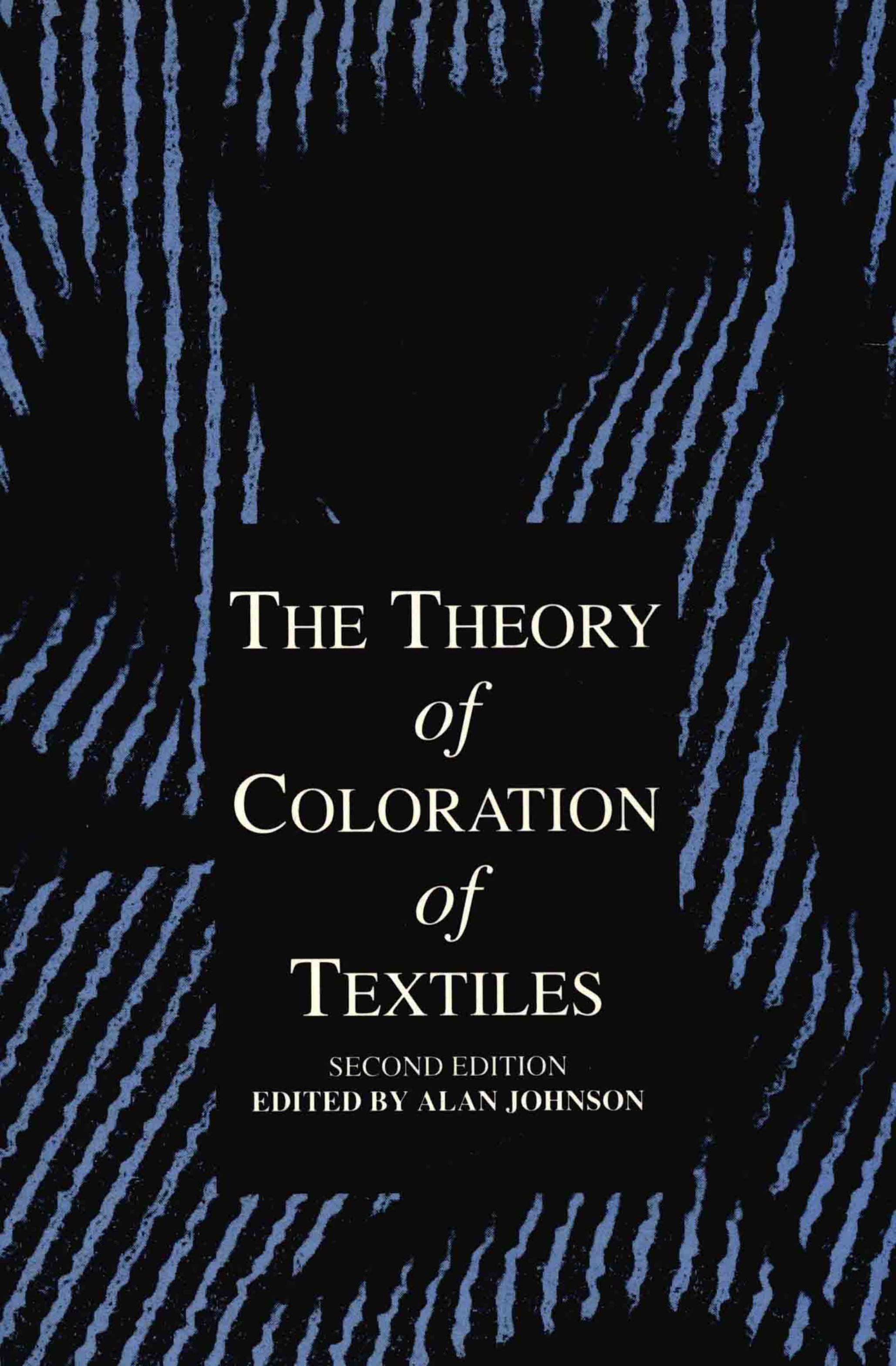

# THE THEORY *of* COLORATION *of* TEXTILES

SECOND EDITION

**EDITED BY ALAN JOHNSON**

# The theory of coloration of textiles

## *Second edition*

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Edited by Alan Johnson

**1989**

**Society of Dyers and Colourists**

**on behalf of the Dyers' Company Publications Trust**

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# The theory of coloration of textiles

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# Preface

The first edition of this book was published in 1975 as the first of a series published under the auspices of the Dyers' Company Publications Trust. From the outset it accomplished all that was expected of it and has been in constant demand, especially by students.

