# INTRODUCTION

## 1.1 SCOPE OF AQUATIC CHEMISTRY

Aquatic chemistry is concerned with the chemical reactions and processes affecting the distribution and circulation of chemical species in natural waters. The objectives include the development of a theoretical basis for the chemical behavior of ocean waters, estuaries, rivers, lakes, groundwaters, and soil water systems, as well as the description of processes involved in water technology. Aquatic chemistry draws primarily on the fundamentals of chemistry, but it is also influenced by other sciences, especially geology and biology.

A theme of this book is that fundamental principles of physical chemistry can be used to identify the pertinent variables that determine the composition of natural water systems. The student of chemistry is perhaps not fully aware that the well known laws of physical chemistry not only apply in the chemical laboratory but also regulate the course of reactions taking place in nature. During the hydrological cycle, water interacts continuously with the earth. Thus a progressive differentiation of geological material is achieved by processes of weathering, soil erosion, and soil and sediment formation. These processes accomplished by nature on a large scale have been likened (Rankama and Sahama, 1950) to the sequence of separations carried out during the course of a chemical analysis. The basic processes—dissolution and precipitation, oxidation and reduction, acid-base and complexation interactions—are the same in nature as in the laboratory. Sillén (1965) likened the evolution of the earth's atmosphere-ocean system to a set of gigantic, coupled acid-base and oxidantreductant titrations in which volatile acids from the interior of the earth were titrated by the bases of the rocks, and the reduced volatiles were titrated by the oxygen of the evolving atmosphere-biosphere system.

While this book treats several topics similar to those found in an analytical chemistry text, it endeavors to consider the spatial and temporal scales of the reactions in nature as distinctly different from those of the laboratory. For example, in chemical analysis, precipitates (frequently of metastable and active compounds) are formed from strongly oversaturated solutions, whereas in natural water systems, the solid phase is often formed under conditions of slight supersaturation; often crystal growth and aging may continue over geological time spans. Interfacial phenomena are particularly important because chemical processes of significance often occur only at phase discontinuities.

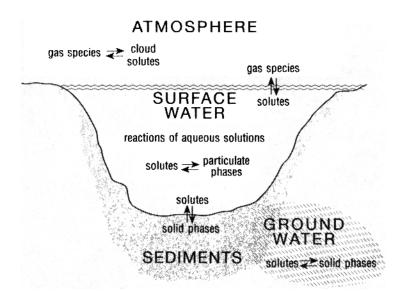


Figure 1.1. Natural water environments of interest in aquatic chemistry. Water links elemental cycles of the atmosphere with those of the sediments. Atmospheric chemistry, water chemistry, sediment geochemistry, soil chemistry, and groundwater chemistry of the elements are needed

Natural water systems typically consist of numerous mineral assemblages and often include a gas phase in addition to the aqueous phase; they almost always involve a portion of the biosphere. Hence natural aquatic habitats are characterized by a complexity seldom encountered in the laboratory. In order to select the pertinent variables out of a sometimes bewildering number of possible ones, it is advantageous to compare the real systems with their idealized counterparts. Figure 1.1 shows in a very general way the kinds of natural water environments of interest to aquatic chemistry. The cycle of water links the elemental cycles of the atmosphere with those of the sediments. Thus atmospheric chemistry, water chemistry, sediment geochemistry, soil chemistry, and groundwater chemistry of the elements are all connected, on a range of time scales. Chemical models aim to capture the most important variables of complex natural water systems.

### Models

To deal with the complexity of natural water systems we employ simplified and workable models to illustrate the principal regulatory factors that control the chemical composition of natural waters. In general, these models must link water composition with that of the atmosphere and the sediments. A model need not be completely realistic in order to be useful. A useful model leads to fruitful generalizations and valuable insight into the nature of aquatic chemical processes, and improves our ability to describe and measure natural water systems. Models are simplifications of a more complex reality. In simplifying, we try to be guided by sound chemical concepts. In accord with the aphorism of Albert Einstein: "Everything should be made as simple as possible, but not simpler."

