Pressure Effects on the Kinetics of Reactions in Aqueous Solution

by

David T. Y. Chen

A Thesis

Submitted in Partial Fulfillment of

the Requirements for the

Degree of

Master of Science

University of Ottawa

April, 1958

K.J. Laidler,
Professor of Chemistry
Research Supervisor.

David Chen,
Candidate.

PREFACE

The work described in the present thesis has been done with the object of gaining further knowledge of the influence of high pressures on the rates of chemical reactions in solution. The reactions studied in the present investigation were all carried out in aqueous solution, and fall into two main classes. One group comprises the hydrolysis in alkaline solution of esters and amides, the other the alkaline fading of certain organic dyes.

Following an introductory section (chapter I), the thesis is divided into two main parts, the first (chapter II) dealing with the hydrolysis of esters and amides, and the second (chapter III) with the alkaline fading of dyes. At the end of each part there is a discussion of the significance of the experimental results obtained, and a final chapter (chapter IV) briefly shows overall significance of the work carried out.

Acknowledgement

The writer is very much indebted to Professor Keith J.Laidler for his kind direction and help.

The work was supported by a grant from the National Research Council of Canada, to whom grateful acknowledgement is made. Thanks are also due to Mr. E.W. Greenwood and other members of the staff of the Canadian Armaments Research and Development Establishment for the design and construction of the high pressure reaction vessel.

Contents

Preface		2
List of Tables		4
List of Figures		5
Abstract		7
Chap. I -	General Introduction	8
	Historical Review of Pressure Effects on Reaction Rates	8
	Theories of Pressure Effects on Reaction Rates	10
	Theories of Volumes of Activation	15
Chap. II -	The Alkaline Hydrolysis of Esters and Amides	19
	Introduction	19
	Experimental Procedure	21
	Results	25
	Discussion	33
Chap. III -	The Alkaline Fading of Organic Dyes	37
	Introduction	37
	Experimental Procedure	40
	Results	46
	Discussion	61
Chap. IV -	General Discussion	66
Claims to Original Research		69
References		71

List of Tables

		Page
Table 1.	Rate constants for the alkaline hydrolysis of methyl and ethyl acetates at different temperatures.	29
Table 2.	Rate constants for the alkaline hydrolysis of methyl and ethyl acetates at different pressures.	30
Table 3.	Rate constants for the alkaline hydrolysis of acetamide and propionamide at different pressures.	31
Table 4.	Summary of results of alkaline hydrolysis of esters and amides.	34
Table 5.	Summary of results for the alkaline fading of brom phenol blue.	49
Table 6.	Rates and equilibrium constants for the fading of phenol phthalein at various temperatures.	53
Table 7.	Rate and equilibrium constants for the fading of phenol phthalein at various pressures.	58
Table 8.	Summary of results for the alkaline fading of crystal violet.	59
Table 9.	Summary of results for the alkaline fading of dyes.	65
Table 10.	Summary of data for reactions in aqueous solution.	68

List of Figures.

		Page
Figure 1	Schematic drawing of the high-pressure reaction vessel.	23
Figure 2	Arrhenius plots for the alkaline hydrolyses of methyl and ethyl acetates.	27
Figure 3	Van 't Hoff plots for the alkaline hydrolyses of the esters and amides.	28
Figure 4	Arrhenius plots for the alkaline hydrolyses of acetamide and propionamide; the open circles are the results of Willems and Bruylants, the closed circles those of the present work.	33
Figure 5	Plots of log (a-x) against time for the fading of brom phenol blue at various pressures.	47
Figure 6	Plots of log (k/k_o) against pressure.	48
Figure 7	Plots of log ($L-L_e$) against the time, for phenol phthalein at four temperatures; L is the photometric density at time t, and L_e that at equilibrium.	51
Figure 8	Plot of the logarithm of the equilibrium constant against 1/T, for phenol phthalein.	52

Page

Figure 9 Plot of log k_1 against 1/T, for phenol phthalein. 55

Figure 10 Plot of log k_{-1} against 1/T, for phenol phthalein. 56

Figure 11 Plot of log K against the pressure, for phenol phthalein. 57

Figure 12 Plot of the volumes of activation against the entropies of activation, for the reactions studied in the present work and for five additional reactions in aqueous solution. 67

ABSTRACT.

The rates of the alkaline hydrolysis of some esters and amides, and of the alkaline fading of certain organic dyes, have been studied over a range of hydrostatic pressures from atmospheric pressure to 16,000 pounds per square inch.

In the case of the ester and amide hydrolyses the results obey van 't Hoff's law, the logarithm of the rate constant varying linearly with the pressure. From the slopes of the lines values of ΔV^{*}, the volume of activation, were calculated; they fell in the range of -10 to -17 cc. per mole. These negative volumes of activation are to be correlated with the negative entropies of activation for the reactions. It is suggested that the results may be explained in terms of the hypothesis that the activated complex is much more polar than the reactants.

In the case of the alkaline fading of dyes the results were somewhat more complicated, the van 't Hoff law not always being obeyed. In the case of crystal violet the rate was found to be independent of the pressure. With brom phenol blue and phenol phthalein the rates were markedly increased by pressure, so that the volumes of activation are negative. These negative volumes of activation are found to be correlated with the entropies of activation for the reactions. An explanation for the results is given in terms of the changes in polarity during the course of the reactions.

Chapter I

General Introduction

HISTORICAL REVIEW OF PRESSURE EFFECTS ON REACTION RATES

The history of high pressure chemical research dates back to the nineteenth century. The earliest application of pressure to a chemical reaction should be ascribed to Berthelot and Pean de Saint Gilles (1) who in 1862 measured the rate of esterification of acetic acid with ethanol at 50 and 100 atmospheres pressure. The pressure was found to cause no significant change in rate. Thirty years later Roentgen (2) made a systematic study of the effects of 500 atmospheres pressure on the rate of inversion of sucrose catalysed by hydrochloric acid. He found the pressure to have an adverse effect on the rate. In 1896 Stearn (3) repeated the same experiment by using both weak and strong acids as catalysts. He obtained the same result as Roentgen in the case of the reactions catalysed by strong acid, but the rate of inversion catalysed by weak acids was increased by pressure. In the same year Rothmund (4) studied the effect of pressure on the rates of inversion of sucrose and the hydrolysis of ethyl and methyl acetates, both catalysed by strong acids. He confirmed Roentgen's result in the case of sucrose inversion, but the rates of hydrolysis of esters were found to be increased at 500 atm. pressure. Tammann and Bogojawlensky (5) in 1897 measured the rate of hydrolysis of methyl acetate catalysed by strong and weak acids as well as weak bases. It was found that all rates were increased by pressure,

the rates catalysed by weak electrolytes being affected by pressure to a greater extent.

After the invention of the high pressure pump by Cailletet in 1870 high pressure techniques developed rapidly. Thus Cohen and his coworkers (6,7,8) were able to use high pressure apparatus up to 1500 atm.at the beginning of this century. Besides repeating the reactions that had been studied before, they also investigated the alkaline hydrolysis of ethyl acetate and the bromate-bromide reaction. In the former case they found an acceleration by pressure, while the latter reaction was retarded by pressure. During the nineteen thirties Conant (9,10) has made a general survey of the effect of pressures up to 12,000 atm. on organic reactions in the liquid phase. Perrin and his coworkers (11,12,13,14) studied the rates of a number of organic reactions up to a pressure of 12,000 atm. Perrin (14) summarized the results by dividing these reactions into three classes, as follows:

(1) "Slow" reactions - These are bimolecular reactions with very low frequency factors; they are markedly accelerated by pressure.

(2) "Normal" reactions - These are bimolecular reactions with normal frequency factors; they are slightly accelerated by pressure.

(3) Unimolecular reactions - These are slightly retarded by pressure.

In 1937 Newitt (15,16) studied some acetic acid

esterifications and Knoevengal condensation reactions up to a pressure of 6,500 atm.

During the present decade, work in the high pressure field has revived considerably. Hamann and his collaborators (17,18,19, 20)have studied the rates of a number of S_N1 and S_N2 solvolysis and Menschutkin reactions as well as the iodination of allyl alcohol up to pressures as high as 30,000 atm. Burris and Laidler (21) investigated some more complicated reactions, and discovered that some bimolecular reactions were retarded by pressure; they therefore modified the "unimolecular reactions" in Perrin's classification to "fast reactions". Weale and Harris (22,23,24) have studied the rates of Menschutkin reactions as well as rearrangements and isomerizations. Except for the rearrangement of N-chloroacetanilide catalysed by hydrochloric acid, which was retarded by pressure, all of the other reactions they studied were found to be accelerated by pressure. They also have measured pressure effects at several temperatures.

Ewald (25) and Nicholson and Norrish (26) have studied several free radical reactions up to a pressure of 10,000 atm.; they were all found to be retarded by pressure.

THEORIES OF PRESSURE EFFECTS ON REACTION RATES

The basic theory of the effect of pressure on the rates of chemical reactions was first formulated by van 't Hoff (27) in 1901. His treatment may be presented using modern notation as follows.

Consider the reaction:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB$$

The equilibrium constant K is defined by the equation

$$K = \frac{[AB]}{[A]\,[B]} = \frac{k_1}{k_{-1}} \tag{1}$$

where the bracketed terms denote activities and the k's denote specific reaction rates. In addition

$$\Delta F = -RT \ln K \tag{2}$$

$$\Delta F = \Delta E + P\Delta V - T\Delta S \tag{3}$$

where ΔF is the change in free energy, ΔE the change in internal energy, ΔV the change in volume, ΔS the change in entropy, P the pressure and T is the absolute temperature. From (2) and (3) we get

$$-RT \ln K = \Delta E + P\Delta V - T\Delta S \tag{4}$$

$$\ln K = -\frac{\Delta E}{RT} - \frac{P\Delta V}{RT} + \frac{T\Delta S}{RT} \tag{5}$$

Differentiation with respect to pressure at constant temperature, assuming that S and E are independent of P, gives

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V}{RT} \tag{6}$$

From equation (6) it can be seen that if ΔV is positive (i.e., the volume increases when reaction proceeds) K decreases with increasing P. This means that pressure reduces the extent of reaction. Conversely if ΔV is negative

(i.e. the volume decreases as reaction proceeds) K increases with increasing P; pressure therefore favors the reaction. Equation (6) can be looked upon as a quantitative statement of Le Chatelier's principle.

The change from A + B to AB involves the activated complex, and one can write the equations

$$\Delta V = V_p - V_r \tag{7}$$

$$\Delta V_1^* = V^* - V_r \tag{8}$$

$$\Delta V_{-1}^* = V^* - V_p \tag{9}$$

$$\Delta V = \Delta V_1^* - \Delta V_{-1}^* \tag{10}$$

where V_r is the total volume of the reactants, V_p the total volume of the products, V^* the volume of the activated complex, ΔV the total volume change, ΔV_1^* the volume of activation for the forward reaction and ΔV_{-1}^* the volume of activation for the backward reaction. Insertion of (1) and (10) into eq. (6) gives

$$\left(\frac{\partial \ln k_1}{\partial P}\right)_T - \left(\frac{\partial \ln k_{-1}}{\partial P}\right)_T = -\left[\frac{\Delta V_1^*}{RT} - \frac{\Delta V_{-1}}{RT}\right] \tag{11}$$

van 't Hoff then made the assumption that eq. (11) can be split into two equations:

$$\left(\frac{\partial \ln k_1}{\partial p}\right)_T = -\frac{\Delta V_1^*}{RT} \tag{12}$$

and

$$\left(\frac{\partial \ln k_{-1}}{\partial p}\right)_T = -\frac{\Delta V_{-1}^*}{RT} \qquad (13)$$

The above equations can also be derived from the thermodynamical formulation of reaction rates according to which the rate constant can be expressed as

$$k_1 = \frac{kT}{h} e^{\Delta S_1^*/R} e^{-\Delta H_1^*/RT} \qquad (14)$$

where ΔS_1^* is the standard entropy of activation and ΔH_1^* the heat of activation. Eq. (14) can also be written as

$$k_1 = \frac{kT}{h} e^{-\Delta F_1^*/RT} \qquad (15)$$

where ΔF_1^* is the standard free energy change in going from the initial state to the activated state. It follows that:

$$\ln k_1 = \ln \frac{kT}{h} - \frac{\Delta F_1^*}{RT} \qquad (16)$$

and $$\left(\frac{\partial \ln k_1}{\partial P}\right)_T = -\frac{1}{RT} \left(\frac{\partial \Delta F_1^*}{\partial P}\right)_T = -\frac{\Delta V_1^*}{RT}$$

Similarly we get

$$\left(\frac{\partial \ln k_{-1}}{\partial P}\right)_T = -\frac{\Delta V_{-1}^*}{RT}$$

From eq. (13) we can see that if ΔV_1^* is negative, i.e. the activated complex has a smaller volume than the reactants, pressure will increase the rate. Conversely, if the volume of

activation is positive, pressure will have an adverse effect on the reaction rate. Moreover if, as in most cases, ΔV_1^* is independent of pressure, this equation can be integrated. Dropping the subscripts we get

$$\ln k = \ln k_o - \frac{\Delta V^*}{RT} P \tag{17}$$

or $$\ln \frac{k}{k_o} = - \frac{\Delta V^*}{RT} P \tag{18}$$

where k_o is the rate constant at zero pressure. The above equations are referred to as van 't Hoff's law. A plot of ln k or ln (k/k_o) against P will give a straight line of slope equal to $- \frac{\Delta V^*}{RT}$, from which the volume of activation can be calculated.

Similarly integration of eq. (6) yields

$$\ln K = \ln K_o - \frac{\Delta V}{RT} P \tag{19}$$

A plot of ln K vs. P will give a straight line and from the slope, which is equal to $- \frac{\Delta V}{RT}$, the value of ΔV can be calculated.

In some cases, however, ΔV^* is not pressure independent. A plot of ln (k/k_o) against P gives a curve instead of a straight line. Nevertheless we can still calculate ΔV^* from the slope of the tangent line at any desired pressure.

Since the effects of pressure on reaction rates are very small, it is necessary to use fairly high pressures (several thousand pounds per square inch) in order to get sufficiently

accurate volume data. Some have even worked up to 15,000 or 30,000 atmospheres. The value of one atmosphere is relatively small as compared to such high pressures; the rate constant determined under atmospheric pressure can therefore be taken as k_o in eq. (18) without introducing much error

THEORIES OF VOLUMES OF ACTIVATION

There are two main theories in connection with the interpretation of ΔV^*. They are: (1) the structural theory of Stearn and Eyring, (2) the electrostriction theory.