The decision to publish a second edition was taken some seven years ago and Mr Bird agreed once again to be the editor. Unfortunately a number of unforeseen circumstances intervened which seriously delayed publication and also led to the change in editorship. I can only hope that my efforts will bear comparison with those of my predecessors.

In planning this edition it was felt that the original chapters entitled 'Influence of fibre structure on dye uptake' and 'The response of fibres to dyeing processes' should be combined into one, and this has been undertaken and the information updated by Dr Ingamells. Other changes involve Chapter 1 on physical chemistry, which has been rewritten by Mr Burdett in place of Dr Marshall who is no longer active in the subject, and Chapter 4 on thermodynamics, where Mr Sumner agreed to contribute a chapter equivalent to that written by the late Dr Peters. The remaining chapters have been updated by their original authors.

Regretfully Professor Giles died shortly after submitting the manuscript of his chapter and before it had been edited. I have therefore carried out the minimum of alterations, leaving it as far as possible as he wrote it: this is particularly obvious in the format of the references. A further cause for regret is the untimely death of Dr Jones in November of last year, but in his case he had been able to cooperate fully in the editing of his chapter. Both of our former colleagues are greatly missed.

In this edition SI units have been used throughout but c.g.s. values are often quoted as well because these are the ones found in the original references. Modern chemical nomenclature has been used where appropriate, so that a number of familiar terms appear in new guises. The most important of these is the replacement of the term molecular weight by relative molecular mass (r.m.m).

My thanks are due to my authors, to members of the Society's staff and to Dr J Macqueen who converted my final version into a form suitable for typesetting.

ALAN JOHNSON

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# CHAPTER 1

# Physical chemistry essential to dyeing theory

**BRIAN C BURDETT**

## 1.1 INTRODUCTION

Physical chemistry is concerned with the influence of physical quantities such as temperature, pressure, concentration and electrical potential on chemical reactions and on the reactants and products of such reactions. The objective is to obtain an understanding of chemical change. Consequently a wide range of different chemical behaviour falls within the investigational methods of physical chemistry.

Initially results are obtained from experimental procedures, after which the results are placed in the form of mathematical equations known as *laws* to formulate general statements or *hypotheses*. An hypothesis attempts to interpret the experimental facts in terms of simpler or more understandable behaviour. In other words, the purpose of an hypothesis is to state the causes of the observed effects. When a particular hypothesis has withstood the test of time and other alternative hypotheses have been eliminated or proved to be unsatisfactory, we refer to it as a *theory*.

Coloration theory rests firmly on physical chemistry. Dyeing or printing of textile substrates depends on the transfer of molecular species (the majority of which are coloured) by diffusion through application media, for example dye solutions or print pastes, adsorption on molecular surfaces of substrates and final diffusion within the structures of the substrates; covalent reactions may occur during the transfer process. As a consequence the physical chemistry of coloration includes a treatment of adsorption, electrical double-layer and related interfacial behaviour, reaction kinetics and thermodynamics, all of which we shall discuss in this chapter.

Emphasis has been placed on simplicity and clarity, so that average readers can follow the presentation while those with greater ability will find that this chapter provides a useful ground work for further study.

## 1.2 THERMODYNAMICS

### 1.2.1 Introduction

Thermodynamics often seems an enigma. This need not be the case, however, if it is realised that thermodynamics is concerned with macroscopic variables such as volume, pressure, temperature and concentration and with the relationships between them. These relationships do not necessarily describe any particular kind of system – thermodynamics is of general applicability, whether for studying the formation of urea from a gaseous reaction involving carbon dioxide and ammonia, or for studying the interaction between acid dyes and wool in an aqueous environment.

It must be stressed also that thermodynamics allows us to make predictions. This is an important and valuable feature of the subject. These predictions, however, concern only the *differences* between the initial and final (or equilibrium) states of the change. Thermodynamics *cannot* predict the rate of change.

It is possible to predict recipes and the controls for a given dyeing process by calculations involving thermodynamic relationships in conjunction with colour physics. The discerning reader will appreciate that such predictions do not deal with the rate at which dye is adsorbed from solution by a substrate, but only with the end result. Relationships that describe change only are developed through thermodynamics.

