CONTENTS

PAGE

INTRODUCTION - - - - - - - - xiv

PART I.—ELEMENTARY THEORY AND ELECTROCHEMISTRY

CHAPTER

I. THE FIRST LAW OF THERMODYNAMICS - 1

The conservation of energy. Units of energy. Application of first law to material systems. Work done in expansion. Heats of reaction. Thermochemical equations. Hess's law. Heats of formation. Heat capacities. Kirchhoff's equation. Application to gases. Energy relations. Isothermal expansion. Adiabatic expansion. The Joule-Thomson effect. Examples.

II. THE SECOND LAW OF THERMODYNAMICS - 30

Spontaneous changes. The Second Law. Maximum work and chemical affinity. Three-stage isothermal dilution processes. Net work. Maximum work of changes of state. Formation of salt hydrates. Heat engines. Carnot's theorem. Maximum work function and free energy. Examples.

III. THE APPLICATION OF THERMODYNAMICS TO CHANGES OF STATE - - - - - 53

The Clausius equation. The Le Chatelier principle. Effect of temperature on vapour pressure. Changes of dissociation pressure with temperature. Examples.

IV. DILUTE SOLUTIONS - - - - - - 65

Expression of concentration. Raoult's law. Henry's law. Deductions from Henry's law. Elevation of the boiling point. Depression of the

CHAPTER PAGE

the vapour pressure. Variation of partial free energy with the composition in very dilute solutions. The activity. Activity coefficients of the alcohols in aqueous solution. Activity of a solute from the vapour pressures of the solvent. Variation of the partial free energy with temperature and pressure. Determination of the activity from freezing point of solutions. Change of activity with temperature. The osmotic pressure of solutions. Examples.

XVI. SOLUBILITY AND MOLECULAR INTERACTIONS IN SOLUTION - - -

Activity coefficients and solubility. Solubility of solids. Causes of deviations from Raoult's Law. Nature of short range forces between molecules. London's interaction energy. Hildebrand's theory of solutions. Entropy of solution. Raoult's law and molecular size. Solutions of long chain polymers. Examples.

XVII. NON-ELECTROLYTES IN WATER - - 377

Structure of liquid water. Associated liquids. The hydrogen bond. Activity coefficients in aqueous solutions. Heats and entropies of hydration. Examples.

XVIII. ACTIVITY COEFFICIENTS AND RELATED PROPERTIES OF STRONG ELECTROLYTES 398

Concentration cells without liquid junctions. Activities of strong electrolytes. Activity coefficients in dilute solutions of single salts and in mixed solutions. The Debye-Hückel calculation of the activity coefficient. Tests of the Debye-Hückel equation. Extension to concentrated solutions. Solvation of ions. Activity coefficients in mixtures of strong electrolytes. Apparent molar volumes of salts. Heats of dilution. Examples.

XIX. IONIC EQUILIBRIA IN SOLUTION AND SALTING-OUT - - - - - 447

Electrical conductivity of solutions of strong electrolytes. The Debye-Onsager theory. True dissociation constant of a weak electrolyte.

CHAPTER PAGE

Dissociation constants of weak electrolytes by electromotive force measurements. Variation of dissociation with temperature. Dissociation constant and ionic product of water. The salting-out of non-electrolytes. The Donnan Equilibrium.

XX. THE STANDARD FREE ENERGIES AND ENTROPIES OF IONS - - - - - 475

Standard free energies of ions in aqueous solutions. Standard entropies of ions in aqueous solutions. Applications. Energy of hydration of ions. Entropy of solution of simple gas ions. Standard free energies of ions in other solvents.

XXI. THE THERMODYNAMICS OF SURFACES - 503

Surface tension and surface energy. Equilibrium at curved surfaces. Gibbs's adsorption equation. Adsorption from binary solutions. Tests of Gibbs's equation. Surface of aqueous salt solutions. Adsorption from ternary solutions. Relation between Gibbs's surface excess and the surface composition. Relations between adsorption, surface tension and concentration. Standard free energies in the surface layer. Traube's rule. Equations of state for the surface layer.

APPENDIX. THE APPLICATION OF STATISTICAL MECHANICS TO THE DETERMINATION OF THERMODYNAMIC QUANTITIES by *W. J. C. Orr, Ph.D.* (Cantab.), University of Glasgow - - - - - 537

The fundamental distribution law. Identification with thermodynamic quantities. Partition functions. The Schrödinger Wave Equation. Perfect gas systems. Monatomic gases. Diatomic gases. Perfect gas mixtures. The crystalline phase. Entropy at absolute zero.

INDEX - - - - - - - - 565