It was Evans and Polanyi (28) who first interpreted the volume of activation in 1935. Although there were not many volume data available at that time, they pointed out that ΔV^* was made up of two parts:

(1) The actual volume difference between the activated complex and the reactants due to change in structure ($\Delta_1 V^*$)

(2) The volume change arising from the reorganization of solvent molecules due to the change of polarity when the reactant molecules pass into the activated complex ($\Delta_2 V^*$)

Stearn and Eyring (29) suggested that it is only the first term that needs to be considered. According to them the volume of activation arises solely from the expansion or contraction of the system due to changes in the lengths of bonds which are partially broken or formed to produce the activated complex. They assumed

that in the activated state a bond is stretched about 10%, with constant cross section. Stearn and Eyring's theory works quite well when applied to the reactions of the Menschutkin type, which are accelerated by pressure, because the activated complex is more compact in structure than the two separated reactant molecules. By making some estimates of bond distances they obtained a value of ΔV_1^* which agrees satisfactory with the experimental value.

In contrast to the structural theory as suggested by Stearn and Eyring, however, Buchanan and Hamann (17) proposed that the second term is frequently more important in predicting the pressure effect. They investigated two unimolecular solvolyses of alkyl halides, and found that their rates were increased by pressure, which means a negative ΔV^*. This result is in contrast to the Stearn-Eyring theory which would predict a positive ΔV^*. A similar situation arises from the work of Burris and Laidler(21), whose results could only be explained by the electrostriction theory. The essence of this theory is that when two ions of opposite sign react together the charges may be partially neutralized. The activated complex is therefore less polar than the individual reactant molecules, and there is therefore less electrostriction of the solvent molecules, which are therefore partially released. Consequently there will be an increase in volume (ΔV^* positive) and a retardation of rate by pressure. Conversely if two ions of the same sign react together there will be an intensification of the electrostatic field, causing an increase in the electrostriction of solvent molecules. This gives a

decrease in volume (ΔV^* is negative) and the rate is accelerated by pressure. Burris and Laidler's work also disclosed two bimolecular reactions which are retarded by pressure. They therefore modified Perrin's third class of reaction as "fast reaction". Thus all the ionic reactions can now be classified into three classes according to the kinetic point of view. They can be explained by the electrostriction theory as follows (21,30):

1. "Slow" reactions These are greatly accelerated by pressure, and have large negative values of ΔV^*. These reactions include Menschutkin reactions and unimolecular solvolyses in which the activated complex is more polar than the reactant molecules. The negative ΔV^* value results from the increase in binding of solvent molecules which also causes a loss of entropy of the system. Therefore ΔS^* is also negative. Since the frequency factor A is equal to $e \frac{kT}{h} e^{-\Delta S^*/R}$, a decrease in ΔS^* means a small value of A. The frequency factors of the reactions of the slow class are therefore abnormally low (sometimes as low as 10^5 litres $mole^{-1}$ $sec.^{-1}$).

2. "Normal" reactions These are only slightly or not affected by pressure, and have very small or zero ΔV^* values. Some of them, like the negative ion displacement reactions, involve an ion and a neutral molecule. The activated complex has about the same polarity as the reactants. There is, therefore, not much change in electrostriction of the solvent molecules, and consequently not much change in volume. Their frequency factors are normal (of the order of $10^9 - 10^{11}$) as predicted by

collision theory, and the entropies of activation are small.

3. "Fast" reactions These are retarded by pressure, and have positive volumes of activation. These reactions involve the approach of ions of opposite sign or the spreading of charges. The electrical field is weakened when the reactants become the activated complex. There is therefore a release or loosening of the bound solvent molecules and consequently positive volumes and entropies of activation. The frequency factors of these reactions are therefore abnormally high (10^{14} - 10^{17}).

The experimental work to be described in the next two chapters was designed with the object of throwing further light on the theoretical basis of pressure effects on reactions in aqueous solution.

Chapter II

The Alkaline Hydrolysis of Esters and Amides

INTRODUCTION

As a general rule reactions between ions and neutral molecules in aqueous solution have frequency factors that may be described as "normal", in that they agree approximately with the kinetic theory of collisions. It is probable that if there are no important electrostatic effects involved in a reaction in solution the frequency of collision is close to that predicted by the kinetic theory. In the case of reactions between ions and neutral molecules there are usually no large electrostatic effects, and the normal frequency factors are to be understood on this basis. For reactions between ions of the same sign or of opposite signs abnormal frequency factors are often obtained, and can generally be explained in terms of electrostatic effects, as was done in the last chapter.

There are, however, certain reactions, involving an ion and a neutral molecule, for which the frequency factors are very much lower than predicted by the kinetic theory of collisions. These are the hydrolyses of substances containing a carbonyl group, such as esters, amides and anilides. For these reactions the frequency factors are always several powers of ten lower than predicted by collision theory, and theories that consider merely the electrostatic interactions between the reactants can give no satisfactory interpretation of this result; the electrostatic interaction between an ion and a dipole is much too small to

account for the low frequency factors. The effects of solvents on reactions of this type have been shown to lead to the conclusion that there is a large dipole moment in the activated complexes for reactions of this type, and a theory in terms of these dipole moments agrees quantitatively with the experimental results using mixed solvents. Unfortunately, however, a satisfactory theoretical treatment of frequency factors along the same lines has not yet been formulated. If there is indeed a large increase of dipole moment when the activated complex is formed there will be an increased electrostriction of solvent molecules, and consequently a loss of entropy. At the same time there will be a contraction resulting from this electrostriction, and an increase in velocity with increasing pressure is to be expected. Studies of the effect of hydrostatic pressure should therefore contribute to an understanding of the exact nature of reactions of this type, and may eventually lead to a more detailed formulation of the structure of the activated complex.

The present work has been carried out with this object in view. For technical reasons (attack of the metal valves by acid) the acid catalysed hydrolyses could not be studied, but an investigation has been made of the alkaline hydrolysis of four carbonyl compounds, over a range of pressures from atmospheric to 15,000 lbs. per square inch. In order to avoid the complications arising from the use of mixed solvents the work was done in pure

aqueous solutions, enough of each substance being soluble to allow satisfactory rate measurements to be made. The four compounds employed were methyl acetate, ethyl acetate, acetamide and propionamide. Activation energies were also determined in the case of the first two compounds, but in the case of the amides the values recently obtained by Willems and Bruylants (32) have been employed. The results did show a marked decrease in volume during the formation of the activated complex, and the significance of this is discussed in more detail later.

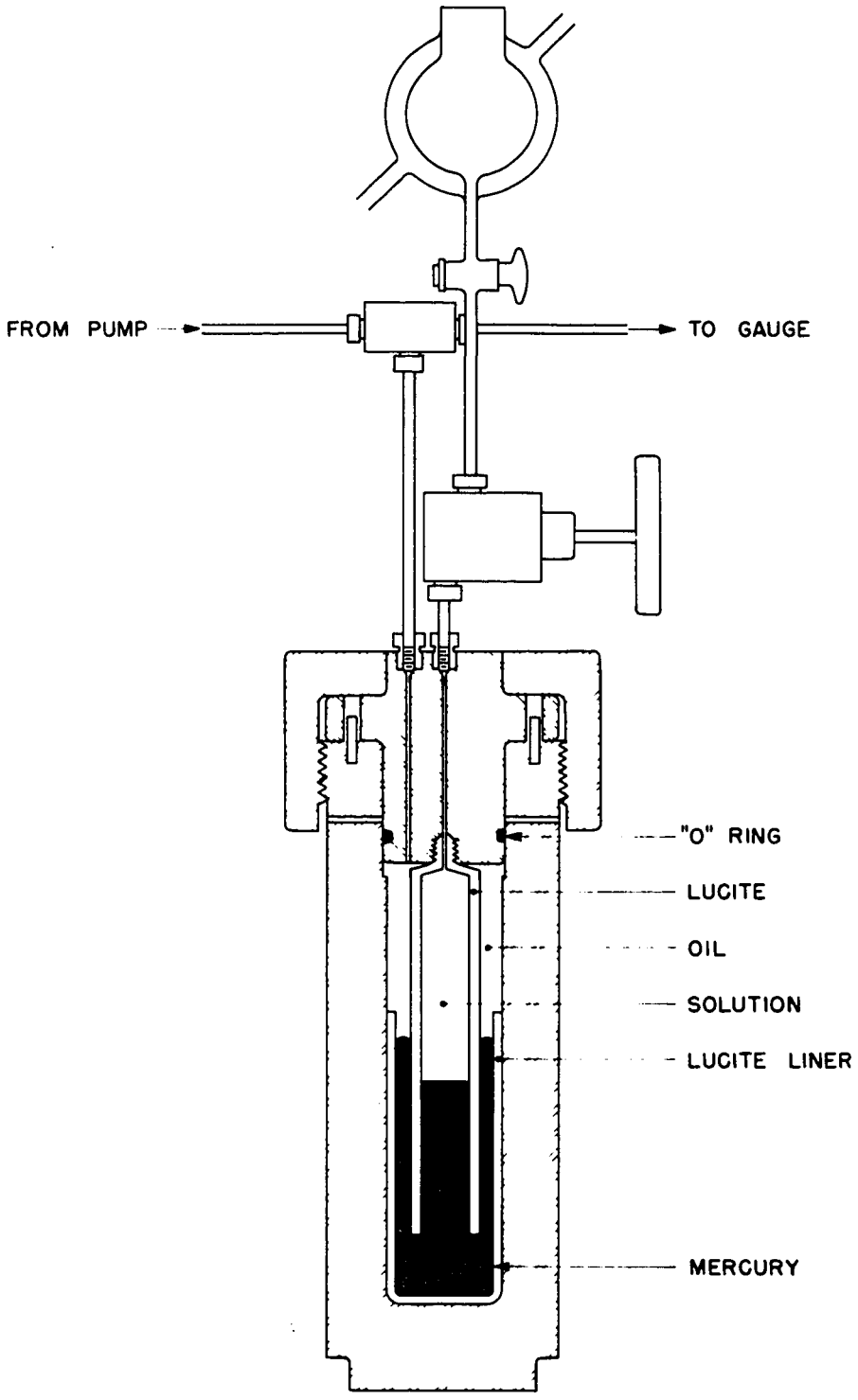
EXPERIMENTAL PROCEDURE

Materials The methyl acetate was purified by refluxing for 6 hrs. with acetic anhydride and then fractionally distilled, the distillate passing at 56° to 57° being collected. The distillate was shaken with anhydrous potassium carbonate, filtered and redistilled. The procedure with ethyl acetate was similar, but the refluxing was done with both acetic anhydride and a few drops of sulphuric acid.

Acetamide was washed in a mixture of benzene and ethyl acetate (50:15 by volume) and recrystallised from methyl alcohol. Propionamide was used as a crystallised Eastman Organics product.

High-Pressure Technique The reaction vessel used for the study of the reactions at high pressures is shown in Fig. 1, which is largely self-explanatory. The vessel is constructed of stainless steel and has a maximum working pressure of 20,000 pounds per sq. in. The pressure is generated by an electrically operated pump.

The reaction mixture is introduced into the vessel by first placing it in the bulb at the top of the apparatus; this is a double-walled glass bulb, and water from the constant temperature bath is constantly circulated through the jacket so as to maintain the bulb at the same temperature as the bath. The mercury level is first brought up to the bottom of the bulb by the application of gentle pressure to the vessel, and the reaction mixture is then introduced into the bulb. The introduction of the mixture into the reaction vessel itself is expedited by the use of a vacuum pump connected to the oil reservoir of the high pressure pump. The high pressure valve is then closed, and the desired pressure applied by means of the pump. When samples are required for analysis the pressure is released, and a sample of solution forced into the upper bulb by the application of gentle pressure. A sample is then pipetted off, and the remainder introduced again into the pressure vessel and the pressure applied. This procedure is carried out at various stages during the course of the reaction. The time taken for these procedures is only a small fraction of the total duration



ure 1 Schematic drawing of the high-pressure reaction vessel. The inside diameter is 2.5", the outside 4.93". Over-all length 14.75". Approximately 100 ml. can be introduced into the inner compartment.

of the experiment, and the correction necessary is therefore very small.

Kinetic Procedure For the determination of the energy of activation of the alkaline hydrolysis of methyl acetate and ethyl acetate the reactions were carried out in flasks maintained in the constant temperature water bath. A mixture was made of 25 ml. each of 0.1 M sodium hydroxide and the ester, and 5 ml. samples were removed at various intervals and mixed with 5 ml. of 0.1 M hydrochloric acid. The excess acid was titrated with 0.1 N $Ba(OH)_2$ solution from a microburette, using phenolphthalein as indicator.

The high pressure runs were carried out at 25°C in the vessel in the manner indicated above. In order to slow down the reactions for the high pressure work the solutions were used at lower concentrations than above. In the case of the ester hydrolyses 25 ml. each of 0.01 M NaOH and ester solutions were mixed and introduced into the vessel. 5 ml. samples were taken at about 800-second intervals and added to 5 ml. of 0.01 M HCl. The excess acid was titrated with 0.01 N $Ba(OH)_2$, using phenolphthalein as indicator.

For the hydrolysis of the amides 10 ml. each of 2 N NaOH and amide solution were mixed and introduced into the pressure vessel. 1 ml. samples were taken at about 1,000-second intervals, added to 2 ml. of 2 N H_2SO_4, and diluted to 100 ml. 10 ml. aliquots were delivered into a Nessler tube and diluted to 25 ml. 10 ml. of 2 N H_2SO_4 followed by 15 ml. Nessler reagent were then added. After

thorough mixing the solutions were examined in an Evelyn photoelectric colorimeter, using filter 515.

RESULTS

All of the reactions studied were kinetically of the second order, and the rate constants were determined by plotting $x/a(a-x)$ against the time, and measuring the slope of the straight line. Hydrolysis of Esters The results obtained for the alkaline hydrolyses of methyl and ethyl acetate at atmospheric pressure and at four different temperatures are shown in Table 1, and the corresponding Arrhenius plots are shown in Fig. 2. The activation energies calculated from these plots are 11.95 and 11.55 kcal. per mole respectively. Potts and Amis (33) have given a value of 11.66 kcal. for ethyl ester, in good agreement. Values of 11.21 and 11.22 kcal. for the two esters have been quoted by Moelwyn-Hughes (34) who, however, gives no reference to the original source. The frequency factors and entropies of activation for the reactions are shown in Table 1.

