THE COLLEGE OF THE BAHAMAS
SCHOOL OF NATURAL SCIENCES & ENVIRONMENTAL STUDIES
CHEMISTRY DEPARTMENT

PHYSICAL CHEMISTRY – CHEM 240

COURSE OBJECTIVES

GENERAL OBJECTIVES

To give students further exposure to some of the fundamental laws, principles, and theories of physical chemistry already encountered in College Chemistry I & II and to introduce certain new concepts.

SPECIFIC OBJECTIVES

1) THE KINETIC THEORY OF MATTER

On completing this course, students will be able to:

a) State the assumptions of the Kinetic Theory of an ideal gas.
b) State the 'fundamental equation derived from these assumptions, viz $pV = Ninc^2$.
c) Use the equation in (b) to verify the following laws:
  (i) Boyle's (ii) Charles's (iii) Dalton's (iv) Avogadro's (v) Graham's
d) Sketch the Maxwell-Boltzmann distribution curve calculated from probability & kinetic theory.
e) State and apply the equation $N = N_1e^{-E/kT}$ for numbers of particles with energy greater than a certain value.
f) Sketch and interpret Andrew's curves showing deviation of real gases from ideal behaviour, and show how they lead to the idea of the critical point.
g) Describe and explain the Joule-Thompson effect.
h) Explain qualitatively the reasons for the deviations in (g) above, and show how these reasons lead to modifications of the Ideal Gas equation.
i) State the Van der Waals equation and rationalise the form of the equation.

2) CHEMICAL ENERGETICS AND THERMODYNAMICS

On completing this course, students will be able to:

a) Define or explain the terms:
  System, surroundings, state of a system, equilibrium system, extensive property, *intensive* property, isothermal process, adiabatic process, work, work of expansion, heat capacity at constant pressure (C_p) and heat capacity at constant volume (C_v).
b) Differentiate between isolated, closed and open systems.
c) Apply the sign conventions for heat and work.
d) Differentiate between state functions and path functions.
e) Differentiate between internal energy (U) and enthalpy (H).
f) i) State the first law of thermodynamics.
  ii) Derive the expressions $\Delta H = \Delta U + p\Delta V$ and $\Delta H = \Delta U + \Delta nRT$ and apply them.
g) Differentiate between reversible and irreversible processes and recognize that spontaneous processes are irreversible, and that maximum work is obtained from a process carried out reversibly.
h) State the second and third laws of thermodynamics.
i) Relate entropy to disorder in a qualitative fashion.
j) Predict the sign of entropy changes for chemical and physical processes.
k) Calculate standard entropy changes for any reaction given a table of absolute entropies.
l) Use the relationship $G = H - TS$ to predict the direction of spontaneous change for a process.
m) Define the standard free energy of formation of a compound and calculate the standard free energy change for any chemical reaction from a table of standard free energies of formation.
n) State and apply the relationship $\Delta G° = -RT\ln K$ between the standard free energy change for a reaction and the equilibrium constant for a process at a given temperature (Van't Hoff's isotherm).
o) State the relationship between AG and cell e.m.f. for redox reactions occurring in galvanic cells ($\Delta G = -nFE$) and use the e.m.f. of cells to calculate various equilibrium constants e.g. solubility products.

p) Apply the Nernst equation.

q) Apply Van't Hoff's isochore which shows the change of equilibrium constant with temperature:

$$\ln K_1 - \ln K_2 = - (H°/R) (l/T_2 - 1/T_1)$$

r) Apply free energy changes to phase equilibrium, and apply the Clausius-Clapeyron equation:

$$l_{np2} - l_{np1} - (H/R) (1/T_2 - 1/T_1)$$

3) PHASE EQUILIBRIA

On completing this course, students will be able to:

a) Define the terms component, phase, phase boundary, as applied to chemical systems.
b) Construct phase diagrams from cooling curves.
c) Draw and interpret phase diagrams to represent conditions under Which phases exist for the following systems:
    i) individual pure substances (one component systems).
    ii) solid/solid, liquid/solid and completely miscible and completely immiscible liquid/liquid two component systems.
d) With reference to c(i) above, define the terms allotropy, enantiotropy, monotropy, transition temperature, vaporisation, condensation, melting, sublimation, metastable, supercooling, critical point and triple point.
e) With reference to two component systems define the terms eutectic point and eutectic mixture.
f) With reference to two component systems define and explain the terms ideal and non-ideal as applied to solutions.
g) Distinguish between volatile and non-volatile solutes.
h) With reference to non-volatile solutes, describe the relationship between vapour pressure and mole fraction, for an ideal solution.
i) State Reoult's Law for an ideal solution.
j) Define the term colligative property and list the colligative properties
k) Explain the elevation of boiling point and the lowering of freezing point, by a non-volatile solute, in terms of vapour pressure/temperature curves.
l) Define the terms osmosis and osmotic pressure.
m) State and apply the equation $\pi V = nRT$.
n) Describe one experimental method of calculating the molar mass of a solute from a change in a colligative property.
o) Perform calculations involving the colligative equations.
p) Apply Raoult's Law to show how the vapour pressure of a mixture of two ideal volatile miscible liquids varies with mole fraction.
q) Use (p) above to draw and interpret vapour composition and boiling point curves especially as applied to fractional distillation.
r) Draw and interpret boiling point/vapour composition curves for non-ideal systems, with specific reference to azeotropes.
s) Describe and explain the process of steam distillation and perform related calculations.
t) i) State the distribution law, and define the term distribution coefficient.
    ii) Explain with examples exceptions to the distribution law.
    iii) Explain the application of the distribution law to:
        α) solvent extraction
        β) liquid phase chromatography

