

✓
PRINCIPLES OF
GENERAL PHYSIOLOGY

VOLUME ONE

The Physico-chemical Background

BY

L. E. BAYLISS

*Department of Physiology
University College, London*

LONGMANS, GREEN AND Co LTD
 6 & 7 CLIFFORD STREET, LONDON W 1
 THIBAUT HOUSE, THIBAUT SQUARE, CAPE TOWN
 605-611 LONSDALE STREET, MELBOURNE C 1
 443 LOCKHART ROAD, HONG KONG
 ACCRA, AUCKLAND, IBADAN
 KINGSTON (JAMAICA), KUALA LUMPUR
 LAHORE, NAIROBI, SALISBURY (RHODESIA)
 LONGMANS, GREEN AND Co INC
 119 WEST 40TH STREET, NEW YORK 18
 LONGMANS, GREEN AND Co
 20 CRANFIELD ROAD, TORONTO 16
 ORIENT LONGMANS PRIVATE LTD
 CALCUTTA, BOMBAY, MADRAS
 DELHI, HYDERABAD, DACCA

Fifth edition © L. E. Bayliss, 1959

PRINCIPLES OF GENERAL PHYSIOLOGY

by W. M. Bayliss, (1860-1924)

First published 1915
Second edition 1918
Third edition 1920
Fourth edition
revised by A. V. Hill and others . . . 1924
New impression 1931
Fifth edition, in two volumes
by L. E. Bayliss 1959

Printed in Great Britain
 by T. and A. CONSTABLE LTD., Hopetoun Street
 Printers to the University of Edinburgh

PREFACE

In the earlier editions of *Principles of General Physiology* there were several chapters and parts of chapters which dealt with certain aspects of physical chemistry. The inclusion of these "background" subjects in a book on physiology was defended, in the Preface to the 2nd edition, in the following passage: "A word seems requisite with regard to certain discussions contained in the earlier chapters, especially some of the questions of physical chemistry. The text-books on the subject do not always give sufficient treatment of those aspects which are of great importance in physiology. Original papers must be referred to in order to disinter some particular fact, and it seemed to me that I could save a certain amount of time and trouble for my fellow-workers. It is true that some of these matters may not seem to belong to a treatise on 'General Physiology', but I know of no more appropriate name, and as far as I can find out these parts of the book have been found useful". The emphasis given to this aspect of general physiology—more by the readers, perhaps, than by the author—gave rise at one time to the danger that "general physiology" would be regarded as the application of physical chemistry to biology, and nothing else. It is the "nothing else" to which objection must be taken: chemistry may be regarded as an application of certain aspects of atomic and molecular physics, and physics as an application of mathematics; but this does not describe the whole contents of these subjects. The study of physical chemistry should be regarded as an essential foundation on which the study of living processes is based.

In the Preface to the 2nd edition, again, a number of passages are quoted from the writings of Claude Bernard (*La Science expérimentale*), and concluded by the following words: "The only interpretation that I can put upon these passages is that the reason why we make an independent science of physiology is because the laws of physics and chemistry exert their influence in a specially complex system. At present we are unable to analyse the workings of this machine to more than a limited extent. We know, for example, that glucose supplied to a living cell is burnt up and that the energy set free is used for particular purposes; but how this happens is as yet beyond our comprehension. Nevertheless, each step in analysis results in reducing some further stage to simpler laws. When we obtain an electrical current from a fish, we make use of a more complex manner of production than that from a galvanic battery, but we are not justified in saying that the vital production of an electrical current differs in any more fundamental way from that by a galvanic battery than this

does from that by a thermopile or a dynamo-machine. From the philosophical point of view, of course, we know neither more nor less of the essential 'nature' of living processes than of those of chemical action or electricity". The developments in physiology during the past 40 years serve only to strengthen this view. There are many aspects of physical chemistry, moreover, which were not discussed in the earlier editions, but which have since become of great importance to physiology. Some, indeed, are new developments, since the 1st edition was prepared. The most obvious, perhaps, are: the whole concept of activation energy and the kinetics of chemical reaction, particularly in solution; the theory of strong electrolytes and G. N. Lewis' concept of "activity"; and the applications of the quantum theory to photochemical reactions. Although the lack of suitable text-books has now been largely remedied, it seemed to me, when undertaking the preparation of a new edition of *Principles of General Physiology* that the discussion on physico-chemical subjects should not be omitted entirely.