Table 2 shows the rate constants obtained for the alkaline hydrolysis of the two esters for a range of pressure up to 12,000 pounds per sq. in. Figure 3 shows a plot of the logarithm of k/k_o against the pressure; k_o is the rate constant at zero pressure, here assumed to be the same as atmospheric pressure. The van't Hoff law is seen to be obeyed accurately with $\Delta V^{\ddagger}$ constant and from the

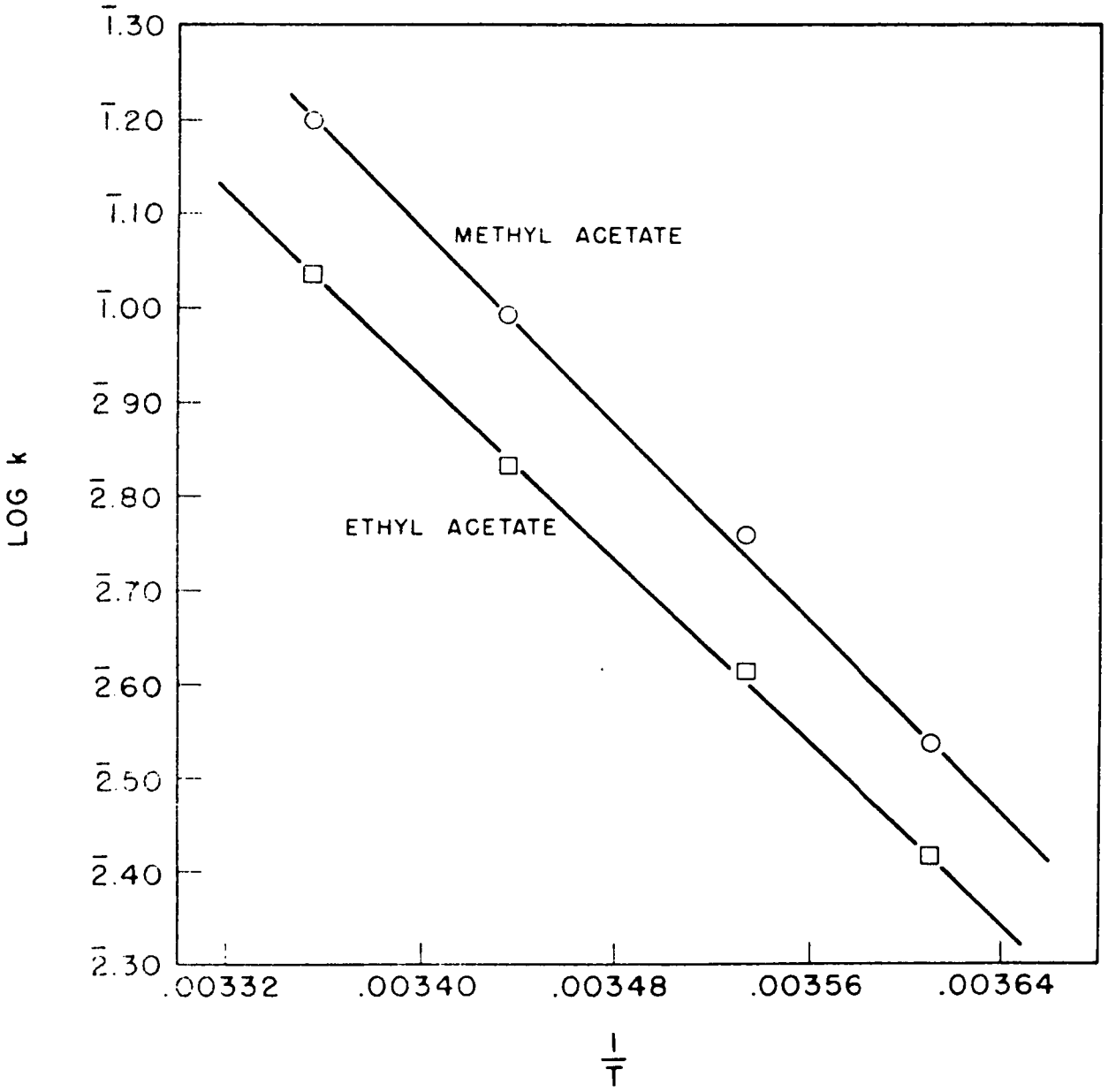


Figure 2 Arrhenius plots for the alkaline hydrolyses of methyl and ethyl acetates.

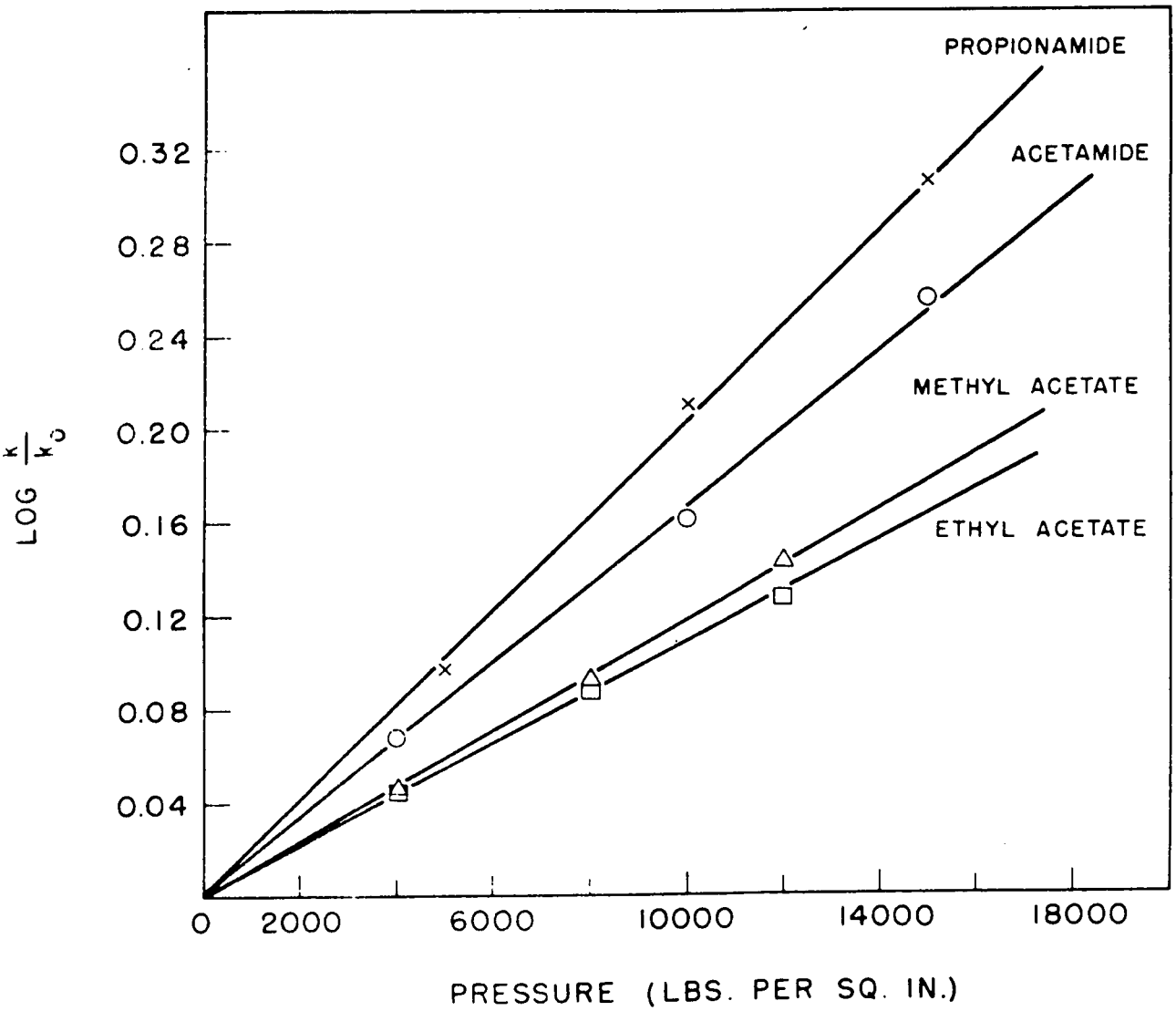


Figure 3 Van 't Hoff plots for the alkaline hydrolyses of the esters and amides.

slope of the curves the values of ΔV^{*} have been calculated; these are shown in Table 2. It is to be noted that in Tables 1 and 2 there is a slight difference between the rates at atmospheric pressure and 25°, and this is attributed to the differences in concentration; there is a small ionic strength effect for these reactions. Cohen and Kaiser (7) have studied the effect of pressure on the alkaline hydrolysis of ethyl acetate at 2.4°C using 0.01 M solutions, and from their results we calculate a ΔV^{*} value of -4.8 cc. per mole. The much smaller value obtained by them is attributed to the much lower temperature they employed.

Alkaline Hydrolysis of Amides Since accurate values of activation energies for the amide hydrolyses have recently been determined by Willems and Bruylants (32) we did not carry out a remeasurement of these quantities. Table 3 shows the rate constants at the various pressures, and the corresponding van 't Hoff plots are included in Fig.3. The volumes of activation are shown in Table 3. Figure 4 shows an Arrhenius plot for the data of Willems and Bruylants and ourselves; our own rates at 25°C are seen to be consistent with theirs at the higher temperatures. The activation energies and entropies are included in Table 4.

Table 1

Rate Constants for the Alkaline Hydrolysis of Methyl and Ethyl Acetates at Different Temperatures

Concentration of both reactants after mixing = 0.05 M

Rate constants in litres $mole^{-1}$ $sec.^{-1}$

Temperature (°C)	Rate Constants for Methyl Acetate	Rate Constants for Ethyl Acetate
4.0	0.0343	0.0258
10.0	0.0573	0.0410
18.0	0.0982	0.0680
25.0	0.158	0.1080
Activation energy (kcal. per mole)	11.95	11.55
Frequency factor (litres $mole^{-1}$ $sec.^{-1}$)	9.28×10^7	3.23×10^7
Entropy of activation (e.u.)	-24.1	-26.2

Table 2

Rate Constants for the Alkaline Hydrolysis of Methyl and Ethyl Acetates at Different Pressures

Concentration of both reactants after mixing = 0.005 M

Rate constants in litres $mole^{-1} sec.^{-1}$ $T = 25.0^{\circ}C$

Pressure (lbs. $in.^{-2}$)	Rate constants for Methyl Acetate	Ethyl Acetate
14.7	0.146	0.080
4000	0.163	0.089
8000	0.181	0.098
12000	0.203	0.107
ΔV^{*} (cc. $mole^{-1}$)	-9.93	-8.77

Table 3.

Rate Constants for the Alkaline Hydrolysis of Acetamide and Propionamide at Different Pressures

Concentration of both reactants after mixing = 1 M.

Rate constants in litres $mole^{-1}$ $sec.^{-1}$ T = 25.0°C

Pressure ($lbs.in.^{-2}$)	Rate Constants for Acetamide	Propionamide
14.7	3.77×10^{-5}	3.00×10^{-5}
4000	4.44×10^{-5}	—
5000	—	3.75×10^{-5}
10000	5.47×10^{-5}	4.86×10^{-5}
15000	6.80×10^{-5}	6.07×10^{-5}
ΔV^{*} ($cc.mole^{-1}$)	-14.2	-16.9

Table 4

Summary of Results

for the Alkaline Hydrolysis of Esters and Amides

Reaction	E (kcal.)	A	ΔS^* (e.u.)	ΔV^* (cc. per mole)
Methyl acetate + OH^-	12.0	9.3×10^7	-24.1	-9.9
Ethyl acetate + OH^-	11.6	3.2×10^7	-26.2	-8.8
Acetamide + OH^-	14.2	9.5×10^5	-33.5	-14.2
Propionamide + OH^-	14.6	1.5×10^6	-32.6	-16.9