Chemical equilibrium appears to be the most helpful model concept initially to facilitate identification of key variables relevant in determining water-mineral relations and water-atmosphere relations, thereby establishing the chemical boundaries of aquatic environments. Molar Gibbs free energies (chemical potentials) describe the thermodynamically stable state and characterize the direction and extent of processes approaching equilibrium. Discrepancies between predicted equilibrium composition and the data for the actual system provide valuable insight into those cases in which important chemical reactions have not been identified, in which non-equilibrium conditions prevail, or where analytical data for the system are not sufficiently accurate or specific. Such discrepancies are incentive for research and the improvement of existing models.

By comparing the actual composition of seawater (sediments + sea + air) with a model in which the pertinent components (minerals, volatiles) are allowed to reach true equilibrium, Sillén (1961) epitomized the application of equilibrium models for portraying the prominent features of the chemical composition of this system. His analysis indicated that, contrary to the traditional view, the pH of the ocean is not buffered primarily by the carbonate system; his results suggest that heterogeneous equilibria of silicate minerals comprise the principal pH buffer systems in oceanic waters. This approach has provided a more quantitative basis for Forchhammer's suggestion of 100 years ago that the quantity of the different elements in seawater is not proportional to the quantity of elements that river water pours into the sea but is inversely proportional to the facility with which the elements in seawater are made insoluble by general chemical actions in the sea. Although inland waters represent more transitory systems than the sea, equilibrium models are also useful here for interpreting observed facts. We can obtain some limits on the variational trends of chemical composition even in highly dynamic systems, and we can speculate on the type of dissolved species and solid phases one may expect.

Thermodynamic models of various systems within overall natural water systems are illustrated in Figure 1.2. Such models are employed in assessing global, partial, and local equilibrium conditions for water, air, and sediment interactions.

Natural waters indeed are open and dynamic systems with variable inputs and outputs of mass and energy for which the state of equilibrium is a construct. Steady-state models reflecting the time-invariant condition of a reaction system may frequently serve as an idealized counterpart of an open natural water system. The concept of free energy is not less important in dynamic systems than in equilibrium systems. The flow of energy from a higher to a lower potential or energy "drives" the hydrological and the geochemical cycles (Ma-

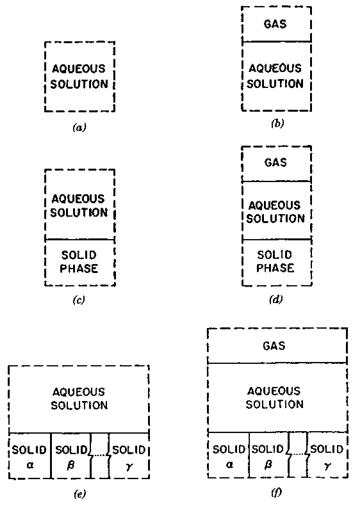


Figure 1.2. Models of various parts comprising overall natural water systems: (a) aqueous solution phase model; (b) aqueous solution and gas phase model; (c) aqueous solution and solid phase model; (d) three-phase aqueous, gas, and solid phase model; (e) aqueous solution plus several solid phases model; and (f) multiphase model for solids, aqueous solution, and a gas phase.

son, 1966; Morowitz, 1968). The ultimate source of the energy flow is the sun's radiation.

## **Ecosystems**

In natural waters, organisms and their abiotic environments are interrelated and interact with each other. Because of the continuous input of solar energy (pho-

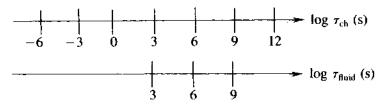
tosynthesis) necessary to maintain life, ecological systems are never in equilibrium. The ecological system, or ecosystem, may be considered a unit of the environment that contains a biological organization made up of all the organisms interacting reciprocally with the chemical and physical environment. In an ecosystem, the flow of energy and of negative entropy is reflected by the characteristic trophic structure and leads to material cycles within the system (Odum, 1969). In a balanced ecological system a steady state of production and destruction of organic material, as well as of production and consumption of O<sub>2</sub>, is maintained.

The distribution of chemical species in waters and sediments is strongly influenced by an interaction of mixing cycles and biological cycles (Buffle and DeVitre, 1994). Radioisotope measurements may often be used to establish the time scale of some of these processes. Similarly, evaluation of the fractionation of stable isotopes aids in the quantitative interpretation of biogeochemical and environmental processes and cycles.