With all this in mind, I felt that the important principles of physical chemistry, and applications which are widespread in all branches of biology, should be brought together and put into a separate volume. This may be found convenient, indeed, by those who wish to understand the physico-chemical background before proceeding to study the principles of general physiology, treated more particularly in the second volume; and by those whose interests lie more, perhaps, in other aspects of biology. Two volumes, moreover, of moderate size, may be less formidable than a single volume whose very dimensions may be daunting. It must be confessed, however, that the dividing line between one volume and the other has been drawn somewhat arbitrarily in many places, and some duplication has been inevitable. The two parts of the book are now largely independent; but this is not alone responsible for its character not being what it was. The times, as well as the author, have changed: many of those unusual features, and what may, perhaps, be called "frills", which were responsible for so much of its personality and charm, have had regretfully to be omitted.

In the treatment adopted, the reader is assumed to have an elementary knowledge of physics, chemistry and biology. Many would say that all students of natural science should have this knowledge: it is essential that students of physiology should have it. Again, all students of science should have some familiarity with the appropriate branches of mathematics; and this, also, is assumed. In the 1st edition (p. 37) reference is made to "the view taken by some, that the introduction of mathematics into biological questions is mischievous". There cannot be many who now hold quite this view, although there may be some who doubt whether mathematics is necessary. When students of general physiology and

experimental biology are concerned directly with the applications of physico-chemical principles, the advantages of such knowledge are obvious enough: the meaning and significance of these principles cannot be fully appreciated without mathematics. But biological studies of all kinds are becoming increasingly quantitative, even when they are not obviously physico-chemical. Although "it may seem hard to add an extra burden to the already large equipment necessary for the physiological investigator", mathematical treatment of biological investigations is often valuable. As Arrhenius has pointed out, the expression of experimental results in a formula, or equation, shows their relation to known laws in a way which is otherwise very difficult or impossible to attain; one is then enabled to see, also, whether all the factors have been taken into account. "A moderate amount of mathematics will probably have to suffice for most of us, enough to be able" (and willing) "to understand and use the fundamental equations". A working knowledge of the principles and uses of the infinitesimal calculus, for example, and of simple applications of the laws of probability, is as desirable in a physiologist as it is essential in a physicist. "A word of caution may be allowed. Although an equation may express in one line what would require pages of verbal description, it must not be forgotten that it is, after all, but a kind of shorthand, and must never be permitted to serve in place of a clear conception of the process itself". (1st edition, p. 40.) The experimenter is always well advised to consider carefully the physical meaning of any equations that he may encounter—particularly those that he has developed himself.

I am grateful to the many authors and publishers who have given permission for reproduction of illustrations which are new to this edition. A great many of these, and all those which have been retained from the previous editions, have been re-drawn, so that they should illustrate more concisely the matters discussed in the text, or that the quality of reproduction should be improved and a uniform style maintained. I am indebted, also, to Dr. M. Grace Eggleton, who has not only read the proofs and made suggestions for improving obscure passages, but also prepared the index. But the most valuable of all my assistance has come, whether they knew it or not, from my colleagues and students in the course of discussion and instruction.

References to some text-books and monographs on physical chemistry, pure and applied to biological studies, the contents of which are relevant to many different chapters, are given on p. viii. Some books are suggested, also, which should be useful to those who wish to start, or continue, studies on mathematics and statistics.

