Unit title: Physical Chemistry of Spectroscopy, Surfaces, Chemical and Phase Equilibria

Unit code:	**J/601/0364**
QCF level:	**5**
Credit value:	**15**

Aim

This unit develops an understanding of physical chemistry topics that have relevance to industrial chemistry through study of phase and chemical equilibria, spectroscopy and surface chemistry.

Unit abstract

This unit covers the kinetic theory of gases, chemical equilibrium, phase equilibria, spectroscopy, surface chemistry and colloids through a programme of related practical and assignment work.

This unit involves interpretation of phase diagrams, calculations involving chemical and phase equilibria and understanding models used to explain spectroscopy and the properties of surfaces.

Understanding equilibria is important in chemical engineering applications. Spectroscopic models are useful in explaining how matter interacts with electromagnetic radiation and the information that may be gained from spectroscopic measurement. Understanding surface chemistry is important in catalysis, the detergent industry and polymer industry.

Learning outcomes

On successful completion of this unit a learner will:

1 Be able to apply the concept of chemical equilibrium

2 Understand physical equilibria in one and two component systems

3 Understand the origins and applications of molecular spectroscopy

4 Understand properties of surface chemistry.

Unit content

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1 Be able to apply the concept of chemical equilibrium

Kinetic theory of gases: inherent assumptions; collision theory; Maxwell distribution of speeds; Boyle's Law; Charles's Law; Avogadro's Hypothesis; relationship between pressure and temperature, ideal gas constant, $pV = nRT$; real gases; deviations from ideal behaviour; other equations e.g. Van der Waals, virial

Calculations: calculations of one term in the ideal gas equation, given the other four, calculation of one variable when another is changed and the rest are held constant (e.g. $p_1V_1 = p_2V_2$)

Equilibrium constants: mole fraction; partial pressure; relationship between partial pressure, total pressure and mole fraction; K_x; K_c; K_p; interconversion of K_x, K_c, K_p; suitable examples

Problems involving chemical equilibrium: numbers of moles of substances in chemical equilibrium with each other; calculation of K_x, K_c, K_p; $\Delta G = \Delta G^\theta + RT\ln K$; $\Delta G = 0$ as a condition for chemical equilibrium; use of $\Delta G^\theta = -RT\ln K$; calculation of K_p from values of ΔH^θ and ΔS^θ; van't Hoff Isochore; $\ln K = -\Delta H^\theta/RT + \Delta S^\theta/R$; shape of plots of lnK versus 1/T; $\ln(K_2/K_1) = -(\Delta H^\theta/R)(1/T_2 - 1/T_1)$; calculation of K_p at different temperatures; interpretation of the magnitude of equilibrium constant

2 Understand physical equilibria in one and two component systems

Simple one-component systems: carbon dioxide; water; sulfur; phase boundaries; triple points; use of phase rule for prediction of the number of degrees of freedom at given points on phase diagrams; interpretation of phase diagrams

Clapeyron and Clausius-Clapeyron equations: calculations; appreciation of the importance of the sign of the change in volume and the enthalpy associated with phase changes in Clapeyron equation; applicability of Clausius-Clapeyron equation; inherent assumptions in Clausius-Clapeyron equations

Liquid-vapour equilibria: mole fraction and percentage composition; composition of liquid phase; composition of vapour phase in equilibrium with liquid phase for an ideal mixture; vapour pressure/composition diagrams and boiling point/composition diagrams for ideal binary mixtures and for binary mixtures, exhibiting positive or negative deviation from Raoult's Law; simple and fractional distillation; azeotropes; carrying out distillation of binary mixtures e.g. petroleum ether, water/methanol, water/propanone

Solid-liquid equilibria: ideal mixtures; interpretation of phase diagrams; eutectic diagram; melting point; composition of liquid and solid phases in equilibrium; carrying out practical work related to construction of a phase diagram; risk assessment of substances involved e.g. acetanilide and benzoic acid

3 Understand the origins and applications of molecular spectroscopy

Spectroscopic techniques: microwave; infrared; visible spectroscopy; wavelength wavenumber, electromagnetic spectrum, Beer-Lambert Law

Theoretical models: energy within molecules: quantised energy levels; types of energy within molecules; transitions between energy levels; rotational levels; vibrational levels; electronic levels; absorption and emission of radiation; population of energy levels