4) CHEMICAL KINETICS AND CATALYSIS

On completing this course, students will be able to:

a) Derive and apply the integrated rate equation for a zero order reaction.
b) Derive and apply the integrated rate equation for a first order reaction.
c) Derive and apply the integrated rate equation for a second order reaction in the case where there is only one reactant or where the two reactants are present initially in the same concentration.

d) Derive and apply the relationships between the half-life and rate constants for zero, first, and second order (as described in c above) reactions.
e) Determine the order of a chemical reaction by:
  i) the integration method.
  ii) the half-life period method.
  iii) the isolation method.
f) Define and explain the term pseudo-first order reaction.
g) Describe various experimental methods of measuring reaction rates e.g.
  i) Prom titre values.
  ii) From polarirnetric measurements.
  iii) From gas volumes, gas pressures and the flow rates of gases.
h) i) State the Arrhenius equation in experimental and logarithmic forms, and use the logarithmic equation to determine the activation energy.
  ii) Relate the Arrhenius equation to the Maxwell-Boltzxnann distribution.
i) Define the term autocatalysis with an example.
j) Explain the term promoter.

5) THE SOLID STATE

On completing this course, students will be able to:
a) Classify solid structures as ionic, atomic/molecular, giant-molecular, or metallic.
b) Classify common ionic crystals according to the radius ratio of the tons.
c) Deduce likely physical properties associated with each type of solid structure.
d) Discuss the principles of x-ray diffraction and its use in determining crystal structure.

COURSE OUTLINE

1) THE KINETIC THEORY OF MATTER (2 weeks)

The kinetic theory as applied particularly to the ideal gas. The use of $pV = Nmc^2$ to explain Boyle's Law, Charies's Law, Graham s Law, Dalton's Law, and Avogadro s Law. The Maxwell-Boltzmann distribution as applied to molecular speeds - derivation to be illustrated. The equation: $N = N_1e^{-E/kT}$ for numbers of particles with energy greater than a certain value. The behaviour of real gases as compared with ideal gases as illustrated by Andrew's curves with mention of the critical point and the Joule-Thompson effect. A qualitative explanation of non-ideal behaviour. A qualitative treatment of the Van der Waals equation.

2) CHEMICAL ENERGETICS AND THERMODYNAMICS (4 weeks)

Definition of thermodynamic terms e.g.:

> System, isolated system, open system and closed system, surroundings, state of a system, equilibrium system, state function and path function, extensive property and intensive property, work, work of expansion, heat capacity at constant pressure (C_p), heat capacity at constant volume (C_V), isothermal process, adiabatic process. Reversible process and irreversible process. Internal energy, enthalpy, entropy.

The first law of thermodynamics. Heat of reaction and internal energy.

The second law of thermodynamics. Entropy changes for chemical reactions and phase transitt.ons. Calculation of entropy changes from tables of absolute entropies.
Gibbs free energy (G) defined as H - TS. $\Delta G' = -RT\ln K$, $\Delta G = -nFE$. The Nerust equation.
Equilibrium constants from cell potentials. Change of equilibrium constant with temperature — the Van't Hoff isochore:

$$\ln(K_2/K_1) = (-\Delta H°/R)\,(1/T_2 - 1/T_1)$$

Eilingham diagrams. The Clausius-Clapeyron equation:

$$\ln(p_2/p_1) = -\Delta H/R\,(1/T_2 - 1/T_1)$$

3) PHASE EQUILIBIA(3 weeks)

Definitions of the terms component, phase, phase boundary. Construction and interpretation of phase diagrams for one and two component systems. Allotropy, enantiotropy, monotropy, transition temperatures, metastability, supercooling, critical and triple points. Simple eutectics. Ideal and non-ideal behaviour of solutions containing either volatile or non-volatile solutes. Colligative properties, and their use for the experimental determination of molar masses. Raoult's Law and deviations from it applications thereof, and interpretation in terms of intermolecular forces. Azeotropic mixtures. Steam distillation. The Distribution Law, and its application to solvent extraction and chromatography.

4) CHEMICAL KINETICS AND CATALYSIS (2 weeks)

Derivation of integrated rate equations for zero and first order reactions, and for second order reactions in the simple case where there is only one' reactant or where the two reactants are present initially in equal concentrations. Relationship between half-life and rate constant for zero, first and second order reactions. Experimental methods for determining the order and rate constants for chemical reactions. The Arrhenius equation and the determination of the Activation energy for a reaction. The relationship between the Arrhenius equation and the Maxwell-Boltzmann distribution. Definitions of autocatalysis and promoters.