L. E. BAYLISS

University College, London, 1958

GENERAL LITERATURE

- Elementary Physical Chemistry.* Lowry and Sugden (1952); Findlay (1955).
Biological Applications of Physical Chemistry. Hitchcock (1953); Bull (1951); West (1956); Wallwork (1956); Dawes (1956); Mansfield Clark (1952); Johnson, Eyring and Polissar (1954).
More Advanced Physical Chemistry. Moore (1956); Moelwyn-Hughes (1956); Guggenheim (1957); Guggenheim and Prue (1955); (and many others).
Physico-chemical Methods. Oster and Pollister (1955, 1956); Reilly and Rae (1940, 1948).
Mathematics. Fleming (1938); Mellor (1912); Kynch (1955); (*More advanced*) Jaeger (1951); (and many others).
Statistics. David (1953); Fisher (1954); (and many others).

ACKNOWLEDGEMENTS

For permission for diagrams based on copyright material we are indebted to the following:—

The Clarendon Press for Figs. 5.3, 5.4, 5.9 from Adam: *Physics and Chemistry of Surfaces*; The Faraday Society for Figs. 5.6, 5.8, 6.2 from *Transactions of the Faraday Society*; The Rockefeller Institute of Medical Research for Figs. 6.3, 7.5, 10.3 (upper), 10.8 from the *Journal of General Physiology*; the American Chemical Society for Figs. 6.5, 9.3 from the *Journal of the American Chemical Society*; the Royal Society for Fig. 6.6 from *Proceedings of the Royal Society*; the Editor for Fig. 6.10 from *Biological Bulletin*; Longmans, Green & Co. Ltd. for Figs. 7.2, 7.4 from Haldane: *Enzymes*; Cambridge University Press for Fig. 9.6 from Lea: *Radiations on Living Cells*; and Fig. 10.2 from Davson and Danielli: *Permeability of Natural Membranes*; Long Island Biological Association for Figs. 10.1, 10.7 from *Cold Spring Harbour Symposia on Quantitative Biology*; J. & A. Churchill Ltd. for Fig. 10.4 from Bayliss: *Modern Views on the Secretion of Urine*; Pergamon Press Ltd. for Figs. 10.5, 10.6 from *Progress in Biophysics and Biophysical Chemistry*; American Society of Biological Chemists Inc. for Fig. 7.3 from *Journal of Biological Chemistry*; University of Chicago Press for Fig. 9.3 from *Botanical Gazette*; American Society of Plant Physiologists for Fig. 9.3 from *Plant Physiology*; The Botanical Society of America for Fig. 9.3 from *American Journal of Botany*.

We are also indebted to The Royal Society of London for the use of an extract from an article by D. Keilin from *Proceedings of the Royal Society*, Vol. 98, series B, 1925.

CONTENTS

Chapter 1—Energy 1

THE LAWS OF THERMODYNAMICS OR ENERGETICS 3

“Free” and “Bound” Energy, 5; Thermodynamic Probability and Entropy, 6; Reversible and Irreversible Processes, 7; The Conversion of Heat into Work, 7; The Inevitable Increase of Entropy, 9; Internal Energy and Total Energy, 10

LIFE AND ENERGY 13

MOLECULAR KINETIC ENERGY AND THE GAS LAWS 16

MATHEMATICS IN PHYSIOLOGY 22

RADIANT ENERGY AND THE QUANTUM THEORY 25

Chapter 2—Chemical Reaction 28

CHEMICAL AFFINITY 29

Valency, 31; Isotopes, 42

THE KINETICS OF CHEMICAL REACTION—ACTIVATION ENERGY 44

The Frequency of Molecular Collisions, 49; The Concept of Activation Energy, 50; Sources of Activation Energy, 57

ENERGY CHANGES IN CHEMICAL REACTIONS 61

Standard Heat Contents, Free Energies and Entropies, 62; Methods of Determining Heats, Free Energies and Entropies, 67; Free Energy Changes and the Equilibrium Constant, 69; The Effect of Temperature on the Equilibrium Constant, 71; Chemical Affinity and the Velocity of Reaction, 73

