

## Fundamentals of Physical Chemistry

22CMA101

Semester 1 2022/23

In-Person Exam paper

This examination is to take place in-person at a central University venue under exam conditions. The standard length of time for this paper is **2 hours**.

You will not be able to leave the exam hall for the first 30 or final 15 minutes of your exam. Your invigilator will collect your exam paper when you have finished.

### Help during the exam

Invigilators are not able to answer queries about the content of your exam paper. Instead, please make a note of your query in your answer script to be considered during the marking process.

If you feel unwell, please raise your hand so that an invigilator can assist you.

You may use a calculator for this exam. It must comply with the University's Calculator Policy for In-Person exams, in particular that it must not be able to transmit or receive information (e.g. mobile devices and smart watches are **not** allowed).

Planck constant,  $h = 6.626 \times 10^{-34} \text{ J s}$

Speed of light,  $c = 2.998 \times 10^8 \text{ m s}^{-1}$

Boltzmann constant,  $k = 1.380 \times 10^{-23} \text{ J K}^{-1}$

Gas constant,  $R = 8.315 \text{ J mol}^{-1} \text{ K}^{-1}$

Avogadro's number,  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Answer **ALL** questions, show **ALL** your working.

1. Answer **ALL** parts

a. SI Units

- i. List the SI base units for length, mass, and time.

[3 marks]

- ii. Explain how the above units are combined to form the SI unit for energy (Joule).

List the different physical quantities involved

[4 marks]

b. Molar masses

- i. How many moles are there in 3.5 micrograms of nickel (molar mass: 58.69 g/mol)? How many atoms does this correspond to?

[3 marks]

- ii. What is the mass of the equivalent amount (same number of moles) of platinum (molar mass: 195.08 g/mol)?

[2 marks]

c. The orange colour of carrots derives from their  $\beta$ -carotene content.

- i. The main absorption peak of  $\beta$ -carotene is at 455 nm. Compute the associated absorption energy; give the result in J and kJ/mol.

*Note:* The equation for Planck's law is  $E=h\nu$  and the speed of light is  $c=v\lambda$ .

[3 marks]

- ii. A wavelength of 455 nm corresponds to blue light. Use this fact to explain why carrots appear orange.

[2 marks]

- iii. What molecular process is initiated when  $\beta$ -carotene absorbs the photon at 455 nm? What process would be initiated if the photon were of significantly lower wavelength (and therefore higher energy)?

[2 marks]

- iv. What would be the colour of  $\beta$ -carotene if it did not absorb visible light but only ultraviolet radiation?

[1 mark]

2. Answer **ALL** parts

For all parts of this question, you **must** show your working and explain the steps that you use. Explain yourself clearly in complete sentences. Method marks can only be given if your method is clearly written.

- a. The half-crown British coin minted between 1816-1919 is made of sterling silver. These half-crowns have a mass of 14.14 g. Sterling silver is 92.5% by weight silver and 7.5% by weight of other metals. At the time of writing, silver is worth £550 per kilogram. Calculate the value of silver contained within a half-crown coin giving your answer to 2 decimal places.
- [1 mark]

- b. Momentum is defined as the mass multiplied by velocity. What is momentum in SI base units?
- [1 mark]

- c. The gas constant in SI base units is given by:  
 $R = 8.31447 \text{ J K}^{-1} \text{ mol}^{-1}$ .
- Given that 1 Torr is defined as exactly  $1/760$  of a standard atmosphere, and that the standard atmospheric pressure is 101.325 kPa, calculate the gas constant in units of  $\text{m}^3 \text{ Torr K}^{-1} \text{ mol}^{-1}$  giving your answer to 3 significant figures.
- Hint:* Energy has the same units as pressure times volume.
- [3 marks]

- d. For the complex number  $z = 5 + 3i$ , calculate:
- i.  $z^*$
- [1 mark]
- ii.  $|z|$  to 3 decimal places
- [2 marks]
- iii.  $\frac{z^*}{z}$
- [3 marks]

Continued...

e. For the given set of simultaneous equations:

$$2y + z = 13 - 4x$$

$$2x + z = 3(3 - y)$$

$$2x + y = 5 - z$$

i. Write down and simplify the associated augmented matrix.

[1 mark]

ii. Use the **Gaussian elimination** method to reduce this matrix to **reduced row echelon form**, and hence find the values of  $x$ ,  $y$  and  $z$  that solve the set of equations above. You **must** clearly explain each step in the solution.

[5 marks]

f. A radioactive nuclide  $A$  decays into another  $B$  by some first order process  $A \rightarrow B$ .

Therefore, the rate of change of the number of nuclei is  $\frac{dN}{dt} = -N\lambda$ . Where  $\lambda$  is the decay constant. If the initial number of nuclei at  $t = 0$  is  $N_0$ , derive an expression for the number of nuclei as a function of time  $N(t)$ .