Rotational spectroscopy: rigid rotor model for diatomic molecules; moment of inertia; rotational quantum number J; statistical weight; rotational constant B; energy of levels; selection rule; differences between levels; spacing of lines; vibrational spectroscopy; simple harmonic oscillator model; vibrational energy changes; normal modes of vibration; energy of levels; selection rule; fundamental vibrational frequency; relationship of infrared spectra to structures; anharmonic oscillator model; comparison between harmonic oscillator model and anharmonic oscillator model; electronic transitions: electronic energy changes; relationship of absorption to atomic/molecular structures, chromophores; energy associated with $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ transitions; effect of solvent on ultraviolet frequencies (blue shift and red shift); effect of conjugated double bonds on wavelength; energy associated with d-d transition in transition metal complexes; Beer-Lambert Law; molar extinction coefficient

Applications: use of vibrational and electronic spectra in qualitative analysis; use of spectra in quantitative analysis; comparison of infrared spectra with different functional groups; comparison of ultraviolet spectra with different chromophores; visible spectra of aqueous solutions of Cu^{2+}, Co^{2+}, Ni^{2+}, MnO_4^-; estimation of molar extinction coefficient for visible and ultraviolet spectra

4 Understand properties of surface chemistry

Solid-gas interface: physical adsorption; chemisorption; meaning of the term 'isotherm'; derivation of the Langmuir isotherm and inherent assumptions; assumptions inherent in the BET isotherm; simple surface catalysis of gas phase reactions e.g. hydrogenation of ethene

Nature and properties of surface-active agents: surface and interfacial tensions; surface activity; surfactants (anionic, cationic, non-ionic); counterions; micelles; reverse micelles; detergency; specific uses of surfactants; change of contact angles and wetting

Charged interfaces: contact angles and wetting; description of the electric double layer; descriptive account of Helmholtz, Gouy-Chapman and Stern models of the double layer with respect to ionic distribution and electrical potential

Colloidal systems: classification; association colloids; polymer solutions; colloidal dispersions; classification of colloidal dispersions; properties of colloidal systems e.g. light scattering, turbidity; stability of colloidal dispersions; observation of properties for specific systems

Learning outcomes and assessment criteria

Learning outcomes On successful completion of this unit a learner will:	**Assessment criteria for pass** The learner can:
LO1 Be able to apply the concept of chemical equilibrium	1.1 account for the relationships between the variables in the ideal gas equation in terms of the kinetic theory of gases 1.2 calculate terms in the ideal gas equation 1.3 write expressions for calculating chemical equilibrium constants 1.4 solve problems involving chemical equilibrium
LO2 Understand physical equilibria in one and two component systems	2.1 analyse pressure/temperature phase diagrams for simple, one-component systems 2.2 perform calculations using the Clapeyron and Clausius-Clapeyron equations 2.3 explain liquid-vapour equilibria and distillation in terms of vapour pressure/composition and boiling point/composition plots for two component systems 2.4 analyse phase diagrams for solid-liquid equilibria which form a simple eutectic mixture
LO3 Understand the origins and applications of molecular spectroscopy	3.1 examine the relationship between spectroscopic techniques and electromagnetic radiation 3.2 review theoretical models used in spectroscopy 3.3 explain the applications of practical spectroscopic techniques
LO4 Understand properties of surface chemistry	4.1 explain the solid-gas interface 4.2 explain the nature and properties of surface active agents 4.3 discuss features of the solid-liquid interface 4.4 discuss the behaviour of colloidal systems

Guidance

Links

This unit has particular links with the following units within this qualification:

- *Unit reference number Y/601/0353: Physical Chemistry*
- *Unit reference number H/601/0355: Chemical Laboratory Techniques.*

Essential requirements

Delivery

Learners must be encouraged to explain relationships in terms of the kinetic theory of gases. Learners must explore the limitations of the ideal gas equation and the reasons for the correction factors introduced in the Van der Waals equation.

The relationship between concentration and pressure should be derived from the ideal gas equation. Learners must be able to write expressions for K_x, K_c and K_p and relate K_p to both K_x and K_c.

The necessary condition for equilibrium $\Delta G = 0$ must be introduced. This then leads to $\Delta G^{\theta} = -RT\ln K$. This relationship may be used for gas phase reactions to calculate K_p from values of ΔG^{θ} which may be calculated from values of ΔH^{θ} and $\Delta S^{\square}$. Learners must be able to comment on the magnitude of the equilibrium constant and where there are significant amounts of reactants and/or products in the equilibrium mixture. The van't Hoff Isochore must be introduced. Learners should be able to use graphs relating to $\ln K = -\Delta H^{\theta}/RT +$ constant and perform calculations using $\ln(K_2/K_1) = -(\Delta H^{\theta}/R)(1/T_2 - 1/T_1)$. Learners must be able to comment on the values of equilibrium constant at different temperatures.

