

THE HOMOGENEOUS CATALYTIC ACTIVATION OF
MOLECULAR HYDROGEN BY CUPRIC SALTS
IN AQUEOUS SOLUTION

by

Ernest Peters

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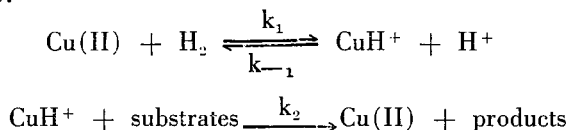
THE HOMOGENEOUS CATALYTIC ACTIVATION OF MOLECULAR HYDROGEN BY CUPRIC SALTS IN AQUEOUS SOLUTION

ABSTRACT

Hydrogen, which is relatively inert at ordinary temperatures, was found to be activated homogeneously in aqueous solution by dissolved cupric salts, as shown by their catalytic effect on the reactions between H_2 and reducible substrates such as $Cr_2O_7^{=}$, IO_3^- , and Ce^{+++} . From kinetic studies of the Cu(II)-catalyzed hydrogenation of $Cr_2O_7^{=}$, it was shown that the catalytic activity of Cu^{++} is greatly influenced by complex-forming reagents. The catalytic activities of cupric complexes were found to decrease in the order: butyrate, propionate > acetate > sulphate > chloride > H_2O (i.e. the uncomplexed Cu^{++} ion) > glycine, ethylenediamine.

In all systems that were studied, the reaction was found to be second order kinetically, the rate being proportional to the concentrations of Cu(II) and H_2 .

The occurrence of an H^+ ion as a product of the initial step of the reaction was postulated to account for the perchloric acid dependence of the rate. The promoting effect of various negative ions, which follows the order of their basicities, was thus explained by assigning to them the role of stabilizing the H^+ ion. The following mechanism was postulated to account for the observed kinetics:



CuH^+ , the activated intermediate suggested by this mechanism, also seems on energetic grounds to be the most plausible of the possible intermediates having reasonable classical structures.

It is suggested that the catalytic activity of Cu^{++} is related to its electron affinity. An attempt is made to extend this interpretation to other homogeneous and heterogeneous hydrogenation catalysts.

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- Studies in the Carbonate Leaching of Uranium Ores. II. Kinetics of the Dissolution of Pitchblende: E. Peters and J. Halpern. Transactions of the Canadian Institute of Mining and Metallurgy, 56: 350-4. 1953.
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- Effect of Complexing on the Homogeneous Catalytic Activation of Hydrogen by Cupric Salts: E. Peters and J. Halpern. Canadian Journal of Chemistry, 34: 554-62. 1956.
- Nature of the Activated Intermediate in the Homogeneous Catalytic Activation of Hydrogen by Cupric Salts: J. Halpern, E. R. Macgregor and E. Peters. Submitted to Journal of Physical Chemistry.

GRADUATE STUDIES

Field of Study: Metal Chemistry

Metallurgical Thermodynamics and Kinetics	C. S. Samis
Theory of Metal Reactions.....	J. Halpern
Structure of Metal Compounds.....	J. Halpern
Metal Surface Chemistry.....	H. G. V. Evans
Theory of Alloys.....	J. G. Parr

Other Studies:

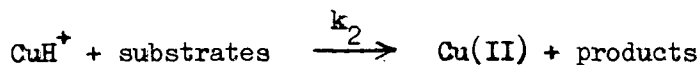
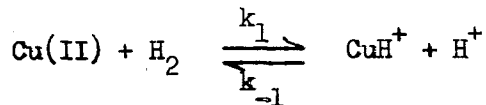
Advanced Physical Metallurgy.....	W. M. Armstrong
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Colloid Chemistry.....	M. Kirsch
Industrial Kinetics and Catalysis.....	D. S. Scott
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Magnetic Properties of Metals.....	H. P. Myers

ABSTRACT

Hydrogen, which is relatively inert at ordinary temperatures, was found to be activated homogeneously in aqueous solution by dissolved cupric salts, as shown by their catalytic effect on the reactions between H_2 and reducible substrates such as $Cr_2O_7^{=}$, IO_3^- , and Ce^{++++} . From kinetic studies of the Cu(II)-catalyzed hydrogenation of $Cr_2O_7^{=}$, it was shown that the catalytic activity of Cu^{++} is greatly influenced by complex-forming reagents. The catalytic activities of cupric complexes were found to decrease in the order: butyrate, propionate > acetate > sulphate > chloride > H_2O (i.e. the uncomplexed Cu^{++} ion) > glycine, ethylenediamine.