5) THE SOLID STATE (1 week)

Solid structures will be classified as ionic, atomic/molecular, giant-molecular or metallic with characteristic properties according to bond-type. Some common ionic crystals will be classified according to radius ratio. Principles of x-ray diffraction as used to determine crystal structure.

6) OPTIONAL TOPICS

These topics may or may not be mentioned briefly in the course according to the interests of the lecturer and the students, and provided that time allows.

a) The liquefaction of gases. Description of the Zartmann (rotating drum) experimental verification of the Maxwell-Boltzmann distribution curve.
b) The concepts of chemisorption and physisorption and their significance to heterogeneous catalysis. The significance of lattice defects.
c) The glass electrode and pH meters.
d) Electron and neutron diffraction, Derivation of the Bragg equation. Calculation of Avogadro's constant front the appropriate density arid unit cell measurements on a crystal.

PRACTICAL COURSE
OBJECTIVES

On completing this course, students will be able to translate the theoretical physico-chemical principles encountered in this course into practical laboratory situations.

SUGGESTED PRACTICALS

Practical exercises for Chemistry 240 will be chosen from the following list, depending on the availability of materials. At least one experiment should be selected from each section.

1) GASES

a) The behaviour of real gases: a work sheet on the deviations of gases from the equation $PV = nRT$. (Hand out prepared.)
b) The relationship between molar mass and rate of effusion. (Handout prepared.) (Gunnell & Jenkins)

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2) TIERMODYNAMICS/THERNOCHEMISTRY

(Expts. 22, 23, 24 pp 177-190, Page J. A.)

a) To find K_a for ethanoic and chlorethanoic acids.
b) To calculate the enthalpy of ionization of a weak acid.
c) To determine the entropy of ionization of ethanoic and chiorethanoic acids.
d) A thermometric titration. (Handout prepared.) (exercise 36, Clift et al.).
e) A determination of the heats of solution of ethane and 1,2 - ethanediol.
g) Determination of the solubility product of a sparingly soluble compound by cell e.m.f. measurements.
g) A determination of various heats of reaction. (Handout prepared.)
h) Entropy and spontaneous endothermic reactions. (Handout prepared.)

3) PHASE EQUILIBRIA

a) The construction of a solid/liquid phase diagram from cooling curves. (Handout prepared.)
b) A study of the relationship between hydrogen bonding and deviations from Raoult's Law for the system $CHCl_3/CH_3COOC_2H_5$. (Hand-out Prepared) (Exercise 6, Hill & Holman)
c) Determination of the triple point of iodine.

4) REACTION KINETICS

a) Determination of the energy of activation for the reaction between bromine and bromate ions. (p51, Hill & Holman).
b) Determination of the rate of racemization of sucrose hetrolarimetry.
c) A calorimetric experiment to determine the first order rate constant for the acid hydrolysis of acetyl salicylic acid.

5) MISCELLANEOUS

a) Interpretation of I.R. spectra.
b) Interpretation of U.V. spectra.
c) Construction of models of close-packed metallic structures (assuming equal radii) i.e. hexagonal close-packed, cubic close-packed/face-centered close-packed and body-entred cubic. Coordination numbers and the fraction of empty space in the structures will be deduced. The radius ratio of ions in interstitial octahedral, tetrahedral, body-centred cubic and triangular sites in ionic crystals will be calculated.

REFERENCES

a) Clift D. A. et al., Chemistry, A Structural View Laboratory ManuaL, Cambridge U. P., 3rd. ed. 1978
b) Gunnell J. & Jenkins E., Selected Experiments in "A"—level *Chemistry,* Oliver & Boyd (p19) 1975

c) Hill G. C., Holman J. S., Chemistry in Context: Laboratory Manual and Study Guide, Thomas Nelson & Sons Ltd., U. K., 1987.
d) Page J. A., Chemistry: Principles & Experiments, Holy, Rineary & Winston Inc., N.Y., (1969).

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EVALUATION

Tests, Assignments	15%
Mid-semester Examination	15%
Laboratory work	20%
Final Examination	50%

TEXTBOOK

Introduction to Physical Chemistry, Brown G. I.., Longman (1983)

READING LIST

1) *Chemistry,* Bailar J. C.et al., 3rd. ad., Harcouzt Brace, Jovanovitch (1989).
2) A—level Chemistry, Rainsden, Low Priced Ed., Stanley Thornes Ltd. England, (1989)

3) Physical Chemistry, Heys H. L., 5th ed., George G. Harp & Co. Ltd. ,(1975)

4) Physical Chemistry, Farmington R. A., Daniel's A., John Wiley & Sons, N.Y., (1978)

5) Chemistry: A Structural View, Starkness D. R. et a., 2nd ed., Cambridge U. P., (1970)