Enzymes: Physical Principles

H. GUTFREUND

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Physical Principles

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Preface

It is customary to state in the Preface why one has written the book, why one has included or omitted some borderline aspects of the subject and for whom one has written the book. This is a good custom provided it introduces the potential reader to the author and his prejudices and helps him to use the book.

My main prejudice is that an understanding of physical principles is more important than the memorizing of facts. In my opinion the present examination system in biochemistry puts too much emphasis on the descriptive. Unfortunately, memorizing the problems which have been solved in the past does not provide a good basis for solving the problems of the future unless concepts and general principles are emphasized.

The book can be used at several levels. A student who has taken one-year university courses in Biochemistry and in Chemistry should be able to work through the whole text and understand most of it sufficiently well to gain a sound knowledge of those aspects of physical chemistry which are essential for the pursuit of modern biochemistry. Those readers who become encouraged by such a first reading to take the study of physical principles more seriously can carry on in a variety of ways. If they find serious gaps in their education in some aspects of physical chemistry, which they wish to remedy, they should study the textbooks or reviews referred to for further reading in that particular field. For those who wish to take up some special topic enough original papers are quoted to introduce them to their chosen topic.

A special word for those who are worried by the sight of a few simple mathematical equations. Equations are used as the simplest way to describe physical relations. It is not necessary to be able to manipulate differential equations or matrix algebra to understand or use 95 per cent. of the text. In most cases phenomena are explained in words as well as in equations. It seems likely to me that most students who have a minimum of mathematical training will get some satisfaction from working their way through all but a few of the derivations. They will suddenly see how simple it really is. Some readers will find the detail in the mathematical treatment patchy. This is done for a purpose; if the student fills in the easy steps he will understand the concepts described. If every simple step is written down in the book, this causes some inhibition of thought processes and is too much of an encouragement for memorizing even algebraic derivations.

The topics treated have been chosen to some extent with an eye for the future. It is difficult to predict what aspects of physical chemistry are going to be important in the future for the study of enzyme molecules. It is likely that a much wider view will be taken of the role of protein molecules as devices for control and transport in addition to their catalytic activity. More emphasis is placed on the quantitative treatment of specificity, recognition and protein assembly than has been the custom in books on enzyme mechanisms. A book which deals with all aspects of the physical chemistry of enzymes in the detail given here on ligand binding equilibria and modern kinetic analysis would fill about four volumes of the present size. Such detailed treatment is given to reaction mechanisms by Jencks (1969) and Bruice and Benkovic (1966), to the size and shape of macromolecules by Tanford (1962), to ionic interactions by Edsall and Wyman (1968) and to protein structure by Dickerson and Geis (1969). Clearly it would have been possible to include a brief discussion of the application of nuclear magnetic resonance to the study of enzyme reactions. I decided reluctantly that adequate treatment of this important subject would be beyond the scope of this book (see Hague, 1971, for references to this subject).

I hope that the present volume will fill a need. In the author's experience the subject-matter dealt with can be covered in a course of 24 lectures. Each lecturer involved in such a course will wish to emphasize different aspects of the subject with supplementary reading.

I have been very fortunate in my friends and collaborators during the last 25 years. I hope they will accept my thanks without being mentioned in a long list of names. A special vote of thanks goes to my colleagues in the Molecular Enzymology Laboratory at the University of Bristol, who have not only helped me to build up an environment which I am enjoying but who have also influenced my thoughts on many problems during almost daily arguments and joint work. Three friends and colleagues have given freely of their time by reading and criticizing the manuscript. Jeremy Knowles (Oxford), John Holbrook (Bristol) and David Trentham (Bristol) deserve much credit for a number of improvements and corrections, but they are, of course, not responsible for the inadequacies which remain. André Persoons and Karel Heremans (Leuven) have made a number of important corrections at the proof stage. For the efficient preparation of the manuscript, proof reading and the preparation of lists of references and the index I am indebted to Mrs. Janet Denton and Mrs. Mary Gutfreund.

Bristol, H. GUTFREUND
August, 1971

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CHAPTER 1

Forces and Structure in Aqueous Solutions

1.1. THE QUANTITATIVE INTERPRETATION OF PHYSICAL MEASUREMENTS

Some thought about units and dimensions, as well as numerical values for certain physical properties, is a good preparation for dealing with physical processes. During the course of this book we shall be dealing with 'fast' reactions, 'large' molecules and 'close' neighbours. We have to be numerate and define how fast is fast, how large is large, and so on. However, the most valuable attribute of the experienced research worker is not only to know how accurate his results and statements have to be, but also what approximations he can make to come to a useful decision. There is no point in a superficial discussion of scientific inference and the statistical design and interpretation of experiments. Wilson (1952) wrote an admirable book on various aspects of this problem and Moroney (1951) presents statistical methods in an entertaining form. In the type of work discussed in the present text one rarely if ever deals with a large number of observations or samples. They are usually of the order of 10 rather than 100. Under these circumstances it is unwise to use statistics as anything but a guide to further work.