Chapter 3—Solutions 76

CONCENTRATION 77

PARTIAL QUANTITIES 78

FREE ENERGY IN SOLUTIONS 79

Free Energy and Vapour Pressure, 81

ACTIVITY 83

THE MEASUREMENT OF ACTIVITY 86

The Vapour Pressure of Aqueous Solutions, 89; The Osmotic Pressure of Solutions, 92; The Depression of the Freezing Point, 99

ACTIVITY AND CHEMICAL REACTION	103
DIFFUSION	105
Activated Diffusion, 108	
TRANSIENT OSMOTIC EFFECTS	111
THE VISCOSITY OF SOLUTIONS	112
<i>Chapter 4—Electrolytes</i>	116
THE CONDUCTION OF ELECTRICITY THROUGH SOLUTIONS	118
Ionic Conductivity, 121; The Degree of Electrolytic Dissociation, 123	
STRONG ELECTROLYTES	124
The Mean Activity of a Salt, 128; The Change of Activity with Concentration, 128; The Relation between Osmotic and Activity Coefficients, 134; Solubilities and Activity Coefficients, 134; The Electrical Conductivity of Solutions of Strong Electrolytes, 135; Ion Association, 136; The Salting-out of Non-electrolytes, 138	
DIFFUSION POTENTIALS AND CONCENTRATION CELLS	138
Diffusion Potentials, 139; Concentration Cells, 143	
THE ACTIVITIES OF THE HYDROGEN AND HYDROXYL IONS	151
The Dissociation of Weak Acids and Alkalies—Buffers, 156; Water as an Electrolyte, 164; The Effect of Temperature on Hydrogen Ion Activity, 165	
AMPHOTERIC ELECTROLYTES	165
The Iso-ionic Point, 167	
<i>Chapter 5—Surface Phenomena</i>	169
SURFACE ENERGY	169
SURFACE TENSION	170
The Surfaces of Solids, 173	
THE SPREADING OF A LIQUID AT AN INTERFACE	174
MONOMOLECULAR LAYERS	177
Polymolecular layers, 181	
ADSORPTION	181
The Adsorption Isotherm, 184; The Kinetics of Adsorption, 185; Saturation, 186; Chemical and Physical Forces in Adsorption, 188; The Effect of Temperature on Adsorption, 190; The Velocity of Adsorption, 191; The Influence of Adsorption on Chemical Reaction, 192; Adsorption from Mixtures—Chromatography, 193	

ELECTRICAL PHENOMENA AT INTERFACES	195
Electrochemical Equilibria at Interfaces—the Gibbs-Donnan Relation, 201; The Electrokinetic Potential, 205; Measurement of the Electrokinetic Potential, 206; Surface Tension and Surface Charge, 214	
ADSORPTION AND THE SURFACE CHARGE	215
DYEING AND STAINING	220
<i>Chapter 6—The Colloidal State</i>	222
DIALYSIS	229
BROWNIAN MOVEMENT	230
THE CONSTITUTION OF COLLOIDAL PARTICLES	233
Giant molecules, 234; Colloidal micelles, 237	
THE STABILITY OF COLLOIDAL PARTICLES	239
The Action of Electrolytes, 240; Complex Colloidal Systems, 246;	
PROTECTIVE ACTION AND SENSITISATION	247
Monomolecular Films of Proteins, 248	
EMULSIONS	249
GELS	251
Imbibition, 255	
BOUND AND FREE WATER	257
PROTEINS	258
Denaturation, 261	
THE VISCOSITY OF COLLOIDAL SOLUTIONS	262
DETERMINATION OF THE SIZE AND SHAPE OF COLLOIDAL PARTICLES	266
Microscopic Observation, 266; The Scattering of Light, 269; Dialysis and Ultra-filtration, 270; The Osmotic Pressure of Colloidal Solutions, 272; Diffusion, Sedimentation and Viscosity, 276	
<i>Chapter 7—Catalysis</i>	285
THE FUNDAMENTAL FACTS OF CATALYSIS	287
Catalysis in Heterogeneous Systems, 290	
ENZYMES	294
The Constitution of Enzymes, 297; The Catalytic Activity of Enzymes, 301	
THE KINETICS OF ENZYME ACTION	310
The Michaelis Equation, 311; The Kinetics of Inhibition, 314; The Schütz Rule, 317; Chain Reactions, 317	