[3 marks]

3. Answer **ALL** parts

For all parts of this question, you **must** show your working and explain the steps that you use. Method marks can only be given if your method is clearly written.

a. Define and explain the following terms:

i. "Chemical Equilibrium"

[2 marks]

ii. "Enthalpy"

[1 mark]

iii. "Entropy"

[1 mark]

iv. "State function". Give an example of a state function.

[2 marks]

Continued...

b. A 3 L reaction vessel contains 0.29 moles of CO<sub>2</sub>, 0.136 moles of H<sub>2</sub>, 0.014 moles of CO and 0.014 moles of water vapour. The reaction is in equilibrium at a temperature of 298 K.

i. Write down a balanced equation for the reaction between CO<sub>2</sub> and H<sub>2</sub> to form water and CO. Hence also write down an expression for the equilibrium constant, K<sub>c</sub>.

[2 marks]

ii. Calculate the value of K<sub>c</sub> and K<sub>p</sub> giving your answers to 3 significant figures. Remember to include the units, or state clearly there are no units if this is the case. Comment on the values obtained.

[5 marks]

c. A 2 L vessel contains argon gas at a pressure of 1 bar and temperature of 298 K. This is connected to a 4 L vessel containing helium gas, also at a pressure of 1 bar and temperature of 298 K.

The valve between the vessels is opened allowing the gases to mix. Calculate the change in entropy of the mixed state compared to the initial state and comment on its sign and value. Give your answer to 3 decimal places.

[7 marks]

#### 4. Answer **ALL** parts

The reaction A→B has the following proposed rate law;  $v = -k[A]^n$ .

a. Define each component of the rate law.

[4 marks]

b. The reaction A→ B has an initial half-life of 126.9 s and 2<sup>nd</sup> half-life of 254.1 s when performed at 35 °C. What is the predicted value of n?

[4 marks]

c. Given that that [A]<sub>0</sub> was 2M what was the rate constant?

[2 marks]

Continued...

d. Assuming that  $A \rightarrow B$  is an elementary reaction how many molecules of A are involved in the transition state?

[1 mark]

e. Calculate the activation energy and pre-exponential factor ( $L \text{ mol}^{-1} \text{ s}^{-1}$ ) for this reaction if the rate constant increases to  $1.20 \times 10^{-2}$  (units withheld) at  $48^\circ\text{C}$ .

[4 marks]

f. The rate constant ( $k_r$ ) determined at  $35^\circ\text{C}$  can be expressed as the following using collision theory (where  $k$  is the Boltzmann constant,  $N_A$  is Avogadro's number, and the reduced mass ( $\mu$ ) is  $1.67 \times 10^{-27} \text{ kg}$  and the reaction cross section ( $\sigma$ ) is  $0.1 \text{ nm}^2$ ).

$$k_r = \rho\sigma \left( \frac{8kT}{\pi\mu} \right)^{1/2} N_A e^{-E_a/RT}$$

Show through appropriate working if the reaction mechanism requires any particular orientation of molecules to react?

[5 marks]

## 5. Answer **ALL** parts

a. State the basic assumptions of the kinetic molecular theory of gases.

[4 marks]

b. A 2.5 L flask at  $15^\circ\text{C}$  contains a mixture of three gases with partial pressure as shown in the table below:

| Gas          | Partial pressure (atm) |
|--------------|------------------------|
| $\text{N}_2$ | 0.32                   |
| He           | 0.15                   |
| Ne           | 0.42                   |

i. Calculate the total pressure of the mixture.

[1 mark]

ii. Calculate the volume at STP occupied by 0.05 g of He and 0.12 g of Ne if  $\text{N}_2$  is selectively removed.

Give your answer in  $\text{dm}^3$ . (1 atm = 101325 Pa)

(Relative masses: He - 4.00 g/mol, Ne - 20.18 g/mol, N - 14.01 g/mol)

[4 marks]

Continued...

- c. The enthalpy of combustion of benzoic acid is commonly used as standard for calibrating constant-volume bomb calorimeters and its value has been accurately measured to be  $-3226.7$  kJ/mol.
- i. Define the terms *calorimeter* and *heat capacity*.  
[2 marks]
  - ii. Describe the steps on how to use a bomb calorimeter.  
[3 marks]
  - iii. Write the equation, including state symbols, for the full combustion of benzoic acid,  $C_6H_5COOH$ .  
[2 marks]
  - iv. Calculate the heat capacity when  $1.9862$  g of benzoic acid is burnt in the calorimeter when the temperature rises from  $21.84$  °C to  $25.67$  °C.  
[Molar mass of hydrogen =  $1.01$  g/mol; Molar mass of carbon =  $12.01$  g/mol; Molar mass of oxygen =  $16.00$  g/mol]  
[4 marks]

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