The accuracy required to prove a point, decide between alternative hypotheses or detect a phenomenon determines the development of techniques. Many of the most fundamental advances in science are due to the improvement of the resolution of measurements. Generally one uses a technique which is just accurate enough to solve the problem in hand. It is of doubtful value to collect accurate information without a purpose in mind. The mere thought that someone will want the information to solve some as yet unknown problem is too random a process for the progress of science. The chances are that the information will be needed for conditions quite different from those used in the old experiment.

For experimental measurements as well as for theoretical calculations in a multi-disciplinary field such as biophysical chemistry it is particularly important to keep the problems in mind and not to let the experimental technique or the computer take one into a blind alley.

A thorough understanding of units and dimensions provides one with a tool for checking the equations set up to describe the physical behaviour of a system. Subsequent numerical calculations are, of course, entirely dependent

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on the units used. Two systems of units are in common use: the MKSA system (meters, kilograms, seconds, amperes) favoured in England and the cgs system (centimeters, grams, seconds) still favoured in the United States literature. In addition to these systems there are in use the practical units. In the areas covered in this book the most commonly used practical units are calories (to interpret heat measurements) and electronvolts (to interpret electrical measurements). It is the aim of this section to help the reader to familiarize himself with various units used rather than to preach a sermon in favour of one convention or another.

Table 1 gives the dimensions and different units for the quantities used in this book. A brief discussion of the different units used for energy measured by different techniques will be used to illustrate a number of points. Energy or work (W) can be expressed by

$$W = \int_{r_1}^{r_2} F \, \mathrm{d}r$$

which is the displacement of a particle over the distance $L = r_2 - r_1$ with the force F acting upon it. The dimensions of force are MLt^{-2}, which is derived from the definition of force in terms of the acceleration (Lt^{-2}) it produces on a unit of mass. Force in cgs units is expressed in dynes (1 dyne = g cm sec^{-2}), while in MKSA units it is expressed in newtons (1 newton = kg m sec^{-2})

$$1 \text{ newton} \equiv 10^5 \text{ dynes}$$

The dimensions of work (ML^2t^{-2}) are derived from those of force times L. In cgs units work is expressed in ergs (1 erg = g cm^2 sec^{-2}), while in MKSA units it is expressed in joules (1 joule = kg m^2 sec^{-2})

$$1 \text{ joule} \equiv 10^7 \text{ ergs}$$

As indicated above, calculations of energy changes derived from calorimetric measurements are often expressed in calories. A calorie is the amount of heat required to raise the temperature of 1 g of water by 1 degree. If a chemical reaction is carried out in a well-insulated vessel (adiabatically) the solution will warm up if the reaction involves a negative heat change (exothermic) and *vice versa*. With a small correction for the difference in specific heat between water and the solution, the heat change in calories is easily calculated from the temperature change:

$$1 \text{ calorie} \equiv 4{\cdot}186 \text{ joules}$$

The above discussion shows the relation between mechanical and thermal energy and now electrical energy will be introduced. Next to thermal measurements, electrical measurements are probably most frequently used

Table 1

Dimensions		c.g.s. units	MKSA units	Practical units
Length	L	cm	m	m$\mu = 10^{-9}$ m
Area	L^2	cm^2	m^2	A $= 10^{-8}$ cm $= 10^{-10}$ m
Volume	L^3	cm^3	m^3	
Mass	M	g	kg	
Time	t	sec	sec	
Velocity	Lt^{-1}	cm sec^{-1}	m sec^{-1}	
Acceleration	Lt^{-2}	cm sec^{-2}	m sec^{-2}	
Force	MLt^{-2}	g cm sec^{-2} (dyne)	kg m sec^{-2} (newton)	newton $= 10^5$ dyne
Work Energy	ML^2t^{-2}	g cm^2 sec^{-2} (erg)	kg m^2 sec^{-2} (joule)	calorie $= 4{\cdot}186$ joules
Power	ML^2t^{-3}	g cm^2 sec^{-3}	kg m^2 sec^{-3}	watt $=$ joules sec^{-1}
Density	ML^{-3}	g cm^{-3}	kg m^{-3}	
Pressure	$ML^{-1}t^{-2}$	g cm^{-1} sec^{-2} (dyne cm^{-2})	kg m^{-1} sec^{-2}	Atmosphere $= 10^6$ dyne cm^{-2}
Electric current		(erg cm)$^{\frac{1}{2}}$ sec^{-1}	Ampere (A)	A $=$ coulomb sec^{-1}
Electric charge		(erg cm)$^{\frac{1}{2}}$	A sec $=$ coulomb	
Electric potential		(erg cm^{-1})$^{\frac{1}{2}}$	volt $=$ joules coulomb^{-1}	
Electrical energy		erg		(e.s.u.)^2 cm^{-1}