Understanding phase equilibria is fundamental to the chemical process industry. Where possible, learners must have the opportunity to carry out practical work linked to construction of phase diagrams. Learners should explore the implications of one-component phase diagrams, the meaning of the phase boundaries and triple points. This should be related to phase rule. The structure of the Clapeyron equation should be related to the structure of one-component phase diagrams.

The relationship between velocity, wavelength, frequency, wavenumber, energy and Planck's constant must be established and the energy differences corresponding to microwave, infrared, visible and ultraviolet electromagnetic radiation calculated. Learners should become familiar with the rigid rotor model for rotation of diatomic molecules, the simple harmonic oscillator and anharmonic oscillator models for infrared and the concept of chromophores for ultraviolet/visible spectroscopy.

Tutors must introduce the importance of physical adsorption and chemisorption to catalysis. Learners must be able to describe surface catalysis. Learners should get the opportunity to observe phenomena relating to surface activity, like surface tension. The formation of micelles and its commercial significance must be explained. The nature of reverse micelles and their application in the oil industry must be explained. Tutors must introduce the three models for describing electrical double-layers on a charged surface. This should be pictorial and descriptive.

Assessment

Learners must perform straightforward calculations involving the ideal gas equation. They should incorporate simple unit conversions – for example cm^3 to m^3, ${}^0C$ to K, bar to Pa etc.

Learners must show how expressions for K_x and K_p and K_c are interrelated using algebra. They must calculate ΔG^θ from values of ΔH^θ and ΔS^θ and calculate K_p from $\Delta G^\theta = -RTlnK$. They need to plot values of lnK against values of 1/T to obtain ΔH^θ, to explain the sign of the slope of the plot in relation to the sign of ΔH^θ and to calculate as a minimum ΔH^θ values from the equation $\ln(K_2/K_1) = - (\Delta H^\theta/R)(1/T_2 - 1/T_1)$.

Learners must complete at least one straightforward calculation using the Clapeyron equation and one with the Clausius-Clapeyron equation.

Learners must provide evidence that they can use the concept of mole fractions or percentage composition. They should demonstrate that they can work out the composition of vapour in equilibrium with a liquid of given composition for an ideal mixture. Learners must relate the vapour pressure, composition plot to a plot of boiling point/mole fraction and explain the principles of simple and fractional distillation of ideal mixtures. Learners must explain the shape of vapour pressure/composition plots and boiling point/composition plots for mixtures exhibiting positive and negative deviation from Raoult's Law. They must also show that they understand the origin of maximum and minimum boiling azeotropes. Where possible, distillation processes should be related to local industrial processes.

Solid/liquid phase diagrams are relevant to chemical process in relation to crystallisation. Learners must provide evidence of carrying out some practical work on this topic to show understanding of how a phase diagram is constructed. Learners must also interpret a given phase diagram for a two component system where a simple eutectic is formed.

In assessing the relationship between spectroscopic techniques and the molecular interactions of the energy of the electromagnetic radiation for learning outcome 3, learners must show that they know the wavelength, frequency and velocity of each type of radiation and understand the nature of the transition caused by the absorption of radiation. Learners must demonstrate their understanding of the aspects of content relating to the rigid rotor model for microwave spectroscopy, simple harmonic oscillator model and anharmonic oscillator models for infrared spectroscopy. They also need to show understanding of d to d transitions in transition metal complexes and of the concept of chromophores and related $\sigma\rightarrow\sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ transitions for ultraviolet spectroscopy of organic molecules in-line with the unit content. Learners must explain how microwave spectroscopy may be used to estimate bond lengths and how qualitative and quantitative infrared and ultraviolet spectroscopy may be used. They also need to demonstrate an understanding of how a Beer-Lambert method may be developed. There should be an awareness of the magnitude of the molar extinction coefficient in relation to the types of compound involved and how that would affect the Beer-Lambert method developed.

The limitations and successes of the Langmuir isotherm and the reasons behind the development of the BET isotherm must be explained. The properties of surfactants in lowering surface tension and in cleaning must be explained, including consideration of formation of micelles and reverse micelles. The Helmholtz, Gouy-Chapman and Stern double layer models must be discussed. Learners must give examples of types of colloidal systems such as polymer solutions, association colloids and colloidal dispersions. They must discuss the properties of colloidal systems, for example light scattering and turbidity. Learners must also discuss factors which affect the properties of colloidal dispersions.

Resources

Learners will need access to appropriate laboratory facilities, technical support and to library and information technology resources.

Employer engagement and vocational contexts

Delivery of this unit will be greatly enhanced by industrial visits and talks from speakers from industry. Understanding phase equilibria is very important in relation to distillation and crystallisation.

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