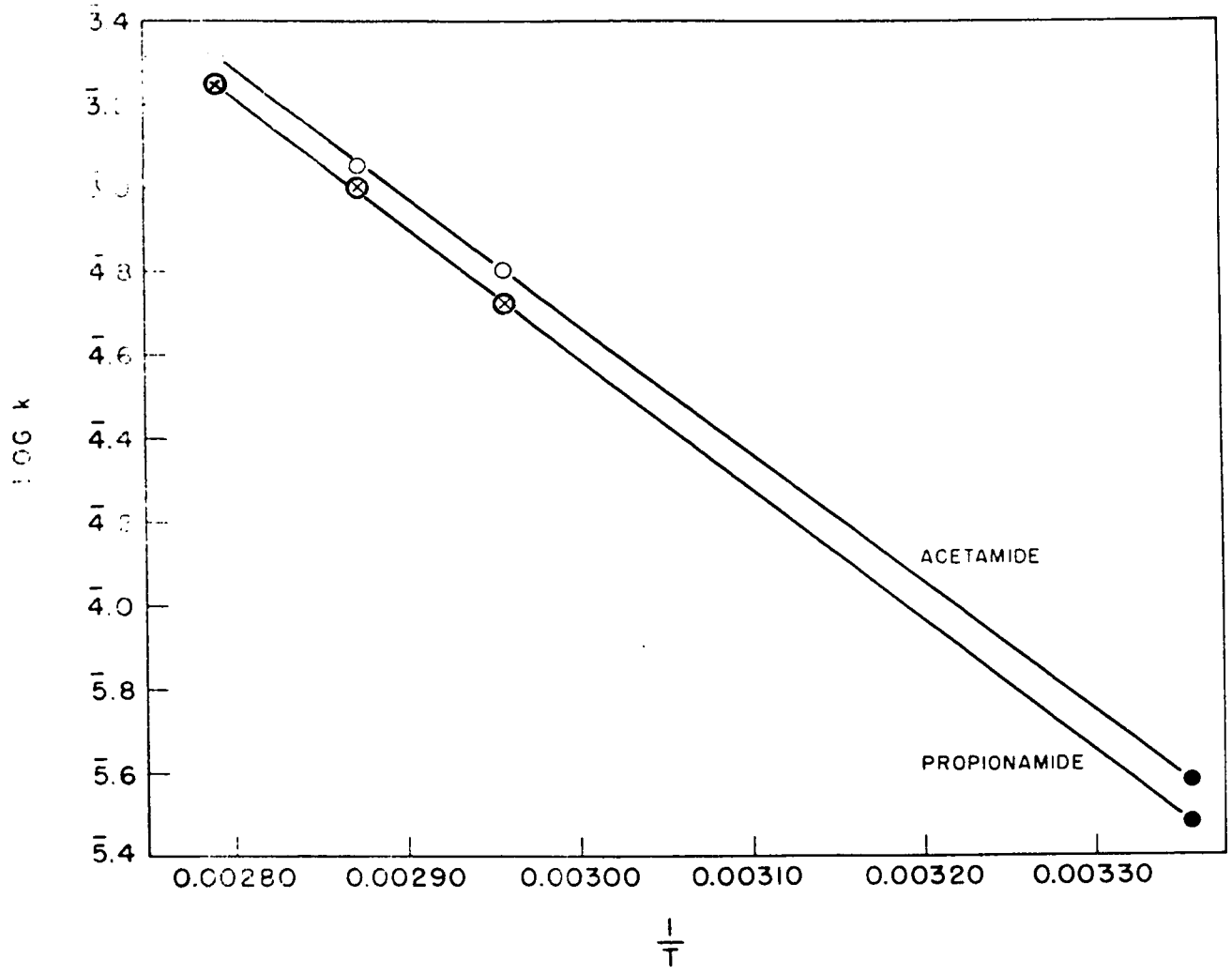
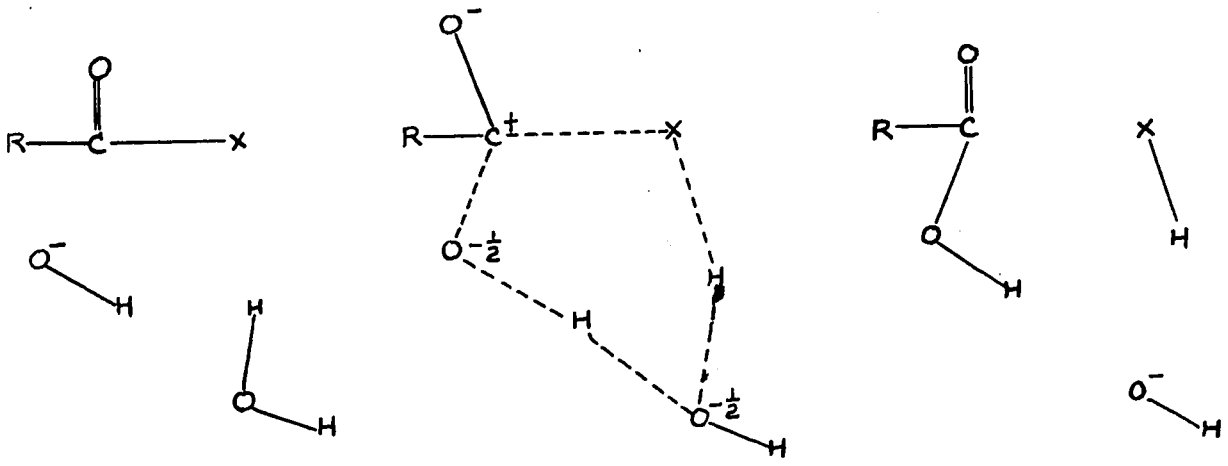


Figure 4 Arrhenius plots for the alkaline hydrolyses of acetamide and propionamide; the open circles are the results of Willems and Bruylants, the closed circles those of the present work.

DISCUSSION

Table 4 shows the main results of the present investigation. It is of interest to consider on what basis we may interpret the values of the volumes of activation that have been obtained for the esters and amides; the values have been seen to fall in the range of -10 to -17 cc. per mole. The work on the hydrolysis of esters and amides in mixed solvents (31) has suggested that the alkaline hydrolysis may be represented according to the mechanism



(initial state) (activated complex) (final state)

The principle on which the ionisation of the activated complex has been formulated is that by the time the activated state has been reached the charge transfers have occurred to just one half of the extent to which they occur in the complete reaction. This type of activated complex has been seen to provide an adequate interpretation of the effects of solvents on the rates.

The empirical equation obtained by Couture and Laidler (35,36) indicates that a unit charge in aqueous solution brings about a diminution of volume of 26 cc. per mole as a result of the electrostriction effect. Considering the hydroxide ion in the initial state of the reaction, we may therefore say that there will be a volume diminution of 26 cc. For the activated complex, contributions must be assigned to the individual charges. The oxygen atom of the carbonyl group bears a full negative charge, and if it were completely surrounded by water a contribution of -26 would be obtained. The rest of the molecule however occupies perhaps one quarter of the volume, and a reasonable estimate is therefore 3/4 of -26, i.e. approximately -18. For the carbon atom in the carbonyl group a reasonable estimate is that three-quarters of the surroundings are occupied by the activated complex itself, and a contribution of 1/4 of -26, namely -6, may be taken. Two other oxygen atoms bear half charges, and in both cases the environs may be said to be occupied to approximately half of the extent by complex, and half by water; a contribution of about 1/4 of -26, namely -6, be therefore be taken in both cases.

The total diminution in volume in the activated state, due to electrostriction, is therefore roughly equal to -18-6-6-6, i.e., -36. As a result of the electrostatic effects alone, therefore, there has been a change of volume from -26 to -36, i.e., a decrease in volume of 10 cc. Structural effects are not likely to be important in this case of the addition of the hydroxide ion to an ester, and the electrostatic effects are probably the main ones. The theory, although crude, therefore appears to give an adequate interpretation of the volume changes taking place in these reactions.

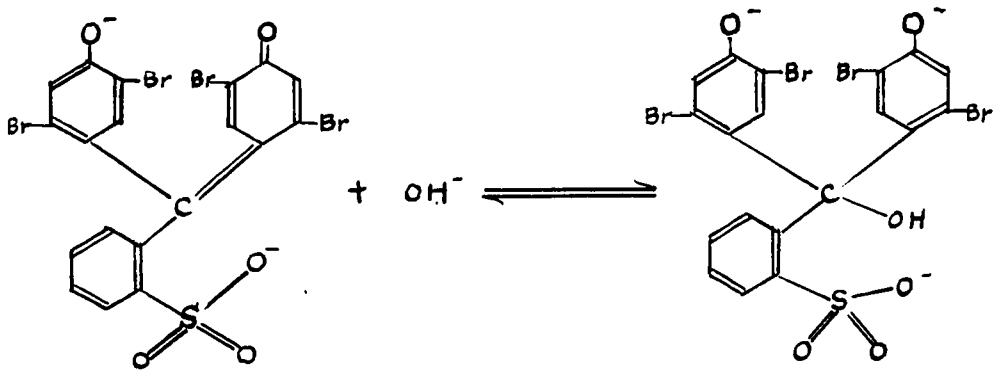
Chapter III

The fading of organic dyes in alkaline solution.

INTRODUCTION

An experimental study was also made of the influenee of pressure on the fading, in alkaline solution, of three organic dyes, viz. brom phenol blue, phenol phthalein and crystal violet. All of these reactions, as seen below, are reactions between two ions; in the first two cases the ions are of the same sign, in the third case of the opposite sign.

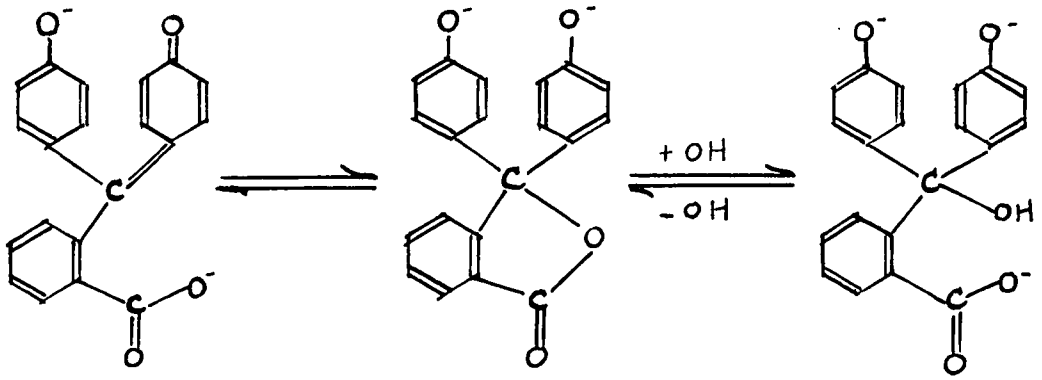
The kinetics of the alkaline fading of brom phenol blue were first studied under atmospheric pressure by Panepinto and Kilpatrick (37) and by Amis and La Mer (38). The results of these workers led to the following proposed mechanism for the reaction, suggested by Amis and La Mer:



The reaction was found to go to completion under the experimental conditions employed.

The alkaline fading of phenol phthalein was studied by Kober and Marshall (39), Biddle and Porter (40), Lund (41),

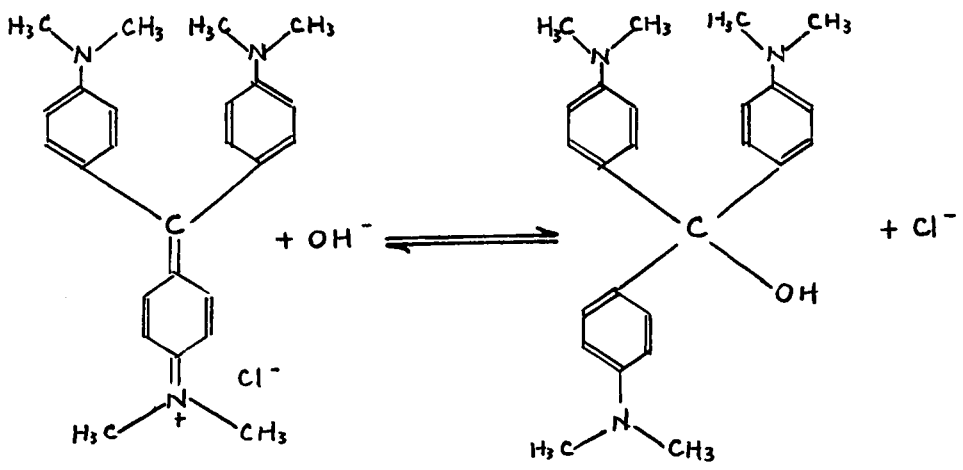
Wygaert and Eeckhout (42), and Barnes and La Mer (43). The mechanism of the reaction can be represented by the following equations:



quinoid form (red) lactone form carbinol form (colourless)

The reaction does not go to completion, and the reverse reaction must therefore be taken into account in the kinetic studies. In the investigation carried out the kinetics have in fact been investigated in both directions over a range of temperatures and pressures.

The kinetics at atmospheric pressure of the fading of crystal violet in alkaline solution was studied by Biddle and Porter (40), Hockberg and La Mer (44), Goldacre and Phillips (45) and in great detail by Turgeon and La Mer (46). The reaction goes essentially to completion under experimental conditions, and again involves the formation of a carbinol, as indicated on the next page.



It is to be seen that the three reactions may be represented schematically by the following equations

$$(B.P.B.)^{=} + OH^{-} \rightleftarrows (B.P.B.)^{\equiv}OH$$

$$(P.P.)^{=} + OH^{-} \rightleftarrows (P.P.)^{\equiv}OH$$

$$(C.V.)^{+} + OH^{-} \rightleftarrows (C.V.)OH$$

The first two therefore involve a reaction between ions of the same sign, the last between ions of opposite sign. According to the simple ideas discussed in chapter I it would therefore be expected that the first two reactions would involve a decrease in volume during the activation process, and would therefore be accelerated by pressure. The third reaction, on the other hand, should involve an increase in volume, and should therefore be retarded by pressure. The results show that these anticipations are realized in the first two cases, but that the third reaction is unaffected by pressure. As will be discussed below, this result

may be due to the fact that the charges do not approach very closely in the formation of the activated complex.

EXPERIMENTAL PROCEDURE

Materials The brom phenol blue used in the investigation was an Eastman product. A stock solution 0.00004M in brom phenol blue was prepared by dissolving 0.0268 g. of the dye in absolute ethanol, adding 4 ml. of 0.01M sodium hydroxide to convert it to the monosodium salt, evaporating the resulting solution in vacuum to dryness, and diluting with water to 1 litre. The phenol phthalein used was C.P. grade Fisher product, and it was thrice recrystallized from absolute methanol. 0.03183 grams of the purified material was dissolved in 50% aqueous ethanol and made up to 100 ml., giving a 0.001 molar solution of phenol phthalein. The crystal violet used was an Anachemia Chemicals Ltd. product, and was purified as follows. 1 gram of the material was dissolved in about 200 cc. of hot H_2O, and filtered. 10% sodium hydroxide solution was added until all of the dye had precipitated as carbinol. The precipitate was collected on a Buchner funnel and washed thoroughly with water. It was then suspended in water, and dilute hydrochloric acid was added to dissolve it. After filtration the carbinol was reprecipitated with excess sodium hydroxide, collected on a Buchner funnel and washed thoroughly with water. It was then suspended in about 50 ml. of water and 5 ml. of 3N hydrochloric acid was added; it was heated until the material was

completely in solution and then filtered while hot. After cooling the crystals of crystal violet chloride were collected on a Buchner funnel, redissolved in hot water, and allowed to recrystallize. The crystals were dried over phosphorus pentoxide in a vacuum desiccator.

Kinetic procedure Since the sodium hydroxide was in excess of the dye, the reactions in the case of brom phenol blue and crystal violet were simple first-order reactions. The phenol phthalein reaction, on the other hand, had to be treated as consisting of opposing first-order reactions.