for the study of energy changes. The electrical measurements are commonly made in terms of volts and amperes. The MKSA system has amperes as a dimension but for practical purposes the following relations should be discussed:

$$\text{amperes} = (\text{erg cm})^{-\frac{1}{2}}\,\text{sec}^{-1} = \text{coulomb sec}^{-1}$$

$$\text{volts} = \text{joules coulomb}^{-1}$$

The coulomb corresponds to $6{\cdot}28 \times 10^{18}$ charges (electrons or protons) and one mole equivalent of charges is $9{\cdot}65 \times 10^{4}$ coulombs (1 Faraday). The number of particles in a mole equivalent is Avogadro's number

$$6{\cdot}28 \times 10^{18} \times 9{\cdot}65 \times 10^{4} = 6{\cdot}03 \times 10^{23}$$

The fractional exponential in the units for amperes given above comes from the relation between charge and force:

$$F = e_1\, e_2/r^2$$ [*]

The force between two charged particles is equal to the product of the number of charges (e_1 and e_2) on each, divided by the square of the distance between them (see Section 1.4.2). If force is expressed in the units g sec^{-2} cm it can be seen from the equation for F that the product of two charges has the units g sec^{-2} cm^{3} or ergs cm. In consequence fractional exponentials occur for the units of single charges. This problem is avoided by the use of amperes in the MKSA system. The charge is defined as amp sec and consequently ampere is the rate at which current flows (coulomb sec^{-1}).

Electrical power is expressed in watts = amps × volts. Therefore,

$$1 \text{ watt} = 1 \text{ joule sec}^{-1}$$

This relation is helpful for the electrical calibration of calorimetric equipment.

A unit which is frequently used to describe such phenomena as ionization and electrode potentials is the electronvolt (eV). One electronvolt is the energy gained by a charged particle when its potential is raised by 1 volt:

$$1 \text{ eV} = 1{\cdot}59 \times 10^{-12} \text{ ergs} = 1{\cdot}59 \times 10^{-19} \text{ joules}$$

and for a mole equivalent this becomes

$$1{\cdot}59 \times 10^{-19} \times 6{\cdot}03 \times 10^{23} = 9{\cdot}65 \times 10^{4} \text{ joules} = 23 \text{ kcal/mole}$$

The interaction of electromagnetic radiation with chemical systems results in energy changes and the relation between these and thermal, electrical and chemical energies can be illustrated by a simple example. The visible range of wavelength is between 400 and 700 mμ (mμ = nm = 10^{-9} m). The energy of electromagnetic radiation expressed per quantum or photon is

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[*] This form of Coulomb's law, used throughout this book, is for cgs units. For MKSA units $F = e_1 e_2/4\pi\varepsilon_0 r^2$, where ε = coulomb²/newton × meter² and $4\pi\varepsilon_0 = c^{-2} \times 10^{7}$ (c is the speed of light).

$$E = h\upsilon = hc/\lambda$$

where h is Planck's constant ($6{\cdot}626 \times 10^{-27}$ erg sec), c is the speed of light (3×10^{10} cm sec^{-1}), υ is the frequency corresponding to the wavelength λ. The energy of one mole equivalent, $6{\cdot}03 \times 10^{23}$, of photons of wavelength 600 mμ (or 600×10^{-7} cm) is given by

$$E = \frac{6{\cdot}626 \times 10^{-27} \times 3 \times 10^{10}}{600 \times 10^{-7}} \times 6{\cdot}03 \times 10^{23}$$

$$= 2{\cdot}01 \times 10^{12} \text{ ergs} = 2{\cdot}01 \times 10^{5} \text{ joules} = 48 \text{ kcal/mole}$$

This means that the maximum energy gained by absorption of light at 600 mμ is 48 kcal/mole. Substitution of different wavelength in the above calculation shows that light of shorter wavelength can produce larger energy changes.

An understanding of all aspects of the interconversion of different forms of energy is of importance both for the design and interpretation of physical measurements and for an understanding of biological processes in molecular terms. Many interesting phenomena involve the interconversion of chemical energy into mechanical energy, in muscle, into electrical energy, in nerve, or into light in bioluminescence. Conversely, the conversion of light energy into chemical energy is the key process in photosynthesis and acts as a control in other photobiological responses.