THE ACTIVATION ENERGY IN ENZYME REACTIONS	321
SPECIFICITY OF ENZYMES	324
<i>Chapter 8—Oxidation and Reduction</i>	326
OXIDATION-REDUCTION SYSTEMS	327
Oxidation-reduction Potentials, 328; Free Radicals in Oxidation-reduction Reactions—Semi-quinones, 336; Autoxidation, 339	
THE OXIDATION SYSTEMS OF THE LIVING CELL	341
Oxidases, 341; Dehydrogenases, 345; The Formation of Carbon Dioxide, 350; The Importance of Cell Structure, 351	
THE ENERGETICS OF LIVING CELLS	352
The Coupling of Chemical Reactions, 354; The Sequence of Oxidative Reactions, 361	
THE RELATION OF OXYGEN PRESSURE TO ITS CONSUMPTION	366
ANAEROBIC METABOLISM	367
<i>Chapter 9—The Actions of Light and other Radiations</i>	370
ABSORPTION OF LIGHT	371
The Mechanism of Light Absorption, 374; The Consequences of the Absorption of a Photon, 376	
GENERAL THEORY OF PHOTOCHEMICAL ACTION	381
The Quantum Yield, 383; Photosensitisation, 385; Photochemical Reactions in Solutions, 386; Relation of Velocity of Reaction to Intensity of Light, 387	
PHOTOSYNTHESIS OF CARBOHYDRATES—THE CHLOROPHYLL SYSTEM	388
The Chemical Nature of the Pigments, 389; Absorption of Light by Chlorophyll and Associated Pigments, 391; Photochemical Reactions of the Chlorophyll System, 393; The Efficiency of the Chlorophyll System, 400	
PHOTORECEPTORS AND VISION	403
PHOTOCHEMICAL ACTIONS OF ULTRA-VIOLET LIGHT	407
Photodynamic Sensitisation, 411	
THE ACTIONS OF IONISING RADIATIONS	412
<i>Chapter 10—The Passage of Substances through Membranes</i>	422
THE PROPERTIES OF MEMBRANES IN GENERAL	423
The Structure of Membranes, 423; The Permeability of a Membrane to a Given Substance, 425; Measurement of Permeability Constants, 431	

THE KINETICS OF PENETRATION THROUGH A MEMBRANE	438
Activated Penetration, 438; Facilitated Penetration, 443; The Penetration of Ions, 449	
ANOMALOUS OSMOSIS	468
ACTIVE TRANSPORT AND SECRETION	471
The Transport of Electrolytes, 475; The Transport of Water, 484; The Theoretical Work Done in Secretion and Active Transport, 489	
SOME NUMERICAL CONSTANTS	495
BIBLIOGRAPHY	497
INDEX	505

from which it falls and on the quantity of water flowing. A mere trickle, even from a considerable height, can do little work. The quantity of water is the capacity factor, and the height above sea level, or velocity is the intensity factor. In electrical energy, the intensity factor is electromotive force or potential difference, and the capacity factor is quantity of electricity or electric charge. In heat energy, the intensity factor is temperature, but the capacity factor is *not* quantity of heat, as measured in a calorimeter. This, although called "quantity" is, in fact, a measure of heat energy. Since the product of the intensity factor by the capacity factor must give the amount of heat energy, the capacity factor must be defined as the quantity of heat, divided by the temperature; this is called "entropy", and its nature and properties will be discussed later. Heat energy, as we shall see, has peculiar properties of considerable importance.

In the sources of power dealt with by the engineer, work is ordinarily done as a result of a fall in the intensity factor, without change in the capacity factor. Thus the same amount of water emerges from a hydro-electric power station as enters it, but at a smaller pressure. But work may also be performed by a system as a result of a change in the capacity factor, at a constant value of the intensity factor. This may occur, for example, in chemical reactions and at interfaces between immiscible substances.

