference in the boiling points of H_2O and H_2Te .

• Use the following information to calculate the heat of formation $\Delta H_{\rm f}^{\circ}$ of methanol CH₃OH(l).

Mark s

3

$$CH_{3}OH(l) \ + \ ^{3}\!/_{2}O_{2}(g) \ \to \ CO_{2}(g) \ + \ 2H_{2}O(g)$$

$$\Delta H^{\circ} = -638.5 \text{ kJ mol}^{-1}$$

$$\Delta H_{\rm f}^{\circ} \text{ of CO}_{2}(g) = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H_{\rm f}^{\circ} \text{ of } H_2{\rm O}({\rm g}) = -241.8 \text{ kJ mol}^{-1}$$

ANSWER:

• Several features of atomic structure and energetics are direct consequences of the wave-like character of the electron. Briefly describe one such feature.

2

• The electrons involved in metallic bonding are typically delocalised throughout the solid metal. Explain, in terms of the quantum theory of the electron, why this behaviour would be expected to decrease the energy of those electrons.

2

• Draw Lewis structures for the following species. (The central atom is underlined.)

Mark s 9

| COCl ₂ | <u>P</u> F ₃ | $H_3\underline{O}^+$ |
|-------------------|---------------------------------------|---------------------------------------|
| | | |
| | | |
| | | |
| H <u>C</u> N | $\underline{\mathrm{S}}\mathrm{Cl}_2$ | <u>C</u> O ₃ ²⁻ |
| | | |
| | | |

Complete the following table.

| Species | $COCl_2$ | PF_3 | H_3O^+ | HCN | SCl_2 | CO ₃ ²⁻ |
|---|----------|--------|----------|-----|------------------|-------------------------------|
| No. of electron pairs around central atom not involved in π bonding | | J | | | | , |
| No. of π bonding orbitals | | | | | | |
| Geometric arrangement of σ and lone pairs | | | | | | |
| Hybridisation of central atom | | | | | | |
| Geometry of molecule or ion | | | | | | |
| Does the molecule have a non-zero dipole moment? | | | | | | |

Mark

2

• Reduction of a metal oxide, MO, follows the reaction

 $MO(s) + C(s) \longrightarrow M(s) + CO(g)$

which has an equilibrium constant $K_p = 2.5$ atm at 1200 K.

- (a) At what pressure would equilibrium be established at 1200 K?
- (b) Below what pressure of CO(g) must the system be maintained at 1200 K to ensure complete conversion of MO(s) into M(s)?

• For each process shown on the left, place a "+" in the boxes below if the quantity at the head of the column is positive or place a "-" if the quantity is negative. If there is no change, place a "0" in the box.

| Process | ΔE | ΔH | ΔS | ΔG |
|---|------------|------------|------------|------------|
| 1 mole of ideal gas at 25 °C and 1 atm → 1 mole of ideal gas at 25 °C and 0.5 atm | | | | |
| $H_2O(1) \rightarrow H_2O(g)$ at 25 °C and 1 atm | | | | |
| $H_2O(1) \rightarrow H_2O(g)$ at 100 °C and 1 atm | | | | |

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORK ONLY.

6

| 2.5 times | • A mixture of H ₂ and D ₂ at 300 K effuses from a very tiny hole in the containing vessel. If 2.5 times as many D ₂ molecules as H ₂ escape from the pinhole in unit time, what is the mole fraction of D ₂ in the original gas mixture? (D stands for the isotope ² H.) | | | | |
|------------|---|--------------------------------|---------------------------------|---|---|
| | | | | | |
| | | ANSV | VER: | | |
| 0.150 M a | y millilitres of 0.100 M Nacetic acid solution to give pK_a of acetic acid is 4. | e a solution with | | mL of | 4 |
| | | | | | |
| | | ANSV | VER: | | |
| volume, | ing a cross in the app V , and temperature, T , T , T from that of an ideal g | where you migh | t observe significa | ant deviation in gas | 2 |
| Conditions | P = 1 atm, $V = 25$ L, T = 300 K | V low, T low, $P = 0.1 atm$ | P low, V high, $T = 1000 K$ | P, V and T are at their critical values | |
| ✓ or X | | | | | |

| • | Three substances, labelled A, B and C combine to give two products, X and Y. The rate law and stoichiometric equation are not known. However, when 0.100 mol of each are present in 100 mL of solution, the rate of production of Y is 6.5×10^{-3} M s ⁻¹ . | | | | |
|---|---|--|--|--|--|
| | What is the value of the rate constant, k , for the | | | | |
| | | | | | |
| | | | | | |
| | | ANSWER: | | | |
| | If the reaction is third order, what are the units | s of k? | | | |
| | The isomerisation $CH_3NC(g) \rightarrow CH_3$ It has an activation energy of 160 kJ mol ⁻¹ and | I ₃ CN(g) obeys first order kinetics. | | | |
| | is 0.41 s^{-1} . Calculate the half-life of this react | | | | |
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |
| | | | | | |
| | F- | | | | |
| | | ANSWER: | | | |

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Numerical Data

Physical constants

Planck constant = $h = 6.626 \times 10^{-34}$ joule second

Speed of light in vacuum = $c_0 = 2.998 \times 10^8$ metre second⁻¹

Avogadro constant = $N_A = 6.022 \times 10^{23} \text{ mole}^{-1}$

Standard atmosphere = 1.013×10^5 pascal

Ideal gas constant = R = 8.314 joule kelvin⁻¹ mole⁻¹

= 0.08206 litre atmosphere kelvin⁻¹ mole⁻¹

 $1 \text{ nm} = 1 \text{ nanometre} = 10^{-9} \text{ metre}$

 $1 \text{ kJ} = 1 \text{ kilojoule} = 10^3 \text{ joule}$

 $1 \text{ kPa} = 1 \text{ kilopascal} = 10^3 \text{ pascal}$

1 L = 1litre = 1dm $^3 = 1$ decimetre $^3 = 10^{-3}$ metre 3

Atomic Weights of Isotopes

Hydrogen, ${}^{1}H$, = 1.008

Deuterium, 2 H, = 2.014

Thermochemical Data at 298 K

| | $\Delta H_{ m f}^{ m o}$ / kJ mol $^{-1}$ |
|---------------------|---|
| NH ₃ (g) | -46 |
| NO(g) | 90 |
| H ₂ O(l) | -285 |

A periodic table is printed on the other side of this data sheet. Atomic weights are included in the periodic table.