Biogeochemical Cycles It is now widely recognized that the earth is one giant biogeochemical system (Schlesinger, 1991). Within this system the atmosphere, the waters of the earth, and the sedimentary reservoirs are linked to the activity of the biosphere. Global cycles of water, carbon, nitrogen, phosphorus, and sulfur are interconnected with one another and have now been affected to a noticeable degree by human activities. The minor element cycles, for example, those of mercury and lead, have been appreciably perturbed over time. Biogeochemical cycles work at local, regional, and global levels (Bidoglio and Stumm, 1994). The elucidation of the scale of these cycles is facilitated by the appropriate integration of stoichiometric (for complete reactions), equilibrium, steady-state, and kinetic (time-dependent) models.

### **Kinetics**

Our understanding of natural water systems has, until recently, been seriously limited by a lack of kinetic information on critical reactions in water, in sediments, and at interfaces. Earlier in atmospheric chemistry (Seinfeld, 1986) and more recently in aquatic chemistry (Brezonik, 1993), a considerable growth of information on rates and mechanisms for reactions central to environmental chemistry has taken place. As a result, we are now better able to assess the characteristic time scales of chemical reactions in the environment and compare these with, for example, residence times of water in a system of interest. Schematically, as shown here, for chemical vs. fluid time scales



we would like to distinguish between *slow* reactions and *rapid* reactions, judged against the time scale of fluid flow (e.g. in a lake, river, or groundwater). The fast reactions are well described by equilibrium models (reversible reactions) or stoichiometric models (irreversible reactions). Kinetic (i.e., time-dependent) descriptions are needed when  $\tau_{\rm ch}$  and  $\tau_{\rm fluid}$  are comparable.

## Water as a Resource and Life Preservation System

Aquatic chemistry is of practical importance because water is an essential resource for humans. We are concerned with the quality of water and its distribution, not with the quantity, because water is an abundant substance on earth. Ecosystem resilience and buffering against change notwithstanding, human activity has become so powerful as to influence global chemical cycles (Schlesinger, 1991) as well as the local and regional chemical and hydrologic cycles. Locally and regionally, groundwater quality has been impaired by release of hazardous chemicals. The restoration of these systems will require the creative integration of chemical, biological, and hydrologic understanding. In the chemical realm, progress in water quality improvement calls for a synthesis of physical, inorganic, organic, and interfacial chemistry.

Conservation of aquatic resources cannot be accomplished by avoiding human influences on the aquatic environment. Control of water pollution and protection of the water resource demand more than waste treatment technology. We need to address questions such as these: To what extent are the oceans able to absorb wastes without harmful effects? Can we improve the fertility of the oceans? How can the ecological balance between photosynthetic and respiratory activities in nutritionally enriched but polluted waters be restored? Answers to such questions call for a greatly improved understanding of the aquatic environment.

Science needs to provide the basis for human harmony with nature, not dominance. "Man masters nature not by force but by understanding" (Bronowski, 1965).

### 1.2 THE SOLVENT WATER

Water is an unusual liquid. It has a very high boiling point and high heat of vaporization; ice has a very high melting point. The maximum density of liquid water is near  $4^{\circ}$ C, not the freezing point, and water thus expands upon freezing. It has a very high surface tension. It is an excellent solvent for salts and polar molecules. It has the greatest dielectric coefficient of any liquid. These unusual properties are a consequence of the dipolar character of the  $H_2O$  molecule. Figure 1.3, from Horne (1969), depicts the electron cloud of the angular water molecule, resulting from the hybridization of s and p electrons to yield two bonding orbitals between the O and the two H atoms, and two non-bonding  $sp^3$  orbitals on the oxygen. The molecule thus has high negative charge density

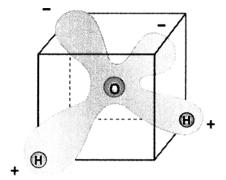


Figure 1.3. Electron cloud depiction for the H<sub>2</sub>O molecule (Horne, 1969).

near the oxygen atom and high positive charge density near the protons. It is a dipolar molecule.

Figure 1.4 (Horne, 1969) shows the measured angle of  $105^{\circ}$  between the hydrogens and the direction of the dipole moment. The measured dipole moment of water is 1.844 debye (a debye unit is  $3.336 \times 10^{-30}$  C m). The dipole moment of water is responsible for its distinctive properties in the liquid state. The O—H bond length within the H<sub>2</sub>O molecule is 0.96 Å (an angstrom unit, Å, is  $10^{-10}$  m). Dipole–dipole interaction between two water molecules forms a hydrogen bond, which is electrostatic in nature. The lower part of Figure 1.4 (not to the same scale) shows the measured H-bond distance of 2.76 Å, or 0.276 nm.