It will be noticed that the intensity factors are what are called "strengths", whereas the capacity factors are of the nature of spaces or masses; the latter sum together when combined, the former do not. If a litre of water at 50° be added to a second litre of water at the same temperature, the energy content of the mixture will be twice that of a single litre, due to doubling the capacity factor; the intensity factor, temperature, on the other hand, is not altered. Similarly, if we have a condenser at a certain electrical potential, and connect it to another at the same potential, the total charge available will be the sum of the two separate charges, but the potential will be unaltered.

In all physico-chemical studies, and particularly in those concerned with the properties of energy, the term "system" will frequently be encountered. The word has, indeed, already been used, and could hardly be avoided without great inconvenience. According to Lewis and Randall: "Whatever part of the objective world is the subject of thermodynamic discourse is commonly called a system" (1923, p. 8). Use of the word, however, is not restricted to thermodynamics. A system is bounded by walls, or surfaces, which, however, are not necessarily physical entities, but may be mathematical abstractions; it may—and usually does—contain matter, but need not; it may be homogeneous, or it may consist of several different "phases", each of which is homogeneous and separated from one another by discontinuities; the matter within it may undergo changes of state, chemical reactions and so forth.

Any particular system which may be considered will thus have external

surroundings; it is defined as "isolated" if it cannot exchange either matter or energy with its surroundings; as "closed" if it can exchange energy, in the form of heat or work, for example, but cannot exchange matter; and as "open" if it can exchange both matter and energy. Each of the phases in a heterogeneous system may, of course, be treated as a system in itself; these may be open systems, for example, even though the whole is closed or isolated. "Classical" thermodynamics is concerned chiefly with closed systems. Open systems are rather more difficult to deal with by thermodynamical methods, but are of particular interest to the biologist, since all living organisms are essentially open systems.

THE LAWS OF THERMODYNAMICS OR ENERGETICS

There are two great laws which define quantitatively the manner in which energy may change from one form to another. The first law states that while energy may be of many kinds, kinetic, thermal, chemical, electrical and so on, which can be converted into one another, there is never any gain or loss. The first law is thus known as the "*Law of Conservation of Energy*".

The fact that energy can neither be created nor destroyed is a matter of universal experience: but it could not become so until such phenomena as light, electricity, and particularly heat, were recognised as forms of energy not essentially different from the more obvious and recognisable form, mechanical energy. The inclusion of heat is of particular importance, since in practice it is never possible to convert one form of energy into another without also generating some heat. Although Boyle and Hooke, in the latter part of the 17th century, had the idea that all forms of energy (as we now regard them) could be conceived as forms of mechanical motion, this was not generally accepted. In the 18th century, heat was regarded as an "imponderable fluid", and called "caloric"; electricity and light were other such fluids. By the close of the 18th century, however, the idea that any "fluid" could be without weight was already becoming inconsistent with experimental observation, and unattractive. The investigations of Count Rumford, moreover, at the end of the century showed that heat could be generated as a result of the performance of mechanical work (and not only, therefore, as a result of combustion processes) and that there was a quantitative relation between work and heat. It is of interest, incidentally, that Rumford's observations and measurements were made during, and as a result of, his concern with the practice of boring cannon. This quantitative relation, however, and the general conception of heat as a form of energy, was not firmly and finally estab-

lished until the work of Joule; and the idea of the conservation of energy was first expressed by him in a classical paper which appeared in 1847.