The kinetic law applying in the case of brom phenol blue is

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \qquad (20)$$

where x is the amount of product at time t, and a is the initial amount of dye. The first-order rate constants were obtained by plotting log (a-x) against time and determining the slopes. The kinetic runs were carried out by mixing 25 ml. of 0.00004 M brom phenol blue with 25 ml. of 0.4 N sodium hydroxide solution, the resulting solutions being 2×10^{-5} M in brom phenol blue and 2×10^{-1} N in sodium hydroxide. 5 ml. samples were taken at intervals of about 1500 seconds and delivered into a colorimeter tube containing 5 ml. of water. The optical densities of the solution were determined in an Evelyn photoelectric colorimeter using

filter 565. The concentrations of the unreacted dye were read from a calibration line, prepared as follows. 10 tubes containing separately 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5 ml. of 0.0004 N brom phenol blue were diluted to 20 ml.; the resulting concentrations of brom phenol blue in each tube were 1.0×10^{-5}, 0.9×10^{-5}, 0.8×10^{-5}, 0.7×10^{-5}, 0.6×10^{-5}, 0.5×10^{-5}, 0.4×10^{-5}, 0.3×10^{-5}, 0.2×10^{-5}, 0.1×10^{-5} respectively. The galvanometer readings were taken by setting the reading of the completely faded sample as 100. The photometric densities of these readings were then plotted against the concentrations of brom phenol blue, and a good straight line was obtained showing that the Lambert-Beer law was obeyed. The high pressure technique was as described previously.

Since the phenol phthalein fading is reversible the mechanism must be represented as

$$(P.P.)^{=} + OH^{-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (P.P.)^{\equiv}OH$$

The rate of disappearance of the dye is therefore given by

$$-\frac{d[(P.P.)^{=}]}{dt} = k_1 [(P.P.)^{=}] [OH] - k_{-1} [(P.P.)^{\equiv}OH] \qquad (21)$$

where k_1 is the second-order rate constant for the forward reaction and k_{-1} is the first-order rate constant for the reverse reaction. Since $[OH^{-}]$ is practically constant we can combine it with k_1 to form a pseudo-first order constant k_1', the resulting

equation being

$$- \frac{d[(P.P.)^{=}]}{dt} = k_1' [(P.P.)^{=}] - k_{-1} [(P.P.)^{\equiv}OH] \qquad (22)$$

The behaviour is therefore that of opposing first-order reactions, which obey the kinetic law

$$k_1' + k_{-1} = \frac{2.303}{t} \log \frac{c_e}{c_e - c} \qquad (23)$$

Here c_e is the equilibrium concentration of the carbinol form of phenol phthalein, and c is the concentration of the carbinol form at any time t. Let c_T be the total concentration of phenol phthalein, c_e' the equilibrium concentration of the pink form of phenol phthalein, and c' the concentration of the pink form at any time t. Then since

$$c_e = c_T - c_e' \qquad (24)$$

$$c = c_T - c' \qquad (25)$$

equation (23) becomes

$$k_1' + k_{-1} = \frac{2.303}{t} \log \frac{c_T - c_e'}{c' - c_e'} \qquad (26)$$

If the absorption of light by the substance obeys the Lambert-Beer law the concentration of the coloured substance is directly

proportional to the photometric density L, according to the following expression

$$c' = \frac{L}{K_1} \qquad (27)$$

where K_1 is the calibration constant whose value depends on the nature of the coloured substance and the characteristics of the filter used. L is the photometric density, equal to $\log (I_o/I)$, where I_o is the intensity of the incident light and I that of the transmitted light. Equation (26) therefore becomes

$$k_1' + k_{-1} = \frac{2.303}{t} \log \frac{L_T - L_e}{L - L_e} \qquad (28)$$

where L_e is the photometric density of the solution at equilibrium, and L that at any time t. From equation (28) it can be seen that a plot of $\log (L - L_e)$ against the time should result in a straight line with a slope equal to $-\frac{k_1' + k_{-1}}{2.303}$, so that the value of the complex rate constant $(k_1' + k_{-1})$ can be calculated. The individual rate constants k_1 and k_{-1} can be found from the equilibrium constant K, which is equal to k_1/k_{-1}. If $k_1' + k_{-1}$ is called k_c then

$$k_1 = \frac{k_1'}{[OH^-]} = \frac{k_c - k_{-1}}{[OH^-]} = \frac{k_c - k_1/K}{[OH^-]} \qquad (29)$$

From this $$k_1 = \frac{k_c}{[OH^-] + \frac{1}{K}} \qquad (30)$$

so that $$k_{-1} = k_c - k_1 \qquad (31)$$

The kinetic runs with the phenol phthalein were carried out by mixing 99 ml. of 0.0101 N sodium hydroxide and 1 ml. of 0.001 N phenol phthalein in a 100 ml. volumetric flask. The resulting solution was 0.01 N in sodium hydroxide and 0.00001 N in phenol phthalein. 10 ml. samples were taken at about 2000-second intervals and the photometric densities of the samples were determined in the Evelyn photoelectric colorimeter using filter 540. The photometric density at equilibrium was determined in each case by allowing the reaction mixture to remain under experimental conditions for at least 24 hours. The value of the rate constant k_c was determined by plotting log $(L - L_e)$ against the time. Phenol phthalein in alkaline solutions shows an adsorption maximum at 550 μ; a calibration line was prepared by plotting the concentration of phenol phthalein, varying from 1×10^{-6} M to 10×10^{-6} M, against the photometric density using filter 540. The Lambert-Beer law was obeyed.

The procedure with crystal violet was similar to that with brom phenol blue. The dye shows an adsorption maximum at 590 μ and the best filter was No. 565. The calibration was carried out by varying the concentration of crystal violet chloride

from 5×10^{-6} M to 0.5×10^{-6}M, and the Lambert-Beer law was found to be obeyed. The kinetic runs were carried out by mixing equal volumes of 0.004 N sodium hydroxide and 0.00001 M crystal violet chloride solutions, so that the resulting concentrations were 0.002 N in sodium hydroxide and 0.000005 molar in crystal violet. Samples were withdrawn at intervals of about 900 seconds and the photometric densities L determined using the colorimeter. The values of log L were plotted against the time, and straight lines obtained in each case. The apparent first-order rate constants were calculated from the slopes of the lines.

EXPERIMENTAL RESULTS

Brom phenol blue Rate constants for the brom phenol blue reaction were determined at a temperature of 25.0°C and at pressures varying from atmospheric to 15,000 pounds per square inch. Plots of log (a - x) against time are shown in Figure 5, and the rate constants, obtained from the slopes, are listed in Table 5; this table shows the apparent first-order constants k_1' and the true second-order constants k_1 obtained by dividing k_1' by the concentration of hydroxide ions. Figure 6 includes a plot of log (k/k_o) against the pressure. The relationship is seen to be not strictly linear. The slope of the line at low pressures corresponds to a volume of activation of -9.2 cc. per mole. At higher pressures the curve is quite linear, and the corresponding volume of activation is then - 19.6 cc. per mole.

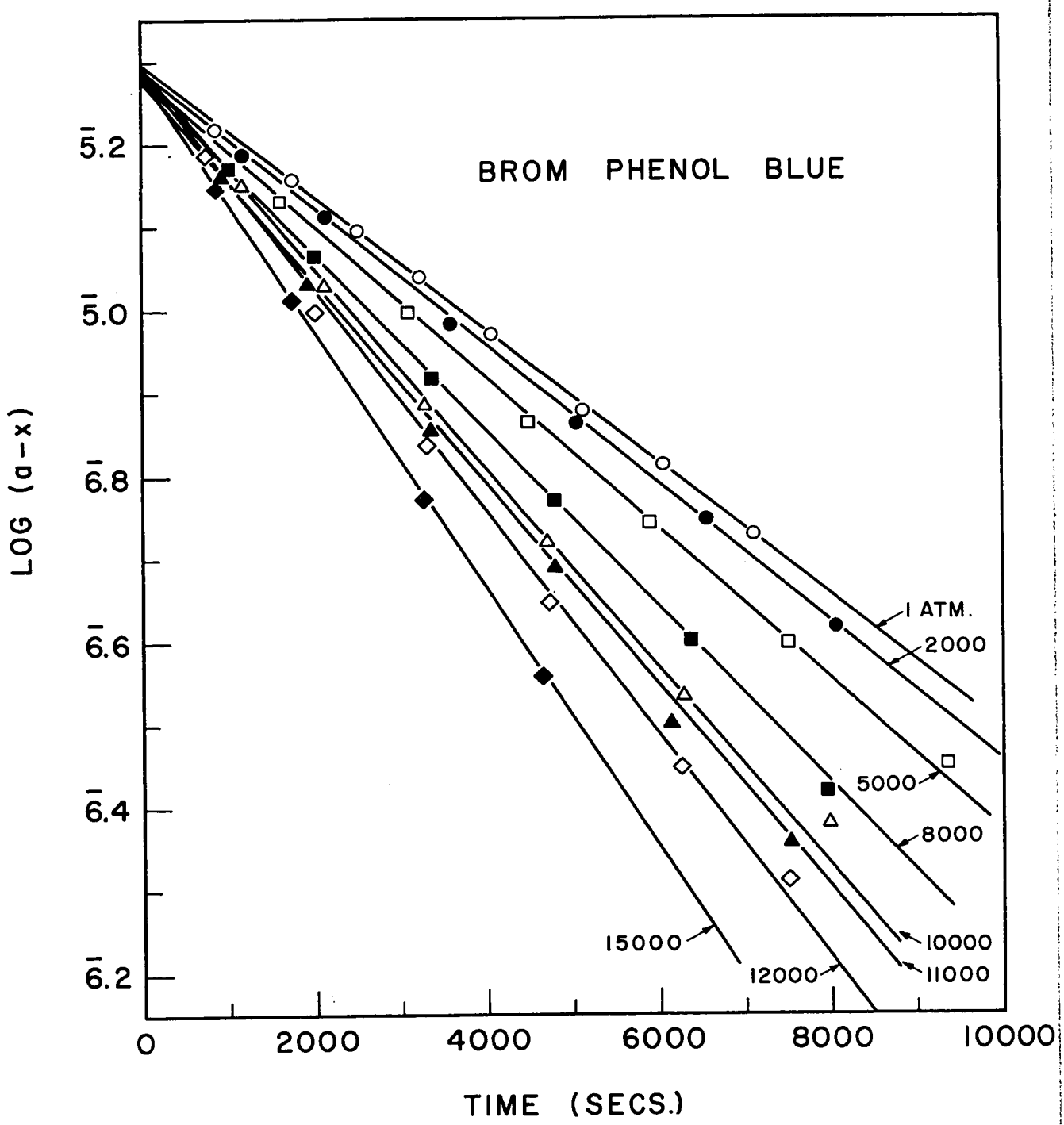


Figure 5 Plots of log (a-x) against time for the fading of brom phenol blue at various pressures.

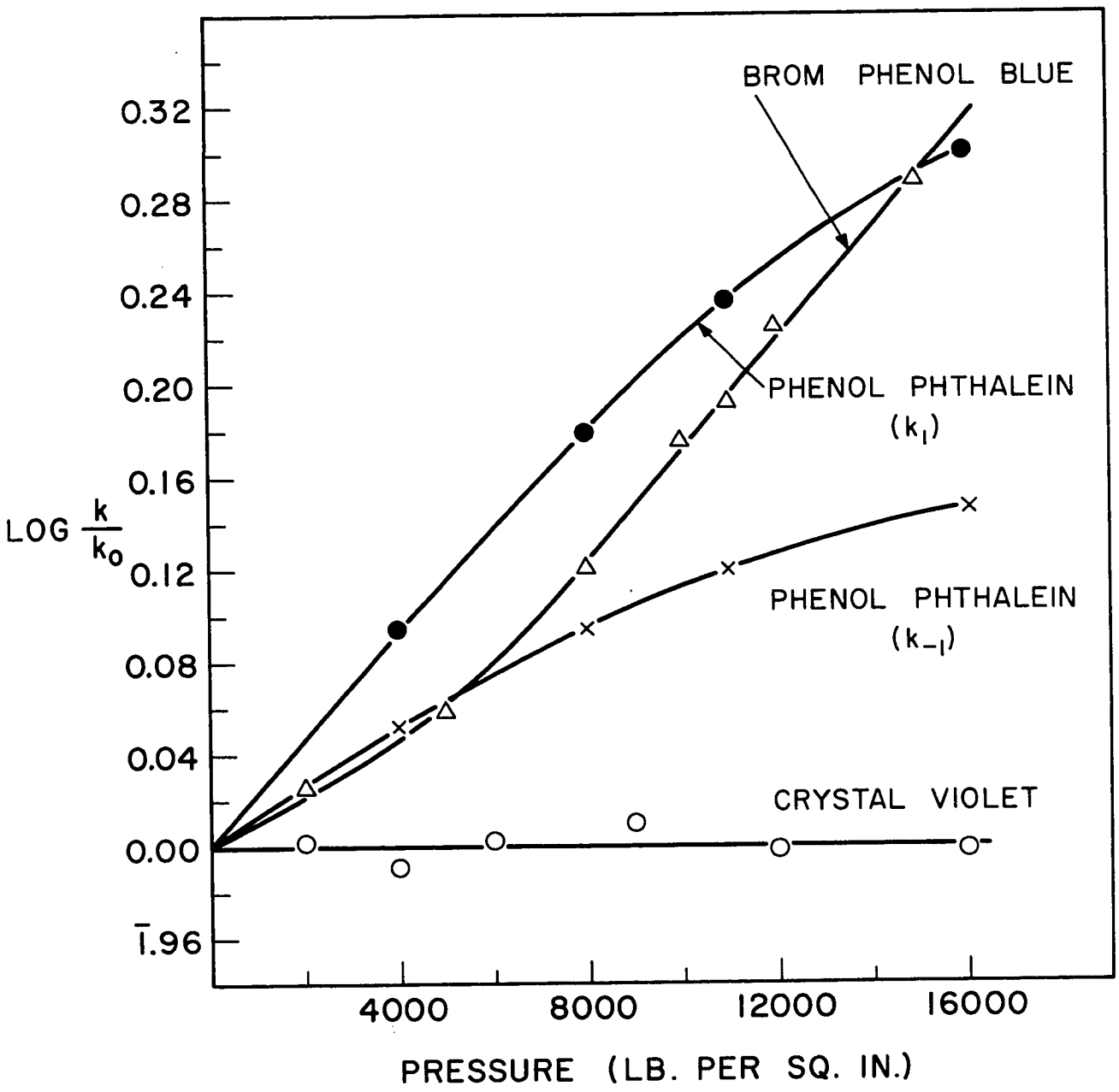


Figure 6 Plots of log (k/k_o) against pressure.