In dealing with change the extent to which the change occurs must be defined. In thermodynamic terms this is equilibrium: a system is said to be *at equilibrium* when it has reached a state where no more macroscopic changes will occur.

### 1.2.2 The First Law of Thermodynamics

The First Law of Thermodynamics deals with three fundamental concepts, namely, energy, work and heat, and the relationships among them.

*Energy*

Thermodynamics is concerned with *internal energy* $U$, that is energy acquired by means of the mass and motion of molecules, intermolecular forces and chemical composition. But thermodynamics is aimed at the *change in energy* rather than absolute values. Thus if $\Delta U$ represents the change in the total internal energy then

$$\Delta U = U_2 - U_1 \tag{1.1}$$

where $U_2$ is the final value and $U_1$ the initial value of the internal energy of the system. The significant features of this relationship are that the energy

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change depends only on the initial and final states, and is independent of the path between them (Figure 1.1).

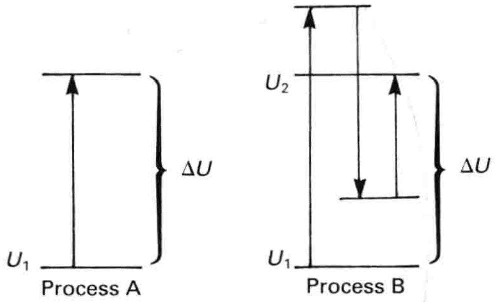

*Figure 1.1 – Two paths between initial ($U_1$) and final ($U_2$) states that have the same $\Delta U$ value irrespective of intermediate stages (reproduced by permission of Prentice Hall Inc., Eaglewood Cliffs, New Jersey, from 'Introductory physical chemistry', by A R Knight, © 1970, p. 5)*

It is convenient to classify all energy leaving or entering a system as either work or heat.

### *Work*

Work $w$ may be defined as the energy *lost* from the system other than by heat transfer. For example, when a gas is formed in a chemical reaction, work is done by the system in pushing back the surrounding atmosphere. Note that *work is done by the system* and, conventionally, it is a *positive* quantity. This type of work is known as pressure–volume or $PV$ work, and the formation of a gaseous product results in an increased volume. If the volume change is represented by $\Delta V$, then the work done is given by

$$w = P\,\Delta V \tag{1.2}$$

where $P$ represents the *constant external* pressure.

For a general situation, Eqn 1.2 would be written as

$$w = \int_{V_1}^{V_2} P\,\mathrm{d}V \tag{1.3}$$

where $P\,\mathrm{d}V$ is the product of external pressure and an infinitesimal volume change at that pressure, and

$\int_{v_1}^{v_2}$ is the sum of all the $P\,\mathrm{d}V$ terms between the limits of $V_1$ and $V_2$.

If $P$ remains constant, then Eqn 1.3 becomes

$$w = P\int_{V_1}^{V_2} \mathrm{d}V = P\,\Delta V \qquad \text{(constant pressure)} \tag{1.4}$$

which is identical to Eqn 1.2. No $PV$ work will ever be done if the volume does not change.

*Heat*

Heat $q$ may be defined as a change in energy shown by a change in the temperature of the system or its surroundings. Thus it is possible to estimate the heat absorbed by a system from a knowledge of the change in absolute temperature $\Delta T$, such that

$$q = C\,\Delta T \tag{1.5}$$

The additional factor $C$ is the heat capacity of the system. Conventionally, $q$ is *positive* when *heat is absorbed by a system*. In Eqn 1.5 $q$ is expressed in joules (J) and $C$ in joules per kelvin (J $K^{-1}$).

*The First Law*

The First Law of Thermodynamics expresses the relationship between the energy change in going from one state to another state and the two mechanisms by which this energy can be changed, i.e. heat and work. The law is sometimes known as the *Law of Conservation of Energy* and states that energy cannot be created or destroyed. Thus whenever energy of one kind is converted into energy of another kind, there exists a definite quantitative relationship between them, which is

$$\Delta U = q - w \tag{1.6}$$

This relationship expresses the statement that the net change in energy is the difference between heat gained and work lost. Note that Eqn 1.6 also states that energy, heat and work all have the same units, i.e. joules (J).