The hydrogen-bonded structure of ice is shown in Figure 1.5a (Gray, 1973), and one of the several models proposed for the structure of water in the liquid state is shown in Figure 1.5b (Nemethy and Scheraga, 1962). In the open tetrahedral ice structure, each oxygen atom is bound to four nearby oxygen atoms by H bonds. The energy of each H bond is estimated to be about 20 kJ mol<sup>-1</sup>. (For comparison, covalent bond energies are typically 20 times greater.) H bonds are of low energy, but they are numerous in ice and water.

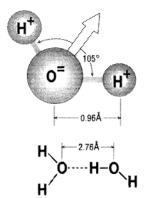


Figure 1.4. Structure of the angular water molecule and the hydrogen bond (Home, 1969).

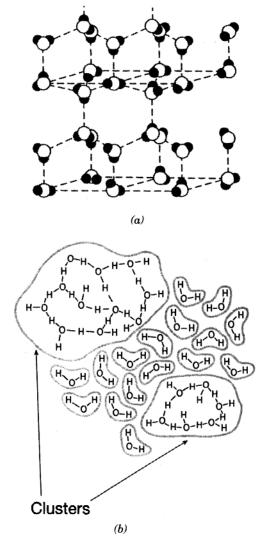


Figure 1.5. (a) Hydrogen-bonded open tetrahedral structure of ice (Gray, 1973). (b) Frank-Wen flickering cluster model of liquid water (Nemethy and Scheraga, 1962).

Upon melting, ice loses its open structure with the "melting" of some fraction of the hydrogen bonds and so the volume of the liquid water decreases, reaching a minimum at 4°C; above this temperature thermal expansion dominates the density.

In Figure 1.5b the Frank-Wen "flickering cluster" model envisions larger clusters of H-bonded water surrounded by noncluster waters, which nonetheless interact with neighbors by dipole-dipole forces. The lifetime of the clusters is estimated at around 100 picoseconds (ps), which is long with respect to the

period of a molecular vibration, approximately 0.1 ps. The persistence (or reformation) of hydrogen bonding in liquid water is a key to understanding the physical properties of water as well as its poorer solvent properties for nonpolar, hydrophobic solutes. The highly structured water linked by H bonds must be disrupted by any solute (Tanford, 1980). When the solute is ionic, the attractive interactions between ion and water molecule favor dissolution. When the solute is a nonpolar molecule, the structural cost to the hydrogen-bonded water makes dissolution an unfavorable process.

### 1.3 SOLUTE SPECIES

Dissolution of *ionic and ionizable solutes* in water is favored by ion-dipole bonds between ions and water. Figure 1.6 illustrates a hydrated sodium ion, Na<sup>+</sup>(aq), for example, from dissolution of NaCl in water, surrounded by six water molecules in octahedral positions. The energy of the ion-dipole bonds depends on the size of the ion and its charge. Higher charge and smaller ionic radii favor the bonding. Further away from the central ion, the water molecules are structured through additional dipole-dipole interactions. In a similar way, the Cl<sup>-</sup>(aq) ion interacts with the solvent water to form ion-dipole bonds, with the hydrogen side (local positive charges) of H<sub>2</sub>O pointing toward the central ion.

The dissolution of *polar molecules* in water is favored by dipole-dipole interactions. The solvation of the polar molecules stabilizes them in solution. *Nonpolar molecules* are difficultly soluble in water because of the already mentioned unfavorable energy cost of disrupting and re-forming the hydrogen-

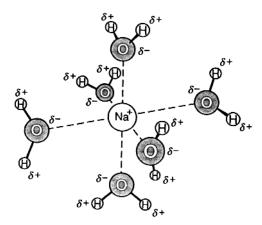


Figure 1.6. Hydrated sodium ion, Na<sup>+</sup>, in aqueous solution. H<sub>2</sub>O molecules form ion-dipole bonds to the central metal ion. The waters are in octahedral coordination to the sodium ion (Gray, 1973).

bonded water. Complicated molecules or ions with both ionic and nonpolar regions, or polar and nonpolar regions, show more complicated behavior in water (surface active species), but the stabilizing and destabilizing contributions of ion-dipole, dipole-dipole, and H-bond disrupting energies can still be recognized.