Table 5

Summary of results for the alkaline fading of brom phenol blue

$T = 25.0^{\circ}C.$

$P(lbs.in^{-2})$	14.7	2,000	5,000	8,000	10,000	11,000	12,000	15,000
$k_1'(sec.^{-1})x10^4$	1.864	1.980	2.134	2.460	2.796	2.899	3.125	3.609
$k_1(M^{-1}sec.^{-1})x10^4$	9.32	9.90	10.67	12.30	13.98	14.50	15.63	18.05
$\frac{k}{k_o}$	1	1.062	1.145	1.320	1.500	1.555	1.677	1.936
$\log \frac{k}{k_o}$	0	0.0261	0.0588	0.1206	0.1761	0.1917	0.2245	0.2869

$\Delta V_1^* = -19.6$ cc. per mole

The energy of activation for the reaction was determined by Amis and La Mer (38), and the results at zero ionic strength are

$E = 12.2$ kcal. per mole

$A = 2.04 \times 10^{10}$ litres per mole per second

$\Delta S^* = -13.34$ calories per degree per mole.

Phenol phthalein Since an activation energy for the phenol phthalein reaction had not previously been determined, the rates of the reaction in both directions were measured over a range of temperatures. Figure 7 shows plots of log $(L - L_e)$ against the time at four temperatures, and the variation is seen to be linear. From the slopes the values of $k_1' + k_{-1}$ can be calculated, and the results are included in Table 6. By allowing the mixtures to stand for over 24 hours at the four temperatures the equilibrium constants were determined, and are also shown in the table. The separated values of k_1' and k_{-1} are also shown and from k_1' the values of k_1 are calculated, and are shown in the table. Figure 8 shows a van 't Hoff plot of the logarithm of the equilibrium constant against the reciprocal of the absolute temperature, and it is seen that a straight line is obtained. The thermodynamical values obtained from this plot are as follows:

$\Delta H = -9.97$ kcal. per mole

$\Delta F = -2.49$ kcal. per mole

$\Delta S = -25.1$ cal. $mole^{-1} deg.^{-1}$

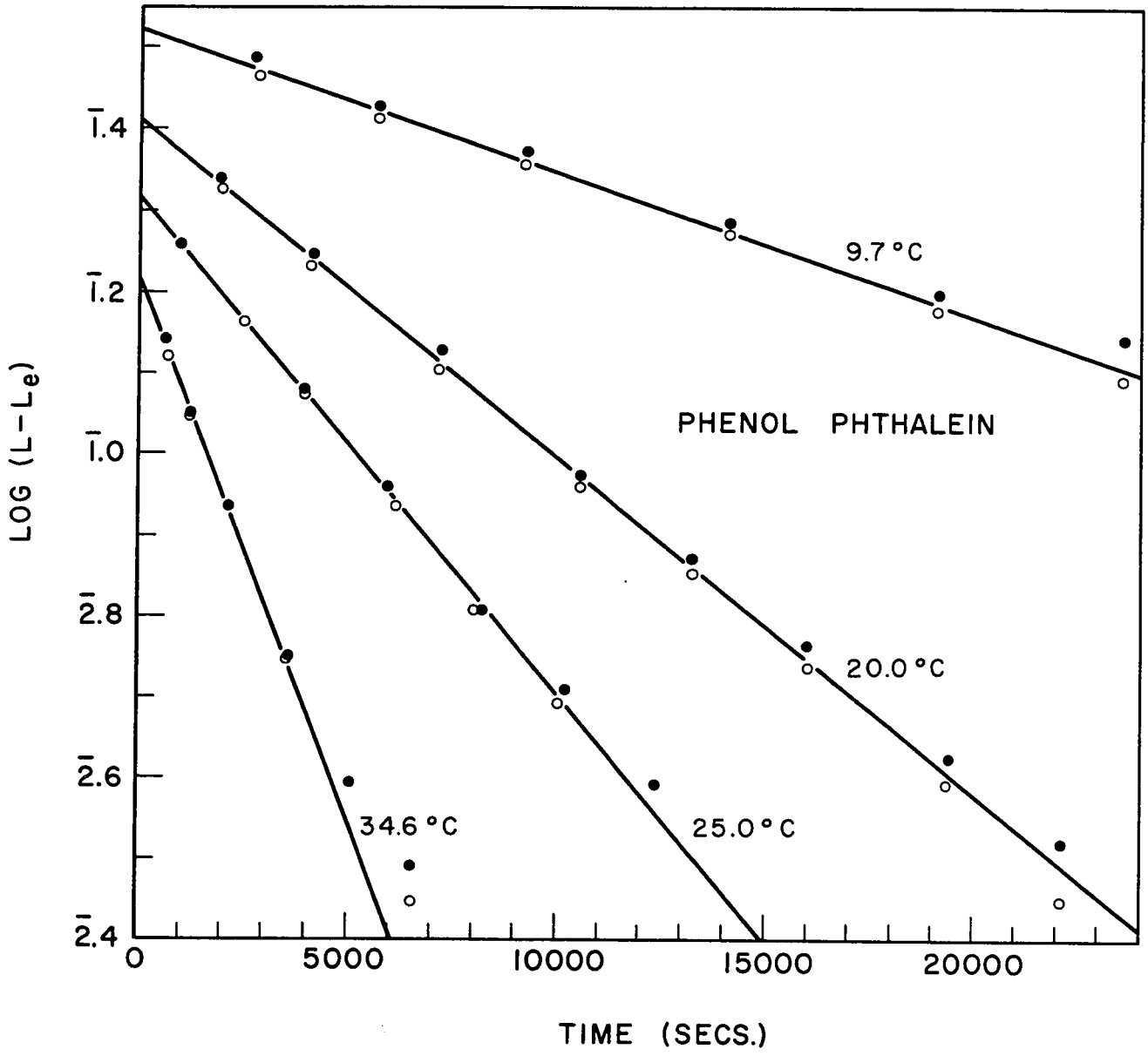


Figure 7 Plots of log(L-Le) against the time, for phenol phthalein at four temperatures; L is the photometric density at time t, and Le that at equilibrium.

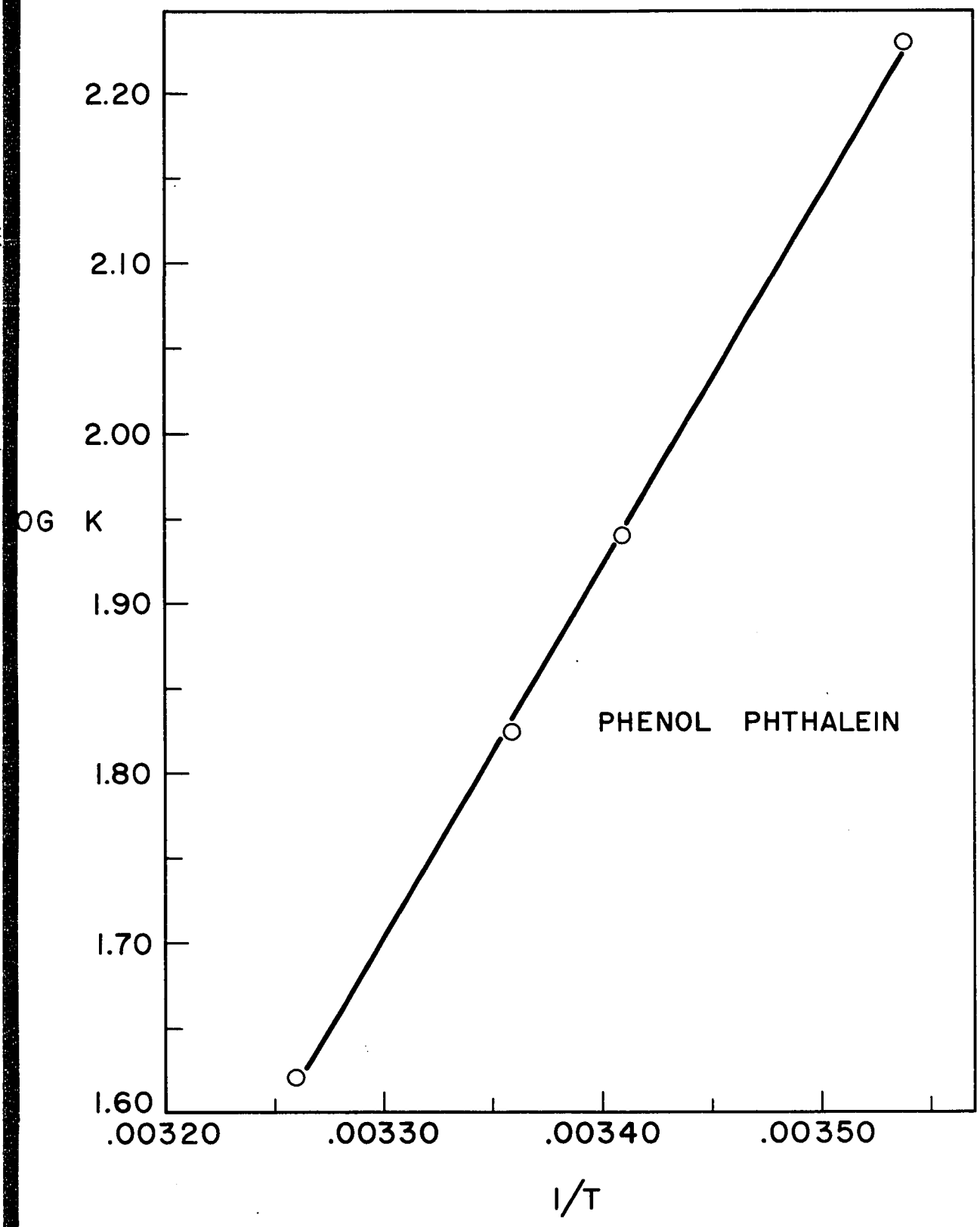


Figure 8 Plot of the logarithm of the equilibrium constant against 1/T, for phenol phthalein.

Table 6

Rate and equilibrium constants for the fading of phenol phthalein at various temperatures

Temperature	9.7°C	20.0°C	25.0°C	34.6°C
$(k_1' + k_{-1}) \times 10^5 (sec.^{-1})$	4.12	9.60	14.3	31.1
K (M^{-1})	74.0	86.9	66.7	41.8
$k_1' \times 10^5 (sec.^{-1})$	2.62	4.46	5.72	9.17
$k_1 \times 10^3 (M^{-1} sec.^{-1})$	2.62	4.46	5.72	9.17
$k_{-1} \times 10^5 (sec.^{-1})$	1.51	5.13	8.58	21.94

$\Delta H = -9.97$ kcal.mole^{-1} $\quad \Delta F = -2.49$ kcal. mole^{-1} $\quad A_1 = 1.14 \times 10^4$ $M^{-1} sec.^{-1}$

$E_1 = 8.59$ " " $\quad \Delta S_1^* = -41.94$ cal.deg.$^{-1}$ mole^{-1} $\quad A_{-1} = 3.06 \times 10^9$ $sec.^{-1}$

$E_{-1} = 18.47$ " " $\quad \Delta S_{-1}^* = -17.12$ " "

Figures 9 and 10 show plots of log k_1 against 1/T and log k_{-1} against 1/T. The Arrhenius law is seen to be obeyed accurately, and the energies and entropies of activation obtained are

$E_1 = 8.59$ kcal. per mole
$A_1 = 1.14 \times 10^4$ litres $mole^{-1} sec.^{-1}$
$\Delta S_1^* = -41.94$ cal. $deg.^{-1} mole^{-1}$
$E_{-1} = 18.47$ kcal. per mole
$A_{-1} = 3.06 \times 10^9$ $sec.^{-1}$
$\Delta S_{-1}^* = -17.12$ cal. $deg.^{-1} mole^{-1}$.

Table 7 shows the results obtained at 25.0°C and at the various pressures employed. Figure 11 shows a plot of the logarithm of the equilibrium constant against the pressure, and from the slope of the straight line a value of ΔV of -8.7 cc. per mole was calculated. The plots of the logarithm of k_1 and k_{-1} against the pressure are included in Figure 6, and from the initial slopes values of -19.7 and -11 cc. per mole are calculated for the volumes of activation for the forward and reverse reactions.

Crystal violet Rate constants for the fading of crystal violet were measured at a temperature of 25.0°C and at pressures varying from atmospheric to 16,000 lbs. per sq.in. The results are summarised in Table 8, which shows the apparent first-order constants k_1' and the true second-order constants k_1 obtained by dividing k_1' by the concentration of hydroxide ions.

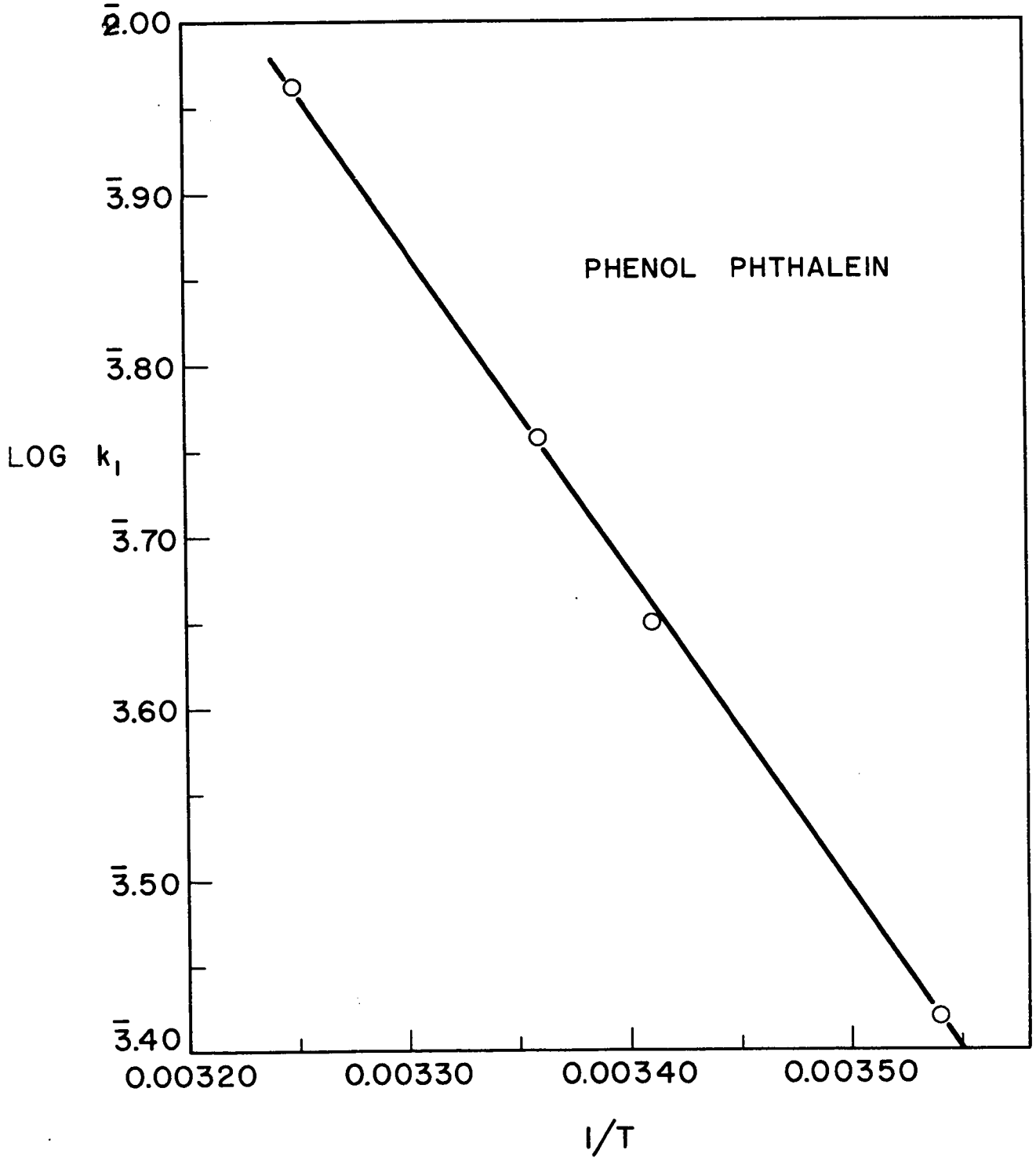


Figure 9 Plot of log k_1 against 1/T, for phenol phthalein.