Table 2. Useful Numbers and Conversions

N Avogadro's number / Number of molecules/mole $\}$ $6{\cdot}03 \times 10^{23}$
C Coulomb $6{\cdot}28 \times 10^{18}$ charges = $2{\cdot}998 \times 10^{9}$ electrostatic units (e.s.u.)
h Planck's constant $6{\cdot}626 \times 10^{-27}$ erg sec
k Boltzmann's constant $1{\cdot}381 \times 10^{-16}$ erg deg^{-1}
R Gas constant $1{\cdot}987$ cal deg^{-1} mole^{-1}
Electronvolt = 23×10^{3} calories/mole
Calorie = 4·186 joules
1 e.s.u. corresponds to $2{\cdot}08 \times 10^{9}$ electronic charges
1 coulomb = $6{\cdot}28 \times 10^{18}$ charges
1 Faraday = $9{\cdot}65 \times 10^{4}$ coulombs

Tables 1 and 2 provide a summary of the statements and derivations given in this section and give numerical values for the constants used throughout the text.

1.2. SOME THERMODYNAMIC DEFINITIONS

1.2.1. Intensive and Extensive Properties

In the present text the formalisms of thermodynamic principles are only briefly stated as an *aide-mémoire.* For a systematic treatment of thermodynamics one of many excellent texts should be consulted (for instance, Hill, 1966 and 1968; Kauzmann, 1967). Katchalsky and Curran (1965) provide an introduction with particular application of thermodynamics to biophysical topics. The concepts mentioned in this section will be used and explained in greater detail in further applications.

Intensive properties such as temperature or pressure are independent of the size of the system. It is common practice during an operation of changing temperature to specify constant pressure. When a quantity is a function of more than one independent variable (intensive property) it is necessary to use partial derivatives. For instance, a change in volume dV due to change in temperature dT and change in pressure dP is expressed by

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial V}{\partial P}\right)_T \mathrm{d}P$$

A useful elementary treatment of partial differential equations is given by Klotz (1964).

Heat, energy, free energy and entropy are extensive properties of a system. This means that they are dependent on the size of the system and have to be expressed as per mole or per litre, etc. The extensive properties used in the present text are:

Total Energy	E	The symbol Δ is used to indicate a difference: ΔE is the energy change during a specified operation.
Gibbs Free Energy	G	
Heat or Enthalpy	H	
Entropy	S	

The physical significance of free energy and equilibria will be discussed in detail in Sections 1.3.1 to 1.3.4. At present we need to accept the definitions that two states of a system are in equilibrium if there is no free energy change in going from one state to the other under the specified conditions, $\Delta G = 0$. *If there is a spontaneous change from one state to the other the system will go towards the state of lower free energy,* $\Delta G < 0$.

The heat change ΔH is identical with the energy change when the operation is carried out at constant volume, a condition applicable to all but exceptional examples discussed here:

$$\Delta H = \Delta E + P\Delta V$$

When the heat of a reaction is measured in a calorimeter an increase in temperature indicates $\Delta H < 0$: the process is exothermic, the heat content of the system decreases during the reaction. In connection with calculation of electrostatic energy it was shown that attractive forces decrease the energy of a system.

The relation between heat and free energy

$$\Delta G = \Delta H - T\Delta S$$

introduces the entropy function S.

1.2.2. Entropy and Organization

Discussions of entropy are often shrouded either in algebraic formalism or in philosophical mystery. This has resulted in some difficulties in the general understanding of this important concept. It is necessary that the meaning of entropy should be properly understood for the subsequent use of thermodynamic principles for the explanation of complex phenomena in macromolecular interactions. This should be possible if a brief description of the physical phenomena due to the entropy of a system is followed by some discussion of the principles involved in the calculation of entropy changes due to changes in the properties of the molecules which make up the system. This very elementary treatment will be supplemented by examples of its use as occasion demands (see also further discussion Section 5.1).

An ideal gas is defined phenomenologically as a gas which behaves according to the ideal gas law:

$$PV = nRT$$

The physical condition for a gas to behave as an ideal gas is that there is no molecular interaction (no forces between molecules) and that the gas molecules can be considered to take up a negligible part of the volume. These conditions usually apply as the pressure becomes very low. Let us consider what would happen if a certain number of gas molecules are transferred from a volume of 1 m^3 to a volume of 10 m^3 under such ideal conditions. The gas molecules will expand spontaneously to fill the larger volume. This spontaneous process will result in a decrease in free energy of the gas and because of the absence of any forces between the molecules there is no heat change: $\Delta H = 0$ and hence

$$\Delta G = -T\Delta S$$

This shows that the decrease of free energy in this idealized process is entirely due to an increase in entropy. The spontaneous process results in an increase in entropy; molecules will distribute themselves in such a way that the entropy of a system is at a maximum.

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