### 1.2.3 Applications of the First Law

In any process there are certain parameters that can be allowed to vary or that can be maintained constant. For example, if a chemical reaction is carried out in a sealed vessel, then the volume of the system will remain constant. Most chemical reactions are not carried out under constant volume, however, but at constant pressure in a reaction vessel open to atmospheric pressure. We shall consider each of these two situations.

*Constant-volume processes*

If a reaction is carried out at constant volume then $\mathrm{d}V = \Delta V = 0$ and, according to Eqn 1.2, $w = 0$. Hence, from Eqn 1.6,

$$\Delta U = q_v \qquad (1.7)$$

where $q_v$ is the heat absorbed at constant volume (a subscript indicates that the property indicated by the subscript is constant). The heat absorbed is, therefore, equal to the increase in the energy of the system in a reaction, and this energy change is a characteristic of the reaction under *any* conditions; the use of constant-volume conditions is a convenient way to determine the numerical value of $\Delta U$. Further, $\Delta U$ may be regarded as the *heat of reaction at constant volume.*

*Constant-pressure processes and enthalpy*

For processes carried out at constant pressure it is convenient to define a new thermodynamic quantity which involves pressure and volume. This quantity is *enthalpy* or *heat content* $H$ and it is defined by the equation

$$H = U + PV \qquad (1.8)$$

The *change in enthalpy* is of more interest than the absolute value, however. Consequently a more suitable equation is as follows:

$$\Delta H = \Delta U + \Delta(PV) \qquad (1.9)$$

For a constant-pressure process, Eqn 1.9 becomes

$$\Delta H = \Delta U + P\,\Delta V \qquad (P \text{ constant}) \qquad (1.10)$$

If only $PV$ work is possible and at constant $P$

$$w = P\,\Delta V$$

(Eqn 1.4) which, with Eqn 1.6, gives

$$\Delta U = q_p - P\,\Delta V \qquad (1.11)$$

Combining Eqn 1.11 with Eqn 1.10 gives

$$\Delta H = q_p \qquad (1.12)$$

The expression indicates that $\Delta H$ is a measure of the heat absorbed in a constant-pressure process. This is a *positive* quantity of heat and for a chemical process we would have an *endothermic reaction*. When heat is liberated, we would have an *exothermic reaction* with a *negative* value for $\Delta H$. In this context, $\Delta H$ is known as the *heat of reaction* (at constant pressure).

Note here the similarities with $\Delta U$. As with $\Delta U$, $\Delta H$ is the enthalpy change for *any* process, not just those at constant pressure. Any change from initial to final states will be associated with a $\Delta H$ value.

An interesting feature of $\Delta H$ refers to reactions involving liquids and solids only. If the pressure remains constant, the difference between the energy change and the enthalpy change depends on $P\ \Delta V$ (Eqn 1.10). For up to moderate pressures, if a reaction involves *only* liquids or solids, the volume change will be very small (if the temperature remains constant) so that $P\ \Delta V$ will be insignificant. Thus Eqn 1.10 reduces to

$$\Delta H = \Delta U \qquad \text{(liquids and solids only)} \tag{1.13}$$

i.e. changes in enthalpy equal changes in internal energy.

*Reversible (ideal) and natural (real) processes*

A careful distinction is made in thermodynamics between various kinds of process, and the most significant is that of describing a process as *reversible*. In such a process the change from initial to final state takes place by a series of infinitesimal steps. A truly reversible process would take an infinitely long time to carry out; consequently, it is an idealised process to which we can compare real processes that occur in nature. A natural or irreversible process is one that takes place by finite steps.

If we consider a gas at pressure $p$ expanding against an external pressure $P$, then the process of expansion will be reversible if

$$p = P + \mathrm{d}p \tag{1.14}$$

At each value of $P$ the system will be in equilibrium, since there is only an infinitely small difference between opposing and driving forces, i.e. internal and external pressures. If d$p$ in Eqn 1.14 becomes finite, the system is no longer in equilibrium and the process is thermodynamically *irreversible*. For our expanding gas the irreversible process is represented by

$$p = P + \Delta p \tag{1.15}$$

Although it is possible to classify thermodynamic processes as reversible or irreversible, other classifications are possible on the basis of maintaining one or other parameter constant. Thus we may have the following:

| | |
|---|---|
| isothermal processes | processes at constant temperature |
| isobaric processes | processes at constant pressure |
| isometric processes | processes at constant volume |
| adiabatic processes | processes in which no heat enters or leaves the system. |