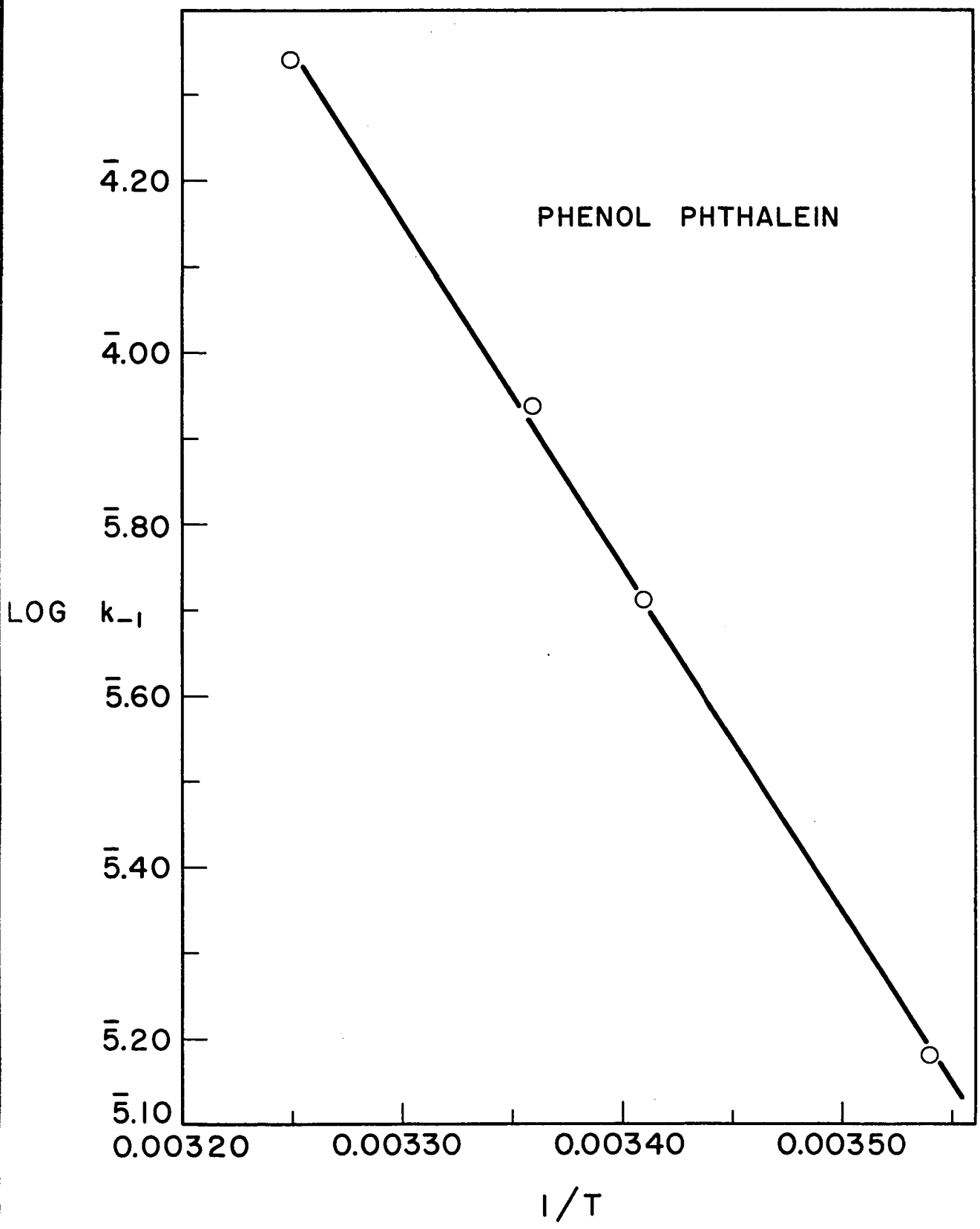


Figure 10 Plot of log k_{-1} against 1/T, for phenol phthalein.

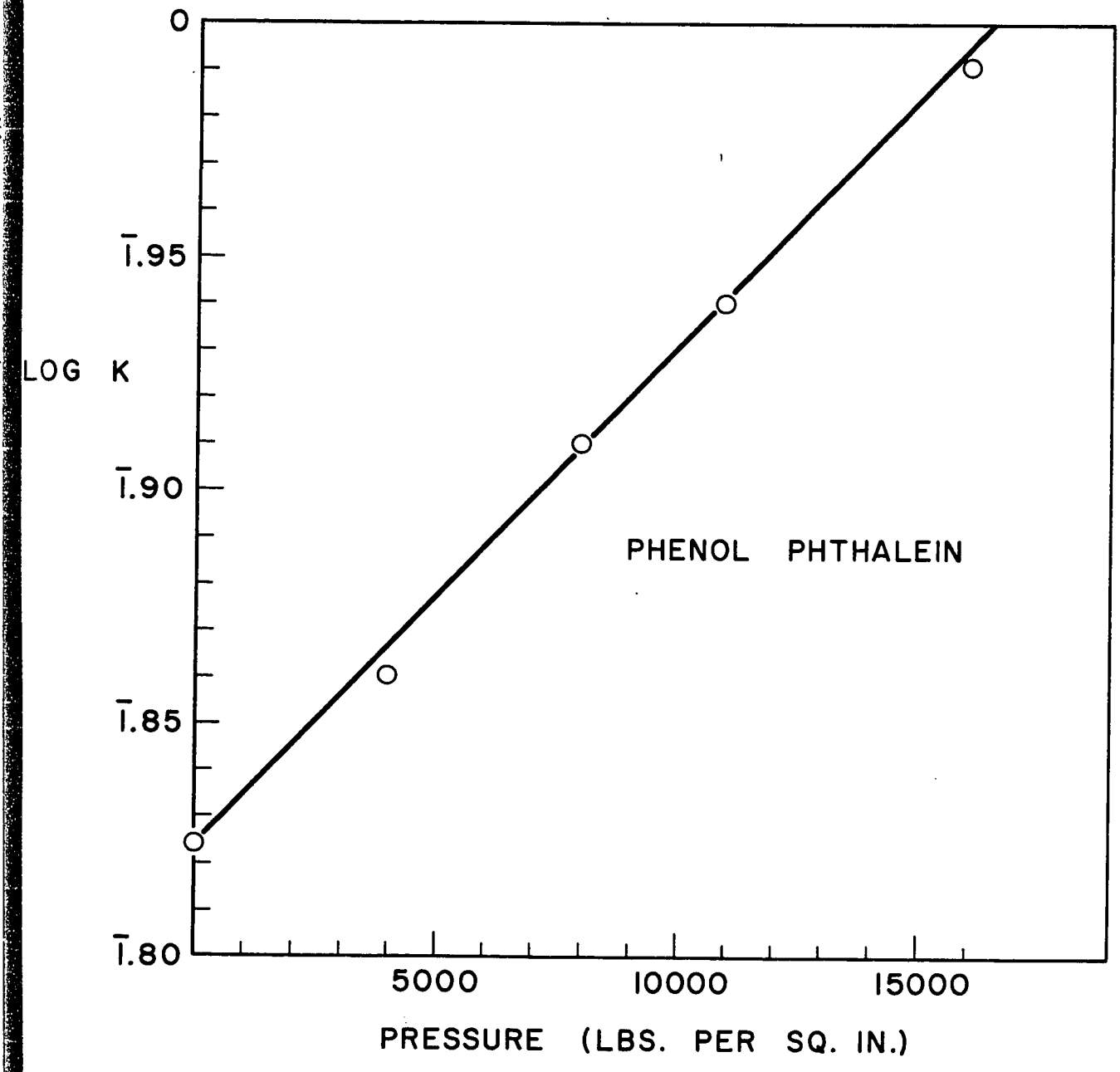


Figure 11 Plot of log K against the pressure, for phenol phthalein.

Table 7

Rate and equilibrium constants for the fading of phenol phthalein at various pressures

$T = 25.0^{\circ}C$

$P(lbs.in.^{-2})$	14.7	4000	8000	11000	16000
$(k_1' + k_{-1}) \times 10^4 (sec.^{-1})$	1.43	1.68	1.93	2.12	2.32
$K\ (M^{-1})$	66.7	73.6	81.2	87.3	98.0
$k_1' \times 10^5 (sec.^{-1})$	5.72	7.12	8.65	9.86	11.5
$k_1 \times 10^3 (M^{-1} sec.^{-1})$	5.72	7.12	8.65	9.86	11.5
$k_{-1} \times 10^5 (sec.^{-1})$	8.58	9.67	10.7	11.3	12.0
$\frac{k_1}{k_o}$	1	1.245	1.512	1.724	1.993
$\frac{k_{-1}}{k_o}$	1	1.127	1.241	1.317	1.398

$\Delta V_1^* = -19.66\ cc.mole^{-1}$

$\Delta V_{-1}^* = -10.98\ cc.mole^{-1}$

$\Delta V = -8.68\ cc.mole^{-1}$

Table 8

Summary of results for the alkaline fading of crystal violet

$T = 25.0^{\circ}C$

P (lbs.in.$^{-2}$)	14.7	2000	4000	6000	9000	12000	16000
$k_1' \times 10^4$ (sec.$^{-1}$)	5.20	5.22	5.09	5.22	5.32	5.18	5.18
k_1 (M^{-1}sec.$^{-1}$)	0.260	0.261	0.255	0.261	0.266	0.259	0.259
$\frac{k}{k_o}$	1	1.004	0.981	1.004	1.023	0.996	0.996
$\log \frac{k}{k_o}$	0	0.0017	$\bar{1}$.9917	0.0017	0.0098	$\bar{1}$.9983	$\bar{1}$.9983

$\Delta V^{\ddagger} = 0$

Pressure is seen to have essentially no effect on the rates, a conclusion that is verified by the plot shown in Fig. 6.

The results obtained by Turgeon and La Mer (46) at atmospheric pressure are, at an ionic strength of 0.0011 M,

$E = 15.1$ kcal. $mole^{-1}$

$A = 3.13 \times 10^{10}$ M^{-1} $sec.^{-1}$

$\Delta S^* = -12.3$ $cal.deg.^{-1}$ $mole^{-1}$.

DISCUSSION

Comparison with previous work It is somewhat difficult to compare the rate constants obtained in the present investigation with those obtained by previous workers, owing to the different conditions employed. The following comparisons may, however, be of interest.

For brom phenol blue the value of the rate constant obtained at 25.0°C and 1 atm. pressure was 0.000932 M^{-1} $sec.^{-1}$. Extrapolation of Amis and La Mer's (38) results to the same ionic strength (0.2 M) gave 0.000854 M^{-1} $sec.^{-1}$.

For the fading of phenol phthalein the present values of K, k_1 and k_{-1} at 25.0°C and 1 atm. pressure are as shown below:

$K = 65.25\ M^{-1}$

$k_1 = 0.00572\ M^{-1}\ sec.^{-1}$

$k_{-1} = 0.0000858\ sec.^{-1}$.

The values obtained by Barnes and La Mer (43) under the same conditions are:

$K = 66.70\ M^{-1}$

$k_1 = 0.00634\ M^{-1}\ sec.^{-1}$

$k_{-1} = 0.0000972\ sec.^{-1}$.

For crystal violet the value of k_1 obtained in the present work was 0.260 M^{-1} $sec.^{-1}$ at 25.0°C. The value of Turgeon and La Mer (46), corrected to the same ionic strength, was

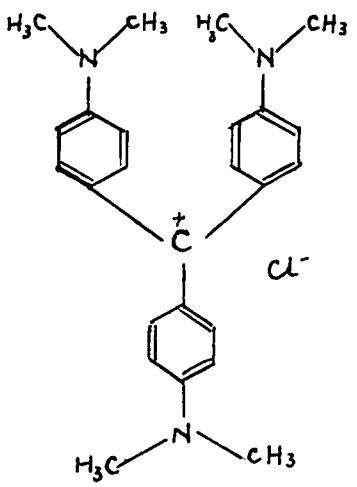
0.256 M^{-1} $sec.^{-1}$. It was found that for this reaction there was some catalysis by the mercury in contact with the solution in the case of the work done in the high pressure vessel; the rate constant in the absence of mercury was 0.207 M^{-1} $sec.^{-1}$.

On the whole the agreement between the results of the present work and those of the previous workers is quite satisfactory.

Significance of the Volumes of Activation The ΔV^* values obtained in the present investigations are listed in the last column of Table 9. Also included in this table are the values of E, A and ΔS^*; the source of these values has been given earlier.

There is again seen to be a fairly good correlation between the volumes and entropies of activation for the reactions. The main discrepancy, although not a very serious one, is found with crystal violet, for which a negative value of ΔV^*, rather than a value of zero, might have been anticipated. A possible explanation for this will now be suggested.