## Speciation

The particular chemical form in which an element exists in water is its speciation. For example, an element can be present as a simple hydrated ion, as a molecule, as a complex with another ion or molecule, and so forth. From what was said previously, bare ions or bare polar molecules do not exist in water. At the least, they would be solvated species. Species of an element are distinguishable from one another stoichiometrically, structurally, and energetically. In addition to aqueous species, one can distinguish elements in different phases, for example, as gaseous species, as solid phases, or in adsorbed states, and on the basis of particle sizes. In the atmosphere, for example, speciation extends over liquid, gas, and aerosol phases (Seinfeld, 1986). The notion of chemical speciation is central to equilibrium and kinetic aspects of aquatic chemistry, as will be evident throughout this book.

## Concentrations and Species of Important Elements in Water

Figure 1.7 illustrates, in the form of an abbreviated periodic table, the river water and marine water concentrations, oceanic residence times, and major

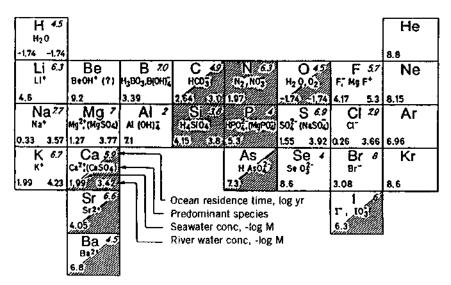


Figure 1.7. Some of the more important elements in natural waters: their concentrations, species, and residence times in river water and seawater (Sigg and Stumm, 1994). Elements whose distribution is significantly affected by biota are shaded.

species for several important elements. For example, consider sulfur: the predominant species present is sulfate,  $SO_4^{2-}$ , the river water concentration is given by log molarity = -3.92, or a sulfate concentration of  $1.2 \times 10^{-4}$  M; the total sulfate concentration in seawater is 0.028 M; and the major ion pair species of sulfate in seawater is  $NaSO_4^-$ (aq); the oceanic residence time is 8 million years. The information presented shows that the elements exist in a variety of oxidation states, protonated versus deprotonated forms, and free (aquated) versus complexed ion forms in water. As will be discussed later, the speciation of an element is influential with respect to its residence time in natural waters.

### SUGGESTED READINGS

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# APPENDIX 1.1 SOME USEFUL QUANTITIES, UNITS, CONVERSION FACTORS, CONSTANTS, AND RELATIONSHIPS

## The Earth-Hydrosphere System (Sigg and Stumm, 1994)

Earth area	$5.1 \times 10^{14} \text{ m}^2$
Ocean area	$3.6 \times 10^{14} \text{ m}^2$
Land area	$1.5 \times 10^{14} \text{ m}^2$
Atmosphere mass	$52 \times 10^{17} \text{ kg}$
Ocean mass	$13,700 \times 10^{17} \text{ kg}$
Groundwater to 750 m	$42 \times 10^{17} \text{ kg}$
Groundwater to 4000 m	$95 \times 10^{17} \text{ kg}$
Water in ice	$165 \times 10^{17} \text{ kg}$
Water in lakes and rivers	$1.3 \times 10^{17} \text{ kg}$
Water in atmosphere	$0.105 \times 10^{17} \text{ kg}$

Water in biosphere	$0.006 \times 10^{17} \text{ kg}$
Total stream discharge	$0.32 \times 10^{17} \text{ kg yr}^{-1}$
Precipitation = evaporation	$4.5 \times 10^{17} \text{ kg yr}^{-1}$

## Some Properties of Water (m kg s units)

Temperature (°C)	$k_BT/10^{-21}$	Density (ρ)	Viscosity/10 <sup>-3</sup> (η)	Surface Tension (γ)	Dielectric Coefficient $(\epsilon)$
5	3.8	999.965	1.5188	0.0749	86.04
20	4.0	998.203	1.0050	0.07275	80.36
25	4.1	997.044	0.8937	0.07197	78.54
30	4.2	995.646	0.8007	0.07118	76.75