*Isothermal expansion*

When a gas expands at constant temperature, the process is said to be isothermal. For an ideal gas, where the internal energy $U$ is dependent solely on the absolute temperature, $\Delta U = 0$. Substituting for $w$ from Eqn 1.3, The First Law (Eqn 1.6) becomes

$$\Delta U = q - w = q - \int_{V_1}^{V_2} P \, \mathrm{d}V = 0 \qquad (1.16)$$

If the expansion is reversible (Eqn 1.14), then the ideal gas law will apply. So, for one mole of ideal gas, $p = RT/V$ and, substituting into Eqn 1.16,

$$q = w = \int_{V_1}^{V_2} P \, \mathrm{d}V = \int_{V_1}^{V_2} p \, \mathrm{d}V = \int_{V_1}^{V_2} RT \, \mathrm{d}V/V \qquad (1.17)$$

Since $RT$ is a constant, then integrating Eqn 1.17 gives

$$q_{\mathrm{rev}} = w_{\mathrm{T}} = RT \ln (V_2/V_1) \qquad (1.18)$$

or, if initial and final pressures are more convenient, then using Boyle's Law

$$P_1 V_1 = P_2 V_2 \qquad (T \text{ constant}) \qquad (1.19)$$

Eqn 1.18 becomes

$$q_{\mathrm{rev}} = w_{\mathrm{T}} = RT \ln (P_1/P_2) \qquad (1.20)$$

*Vaporisation and sublimation*

During vaporisation or sublimation of a pure substance a phase change takes place at constant temperature. If the external pressure is constant and equal to the vapour pressure at that temperature, there will be true equilibrium between the condensed phase and the vapour, and a reversible process will occur. As heat is added to the system to maintain constant temperature, more vaporisation takes place. The temperature will increase only after all the condensed phase has vaporised or sublimed.

If $P$ is the vapour pressure of the condensed phase at a particular temperature and $\Delta V$ is the change in volume per mole as the substance vaporises, then, using Eqn 1.10, we have

$$\Delta H_{\mathrm{vap}} = \Delta U_{\mathrm{vap}} + P\,\Delta V \tag{1.21}$$

For sublimation, $\Delta H_{\mathrm{sub}}$ and $\Delta U_{\mathrm{sub}}$ replace $\Delta H_{\mathrm{vap}}$ and $\Delta U_{\mathrm{vap}}$ in Eqn 1.21.

For vaporisation, the First Law (Eqn 1.6) becomes

$$\Delta U_{\mathrm{vap}} = q_{\mathrm{vap}} - w = q_{\mathrm{vap}} - P\,\Delta V \tag{1.22}$$

which, when combined with Eqn 1.21, gives

$$\Delta H_{\mathrm{vap}} = q_{\mathrm{vap}} \tag{1.23}$$

This relationship provides a definition of the heat of vaporisation $\Delta H_{\mathrm{vap}}$, as the heat absorbed when one mole of liquid phase is converted to the vapour phase at constant pressure. A similar definition applies for the heat of sublimation of a solid to a vapour, $\Delta H_{\mathrm{sub}}$.

### 1.2.4 Thermochemistry

Thermochemistry is that part of thermodynamics that deals with heat and energy changes in chemical processes. Different substances have different amounts of internal (chemical) energy, so that the total energy of the products of a chemical reaction is usually different from that of the reactants. Consequently, chemical change is accompanied by the liberation or absorption of energy which may appear in the form of heat. Thus we have the equations

$$\Delta U = \Sigma U(\text{products}) - \Sigma U(\text{reactants}) \tag{1.24}$$

$$\Delta H = \Sigma H(\text{products}) - \Sigma H(\text{reactants}) \tag{1.25}$$

for the net changes in energy and enthalpy, respectively. If heat is liberated during the reaction, the process is *exothermic* (negative value for $\Delta H$), but if heat is absorbed it is *endothermic* (positive value for $\Delta H$). The quantity $\Delta H$, expressed by Eqn 1.25, is the enthalpy change or heat of reaction, and this equation forms the basis of thermochemistry.

*Thermochemistry equations and Hess's Law*

The changes that can take place in a chemical reaction can be represented

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