When the hydroxide ion reacts with crystal violet it approaches the central carbon atom, which is at a considerable distance from the positive charges on the molecule, which reside for the most part on the nitrogen atoms. It is true that there is some resonance involving structures like



but owing to the much higher basicity of the nitrogen atom as compared with the carbon atom these structures will not be as important as those in which the positive charge resides on one of the three nitrogen atoms. When the hydroxide ion attacks the carbon atom there is not therefore a very close approach of the ions of opposite sign, and the zero volume of activation may be understood on this basis.

On this view the negative entropy of activation is not to be regarded as arising from electrostriction changes. A loss of entropy of 7.9 e.u. is actually to be expected from the fact that two molecules become one in the activated state (the "cratic" term of Gurney (47)). The remaining loss of entropy may well be due to structural factors; there might, for example, be some interference between the benzene rings when the bonds emanating from the central carbon atom are forced out of the plane.

In the case of the reactions between hydroxide ions and brom phenol blue and phenol phthalein it may be seen from the equations for the reaction that there must be a fairly close approach of the ions of like sign during the course of reaction. On this basis it is possible to understand the strongly negative values observed for the entropies and volumes of activation.

TABLE 9

Summary of Results for the Alkaline Fading of Dyes

Dye	Reaction Type	E (kcal.)	A ($M^{-1}sec.^{-1}$)	ΔS^* (e.u.)	ΔV^* (cc.)
Brom phenol blue	$D^{=} + OH^{-} \longrightarrow DOH^{\equiv}$	12.23	2.04×10^{10}	-13.34	-9.19
Phenol phthalein	$D^{=} + OH^{-} \longrightarrow DOH^{\equiv}$	8.59	1.14×10^{4}	-41.9	-19.7
	$DOH^{\equiv} \longrightarrow D^{=} + OH^{-}$ (reverse reaction)	18.47	3.06×10^{9}	-17.1	-11.0
Crystal violet	$D^{+} + OH^{-} \longrightarrow DOH$	15.1	3.13×10^{10}	-12.3	0

Chapter IV

General Discussion

The main results of the present investigation are summarised in Table 10, which includes, for comparison, certain additional data obtained in aqueous solution.

It is to be noted that there is some correlation between the entropies of activation and the volumes of activation. This is shown in Fig. 12, in which the volumes of activation have been plotted against the uncorrected entropies of activation. A rough correlation of this kind is to be expected in view of the fact that the charges and charge distributions on the reacting molecules and the activated complexes influence both the entropies and the volumes. However, as has recently been discussed in some detail (30, 48), an exact correlation between entropies and volumes of activation is not to be expected in view of the fact that entropies and volumes do not depend upon these charges and charge distributions in exactly the same manner; volumes in fact depend upon the first power of the charge (35, 36) and entropies upon the square of the charge (49, 50, 51).

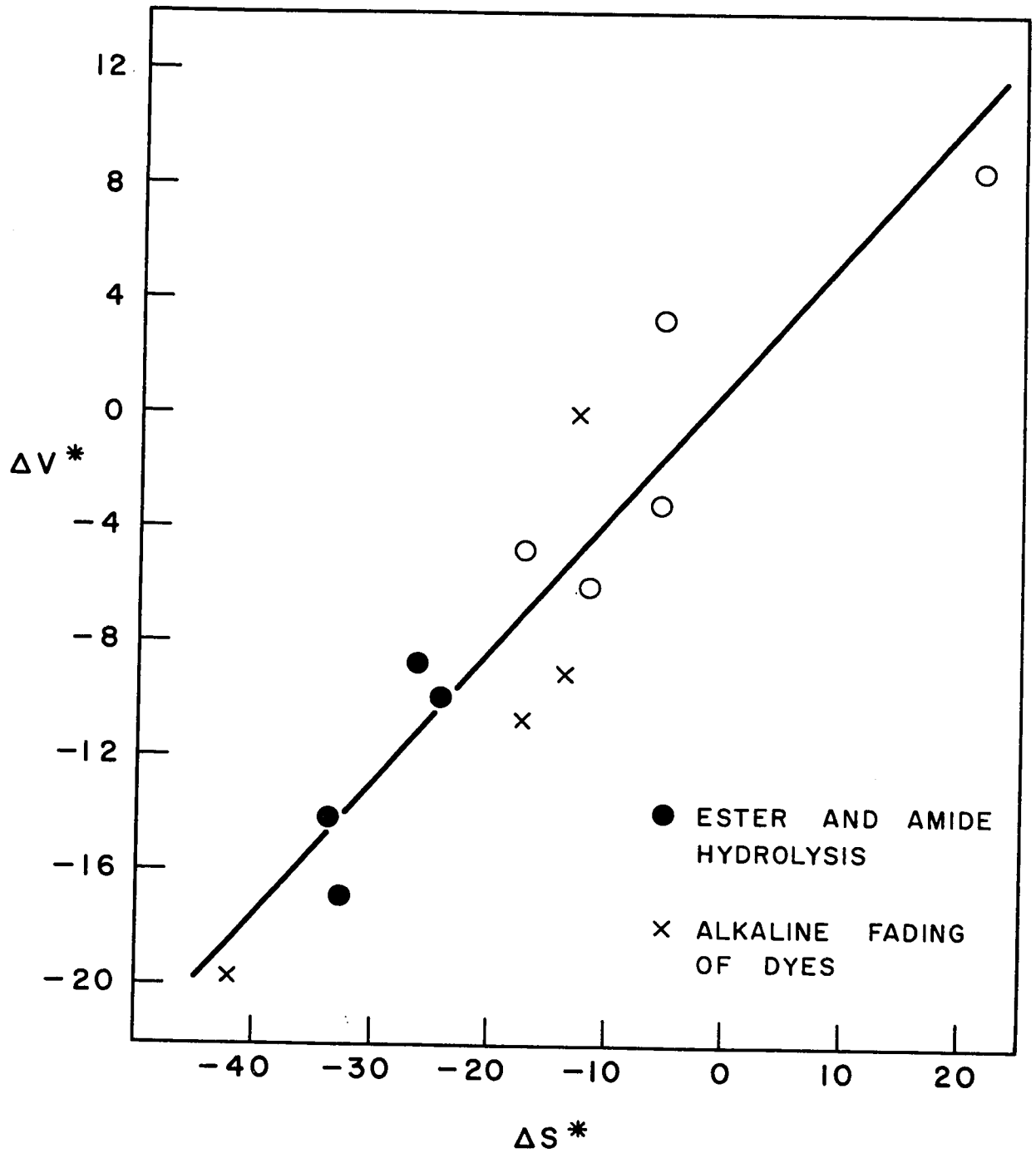


Figure 12 Plot of the volumes of activation against the entropies of activation, for the reactions studied in the present work and for five additional reactions in aqueous solution.

Table 10

Summary of Data for Reactions in Aqueous Solution

Reaction	E (kcal.)	A	ΔS^* (e.u.)	ΔV^* (cc per mole)	Ref.
Methyl acetate + OH^-	12.0	9.3×10^7	-24.1	-9.9	*
Ethyl + OH^-	11.6	3.2×10^7	-26.2	-8.8	*
Acetamide + OH^-	14.2	9.5×10^5	-33.5	-14.2	*
Propionamide + OH^-	14.6	1.5×10^6	-32.6	-16.9	*
Brom phenol blue + OH^-	12.2	2.0×10^{10}	-13.3	-9.2	*
Phenol phthalein + OH^- (k_1)	8.6	1.1×10^4	-41.9	-19.7	*
Phenol phthalein + OH^- (k_{-1})	18.5	3.1×10^9	-17.1	-10.6	*
Crystal violet + OH^-	15.1	3.1×10^{10}	-12.3	0	*
$CH_2BrCOO^- + S_2O_3^=$	13.3	1.6×10^9	-17.0	-4.8	21
$CH_2ClCOO^- + OH^-$	22.7	5.7×10^{10}	-11.6	-6.1	12,14
$CH_2BrCOOCH_3 + S_2O_3^=$	17.2	1.0×10^{14}	- 5.7	-3.2	21
$Co(NH_3)_5 Br^{++} + OH^-$	23.6	5.0×10^{17}	21.7	8.5	21

* Present work

Claims to Original Research.

1. Measurements have been made for the first time of the rates of the alkaline hydrolyses of methyl acetate, ethyl acetate, acetamide and propionamide over a range of hydrostatic pressures from 0 to 15,000 lbs. per square inch.

2. The results have been analysed with reference to van 't Hoff's law, and the resulting volumes of activation interpreted in terms of the detailed mechanism of the reactions.

3. An experimental determination has been made, for the first time, of the energies and entropies of activation for the alkaline hydrolyses of methyl and ethyl acetates in pure aqueous solution.

4. An experimental study has been made of the rates of the alkaline fading of brom phenol blue, phenol phthalein and crystal violet over a range of hydrostatic pressures from 0 to 16,000 lbs. per sq. in.

5. In the case of the fading of phenol phthalein, a study was made of the equilibrium constant of the reaction over a range of hydrostatic pressures. From the results the effect of pressure on the reverse reaction was deduced.

6. A determination has been made, for the first time, of the heat and entropy of reaction, and of the energies and entropies of activation, for the alkaline fading of phenol phthalein in alkaline solution.

7. The pressure results with the dyes have been analysed using the van 't Hoff law and the resulting volumes of activation discussed with reference to the reaction mechanisms.

8. For the ester and amide hydrolyses, and the alkaline fading reactions, a good correlation has been discovered between the measured entropies and volumes of activation.

REFERENCES

1. Berthelot, M and Pean de Saint Gilles, L., Annes.Chim. (Phys.) 36, 231 (1862)
2. Roentgen, W.C., Ann. Phys. Lpz. 45, 98 (1892)
3. Stern, O., ibid, 59, 659 (1896)
4. Rothmund, V., Z.Phys. Chem. 20, 168 (1896)
5. Tammann, G. and Bogojawlensky, A., ibid, 23, 13 (1897)
6. Cohen, E., and de Boer, R.B., ibid, 84, 41 (1913)
7. Cohen, E., and Kaiser, H.F.G., ibid, 89, 338 (1915)
8. Cohen, E. and Valeton, A.M., ibid, 92, 443 (1917)
9. Bridgman, P.W. and Conant, J.B., Proc.Nat. Acad, Sci, 15, 680 (1929)
10. Conant, J.B., and Tongberg, C.O., J. Am. Chem. Soc. 52, 1659 (1930)
11. Gibson, R.O., Fawcett, E.W., and Perrin, M.W., Proc. Roy. Soc. 150A 223 (1935)
12. Williams, E.W., Perrin, M.W., and Gibson, R.O., ibid, 154A, 684 (1936)
13. Perrin, M.W., and Williams, E.W., ibid, 159A, 162 (1937)
14. Perrin, M.W., Trans. Far. Soc., 34, 144 (1938)
15. Newitt, D.M., Linstead, R.P., Sapiro, R.H., and Boorman, E.J., J. Chem. Soc., 876 (1937)
16. P'eng, S.L., Sapiro, R.H., Linstead, R.P., and Newitt, D.M., ibid, 784 (1938)
17. Buchanan, J., and Hamann, S.D., Trans. Far. Soc. 49, 1425 (1953)
18. David, H.G., and Hamann, S.D., ibid, 50,1188 (1954)

19. David, H.G., Hamann, S.D., and Lake, S.J., Aust. J. Chem. 8, 285 (1955)

20. Hamann, S.D., and Teplitzky, D.R., Disc. Far. Soc., 22, 114 (1956)

21. Burris C.T. and Laidler, K.J., Trans.Far. Soc. 51,1497 (1955)

22. Weale, K.E., J. Chem. Soc., 2959, (1954)

23. Harris, R.T., and Weale, K.E., ibid., 953 (1956)

24. Weale, K.E., Disc. Far. Soc. 22, 122 (1956)

25. Ewald, A.H., ibid, 22, 138 (1956)

26. Nicholson, A.E., and Norrish, R.G.W. ibid, 22, 97 (1956)

27. van't Hoff, J.H., Vorlesungen über theoretische und physikalische Chemie, vol.1, 236 (1901)

28. Evans, M.G., and Polanyi, M., Trans. Far. Soc. 31, 875 (1935)

29. Stearn, A.E., and Eyring, H., Chem. Rev., 29, 509 (1941)

30. Laidler, K.J., Disc. Far. Soc. 22, 88 (1956)

31. Laidler, K.J. and Landskroener, P.A., Trans. Far. Soc. 52, 200 (1956)

32. Willems M., and Bruylants, A., Bull. Soc. Chim., Belg. 60, 191 (1951)

33. Potts, J.E. and Amis, E.S., J. Am. Chem. Soc., 71, 2112 (1949)

34. Moelwyn-Hughes, Kinetics of Reactions in Solution, (Clarendon Press, Oxford 1947), p.324

35. Couture A.M., and Laidler, K.J., Can. J. Chem., 34, 1209 (1956)

36. Couture, A.M., and Laidler, K.J., ibid. 35, 207 (1957)

37. Panepinto, F.W., and Kilpatrick, M., J. Am. Chem. Soc. 59, 1871 (1937)

38. Amis, E.S., and La Mer, V.K., ibid, 61, 905 (1939)

39. Kober, P.A., and Marshall, J.T., ibid, 33, 59 (1911)

40. Biddle, H.C., and Porter, C.W., ibid, 37, 1571 (1915)

41. Lund, H., J. Chem. Soc., 1844 (1930)

42. Wygaerts, M., and Eeckhout, J., Natuurw. Tijdchr., 17, 163 (1935)

43. Barnes, M.D., and La Mer, V.K., J. Am. Chem. Soc., 64, 2312 (1942)

44. Hockberg, S., and La Mer, V.K., ibid, 63, 3110 (1941)

45. Goldacre, R.S., and Phillips, J.N., J. Chem. Soc., 1724 (1949)

46. Turgeon, J.C., and La Mer, V.K., J. Am. Chem. Soc., 74, 9588 (1952)

47. Gurney, R.W., Ionic Processes in Solutions (McGraw-Hill Book Co. New York 1953, p.89

48. Laidler, K.J., J. Chim. phys., 54, 485 (1957)

49. Laidler, K.J., Can. J. Chem., 34, 1107 (1956)

50. Laidler, K.J., and Pegis, C., Proc. Roy. Soc., A241, 80 (1957)

51. Couture, A.M., and Laidler, K.J., Can. J. Chem., 35, 202 (1957)