## The International Units

Physical Quantity	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	S
Electric current	ampere	Α
Temperature	kelvin	K
Luminous intensity	candela	cd
Amount of material	mole	mol
The main derived units are:		
Force	newton	$N = kg m s^{-2}$
Energy, work, heat	joule	J = N m
Pressure	pascal	$1 Pa = N m^{-2}$
Power	watt	$W = J s^{-1}$
Electric charge	coulomb	C = A s
Electric potential	volt	$\mathbf{V} = \mathbf{W} \; \mathbf{A}^{-1}$
Electric capacitance	farad	$F = A s V^{-1}$
Electric resistance	ohm	$\Omega = V A^{-1}$
Frequency	hertz	$Hz = s^{-1}$
Conductance	siemens	$S = A V^{-1}$
Amount of photons	einstein	einstein
Dipole moment	debye	D

## **Useful Conversion Factors**

## Energy, Work, Heat

1 joule = 1 volt coulomb = 1 newton meter  
= 1 watt second = 
$$2.7778 \times 10^{-7}$$
 kilowatt hours  
=  $10^7$  erg

= 
$$9.9 \times 10^{-3}$$
 liter atmospheres  
=  $0.239$  calorie  
=  $1.0364 \times 10^{-5}$  volt faraday  
=  $6.242 \times 10^{18}$  eV  
=  $5.035 \times 10^{22}$  cm<sup>-1</sup> (wave number)  
=  $9.484 \times 10^{-4}$  BTU (British thermal unit)

### Power

1 watt = 1 kg m<sup>2</sup> s<sup>-3</sup>  
= 
$$2.39 \times 10^{-4}$$
 kcal s<sup>-1</sup> = 0.860 kcal h<sup>-1</sup>

## Entropy (S)

1 entropy unit, cal  $\text{mol}^{-1} \text{ K}^{-1} = 4.184 \text{ J mol}^{-1} \text{ K}^{-1}$ 

### Pressure

1 atm = 760 torr = 760 mm Hg  
= 
$$1.013 \times 10^5$$
 N m<sup>-2</sup> =  $1.013 \times 10^5$  Pa (pascal)  
=  $1.013$  bars

Coulombic Force Coulomb's law of electrostatic force is written, in SI units, as

$$F = \frac{q_1 q_2}{4\pi\epsilon\epsilon_0 d^2} \tag{1}$$

The charges  $q_1$  and  $q_2$  are expressed in coulombs (C), the distance d in meters (m), and the force F in newtons (N). The dielectric constant  $\epsilon$  is dimensionless. The permittivity in vacuum is  $\epsilon_0 = 8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ . Thus to calculate a coulombic energy E, we have

$$E(\text{ joules}) = \frac{q_1 q_2}{4\pi\epsilon\epsilon_0 d}$$
 (2)

## Some Important Constants

Avogadro's constant, N 6.022 ×  $10^{23}$  mol<sup>-1</sup>
Electron charge, e 1.602 ×  $10^{-19}$  C
Faraday, F 96,485 C mol<sup>-1</sup> (charge of 1 mol of electrons)
Electron mass,  $m_e$  9.109 ×  $10^{-31}$  kg
Atomic mass unit 1.66054 ×  $10^{-27}$  kg
Permittivity of vacuum,  $\epsilon_0$  8.854 ×  $10^{-12}$  J<sup>-1</sup> C<sup>2</sup> m<sup>-1</sup>
Molecular vibration period,  $\nu$  6.2 ×  $10^{-12}$  s

Earth gravitation, g Speed of light in a vacuum, c Gas constant, R

Molar volume (ideal gas, 0°C, 1 atm)

Planck constant, h

Boltzmann constant, k<sub>B</sub>

Ice point

 $9.806 \text{ m s}^{-2}$   $2.998 \times 10^8 \text{ m s}^{-1}$   $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$   $0.082057 \text{ liter atm deg}^{-1} \text{ mol}^{-1}$   $1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$  $22.414 \times 10^3 \text{ cm}^3 \text{ mol}^{-1}$ 

 $6.626 \times 10^{-34} \text{ J s}$   $1.3805 \times 10^{-23} \text{ J K}^{-1}$ 273.15 K

## **Useful Relationships**

 $\ln x = 2.303 \log x$   $RT_{298.15} \ln x = 5.71 \log x \text{ (kJ mol}^{-1})$   $RTF^{-1} = 25.69 \text{ mV at } 298.15 \text{ K}$  $\ln 10 RTF^{-1} = 59.16 \text{ mV at } 298.15 \text{ K}$ 