The second law of thermodynamics may be stated in several different ways; and in none of them is its meaning and significance as simple and obvious as is that of the first law. As stated in one form, the law defines limits to the extent to which a given amount of heat energy can be converted into mechanical work. As Nernst (1923) put it: "while external work and the kinetic energy of moving bodies can be transformed into one another completely and in many ways, and can also be converted into heat, as by applying the brakes to a railway train in motion, the reverse change of heat into work is only possible under certain conditions". In fact, only a fraction of the heat available in the engine of the train can ever be converted into useful work for driving it. That heat had this peculiar property was first realised by Carnot in 1824, but the second law of thermodynamics was not properly established until the latter half of the 19th century. Study of the relation between heat and mechanical work led to the development of "thermodynamics", as is implied by the meaning of the word; the work of Joule, Helmholtz, Clausius and Kelvin being of particular importance in this development. Such a study was very relevant during the 19th century, owing to the development of the steam engine and the application generally of mechanical power to industrial processes. But just as the first law applies generally to all forms of energy and not only to heat and mechanical energy, so also can the second law be expressed in a more general way. As put by Clausius, the second law states that heat will never pass spontaneously from one object or system to another which is at a higher temperature—a statement which is supported by universal experience. But it is equally a matter of common observation that water flows downhill, not uphill, for example, and that a motor-car tyre will deflate spontaneously but will never pump itself up. These, and other similar observations, suggest and illustrate a very general way of stating the second law of thermodynamics; "A system will change of itself only if it can do work in the process." As thus stated, the law not only covers the facts of common observation, but may be extended to the less obvious problems of chemical reactions, and is of great value in predicting which reactions will go spontaneously and which will not.

Since the study of thermodynamics involves all kinds of energy, and not only those implied in the strict meaning of the word, and its laws are of universal application, there is some reason, particularly when we are studying physical chemistry rather than engineering, for using the word "energetics". In the late 19th and early 20th centuries, "energetics" was commonly used in place of "thermodynamics", but it seems now to be rather out of fashion. To the biologist, the word "thermodynamics" seems particularly inappropriate. As we shall see, application of the second law

makes it quite certain that living organisms, however they may work, cannot possibly operate as heat engines.

"FREE" AND "BOUND" ENERGY

The restriction set by the second law to the fraction of the heat energy which can be converted into mechanical work, led Helmholtz, in 1882, to distinguish between "free energy" and "bound energy". Of all the energy contained in a system, that part which can be converted into other forms of energy is "free", and that part which cannot, and is thus of no practical value, is "bound". The statement of the second law, given above, can thus be put into the form: "Free energy always decreases, if it possibly can, but never increases." This fact, derived from universal experience, is sometimes known as the *Principle of Carnot and Clausius*. It does not follow, of course, that if a process results in a diminution of free energy, it will invariably occur at a measurable rate. The descent of a heavy object from the top storey of a house to the bottom is attended by a diminution of free energy, but it will not occur unless the supporting floors are removed. The reaction between hydrogen and oxygen involves a diminution of free energy, but it does not occur at room temperature to a detectable extent unless started by a spark. The second law does tell us, however, that if all constraints are removed from the heavy object, it will travel downwards, not upwards, and that no kind of "triggering" will result in a spontaneous decomposition of water into hydrogen and oxygen at room temperature.

In practice, it is impossible to convert one form of energy into another without generating heat (we shall consider this in more detail later); part, at least, of this heat will be "bound", and cannot be converted into other forms of energy. We can thus express the second law in still another form: "Bound energy always tends to increase, but can never decrease." The term "bound energy" is now little used, but the concept of "free energy", and its distinction from other kinds of energy which a system may contain, is one of considerable importance; it will be found essential in all our subsequent applications of thermodynamics, or energetics, to physico-chemical problems.

The Condition of Equilibrium. Two systems are said to be in true and complete (or "thermodynamic") equilibrium with one another when the circumstances are such that there is no net transfer of matter or energy from one to the other, in spite of the fact that there is no constraint on such a transfer. This does not mean that there is no transfer at all from one system to the other, but that the rate of transfer in one direction is identical with that in the other; in fact, the absence of constraint is shown by the existence of such a reciprocal transfer. The same definition applies, also, to the condition that a single system shall be in equilibrium with its

surroundings, and to the condition that the various constituents of a system shall be in equilibrium with one another. It is clear from what has just been said that two such systems in equilibrium with one another must possess the same amount of free energy; if they did not, there would be some change from one to the other. In these circumstances, we can make a small, or more strictly an infinitesimal, transfer of heat, for example, or of actual molecules from one of the systems to the other, without affecting the free energies, or performing any work during the transfer. This is an important generalisation, and we shall find this definition of a state of equilibrium being used repeatedly in subsequent chapters.

THERMODYNAMIC PROBABILITY AND ENTROPY

A natural, or spontaneous, change can be described as one which proceeds from a less to a more probable state. This is, to some extent, a self-evident statement, but useful deductions can be made from it, if we consider what are the properties of a state that make it more or less probable.

Suppose we had a completely empty box and inserted a single molecule into it. If we then divided the box into two equal parts, and examined one of them, the chance of finding the molecule would be one-half—i.e. if we made a very large number of such examinations, the number of occasions on which we found the molecule would be the same as the number on which we failed to find it. If we put two molecules in the box, the probability that both would be in the same part, according to the laws of chance, would be $\frac{1}{2} \times \frac{1}{2}$ or $\frac{1}{4}$; and if there were N molecules, the chance would be $(\frac{1}{2})^N$. In the circumstances dealt with in ordinary practice, therefore, where N is very large, it would be extremely improbable to find all the molecules in one half of the box; and the most probable condition is that there should be a uniform distribution throughout the box, i.e. that there should be a maximum degree of what Willard Gibbs has termed “mixed-up-ness”, but which may also be called “thermodynamic probability”. This principle is of quite general application. A system of any kind which is less “mixed-up” in one state than another is also less “probable”; it will change from the one state to the other if it is allowed to. Conversely, a system can only be brought into a more “organised” or less “mixed-up” state if work is performed on it.

Now the thermodynamic probability of a system is also a measure of its entropy content. The connection between this very general meaning of the term “entropy” and its particular meaning as a measure of the capacity factor in heat energy, is not immediately obvious. In a later section, some particular cases will be discussed in which the connection can easily be seen. For the moment, we will merely note that according to the kinetic theory of gases, to be considered later, heat is an expression of the kinetic

energy of random motion of the molecules; this motion, being random, is more probable than an ordered, or directed, motion which is capable of performing external work. If we have a system which possesses free energy, therefore, it will always tend to change, if allowed to, in such a way as to increase its randomness, with the production of heat and an increase in entropy. Once the energy is in this random, more probable, state, it will not spontaneously re-organise itself into a less probable state; the second law of thermodynamics may be stated in the form: "Entropy will never spontaneously decrease."

REVERSIBLE AND IRREVERSIBLE PROCESSES

The unrestrained flow of energy from a high potential to a low potential, is an irreversible process: the randomness, and entropy, of the system is increased, and no alteration of the conditions will reverse the flow unless an external source of energy is provided. If, on the other hand, the tendency for the system to change is always opposed to such an extent that the change is only just permitted, then a very small (infinitesimal in the limit) increase in the opposition will reverse the change. In such a reversible process (which, of course, will only proceed at an infinitesimal rate) the flow of energy is controlled and ordered, and there is no degradation into chaotic motion; entropy is not increased. It is only by the use of a reversible process, in conditions such that the system is in thermodynamic equilibrium, that the free energy of a system can be converted into work, and measured.

Lewis and Randall (1923) instance as the most nearly reversible process encountered in practice, the measurement of the E.M.F. of a battery by means of a potentiometer and sensitive galvanometer. By continually adjusting the potentiometer so that a just perceptible current flows out of the battery, it would be possible to make the battery do very nearly the theoretical maximum amount of electrical work, although it would obviously take a very long time. If the opposing potential were made too great, no current would flow from the battery and no work would be done; if there were no opposing potential at all, no useful work would be done in spite of the fact that a very large current would flow, since electrical work is measured as the product of the current and the potential difference. There would probably be a large dissipation of energy in the resistance of the connecting wires, but this would be in the form of heat, and the entropy of the system would increase.

THE CONVERSION OF HEAT INTO WORK

We are now in a position to show, simply, how our first statement of the second law of thermodynamics, which puts restrictions on the conversion of heat into work, is an inevitable consequence of the other, more general