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The occurrence of an H^+ ion as a product of the initial step of the reaction was postulated to account for the perchloric acid dependence of the rate. The promoting effect of various negative ions, which follows the order of their basicities, was thus explained by assigning to them the role of stabilizing the H^+ ion. The following mechanism was postulated to account for the observed kinetics:



CuH^+ , the activated intermediate suggested by this mechanism, also seems on energetic grounds to be the most plausible of the possible inter-

mediates having reasonable classical structures.

It is suggested that the catalytic activity of Cu^{++} is related to its electron affinity. An attempt is made to extend this interpretation to other homogeneous and heterogeneous hydrogenation catalysts.

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THE HOMOGENEOUS CATALYTIC ACTIVATION OF MOLECULAR HYDROGEN
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INTRODUCTION

HYDROMETALLURGICAL APPLICATIONS OF HYDROGENATION REACTIONS

The use of hydrogen as a metallurgical reducing agent in the preparation of metals from their compounds has been appreciated for many years, but commercial interest in this application is of comparatively recent origin. This interest has resulted largely from the increased use of hydrometallurgical "leaching" processes in the treatment of certain low grade ores of copper, nickel, cobalt, uranium, and vanadium, which yield solutions from which the metals or their lower oxides can be conveniently displaced by hydrogen. From thermodynamic considerations of the metal precipitation reactions, it is apparent that the application of this procedure is essentially limited to those metals which lie below or immediately above hydrogen in the electromotive series. Some measure of favourable displacement of the reduction equilibrium can usually be achieved by increasing the partial pressure of hydrogen or the temperature. In addition the formation of an insoluble compound (such as an oxide) of the metal in a lower valence state, may sometimes be utilized to advantage.

From a kinetic standpoint, molecular hydrogen is relatively inert, and usually requires the presence of a catalyst to react at temperatures much below 600°C. The most active catalysts are the transition metals including Ni, Pt, and Pd, and certain metallic oxides such as Cr_2O_3 , ZnO, CuO, and their mixtures (1). Early attempts by Ipatieff and his co-workers (2) to displace metals from solution at temperatures up to 300°C. and with hydrogen pressures up to 600 atm. therefore met with varying degrees of success,

depending on the catalytic activity of the dissolved metal salts, the precipitated products, or the walls of the container. In the course of these investigations, Ipatieff succeeded in precipitating Cu, Bi, Pb, Co, Ni, and Fe by hydrogen, either in metallic form or as oxides of lower valence, from aqueous solutions of their salts. In recent years a number of processes have been developed which utilize hydrogenation reactions of this type to yield metallic Ni and Co as well as the oxides UO_2 and V_2O_3 from alkaline leach solutions (3,4,5). In each case a heterogeneous hydrogenation reaction is involved (6). In the precipitation of the oxides an extraneous catalyst, such as metallic Ni, must be present to catalyze the reduction of the dissolved salt (4,5).

HYDROGENATION CATALYSIS

Both from the standpoint of applications such as these, and as a matter of fundamental interest, great importance attaches to the understanding of the mechanism of hydrogenation catalysis. In general, the detailed mechanism by which hydrogenation catalysts function is not fully understood, in spite of their widespread application and the extensive study to which they have been subjected. The low reactivity of molecular hydrogen has been attributed to its high dissociation energy (103 kilocalories (7,8)) coupled with its closed shell ground state electronic configuration. Thus in the homogeneous gas phase reactions of hydrogen with other electronically saturated molecules, a substantial portion of the dissociation energy must usually be expended in the activation process, as evidenced by the suggested value (9) of 61 kilocalories for the activation energy of the $H_2 - CO$ reaction, by the high ignition temperature (580°C.) of hydrogen-oxygen mixtures, and by the immeasurably low rate of the $H_2 - CO_2$ reaction at temperatures below 600°C. (10).

The heterogeneous activation of molecular hydrogen, which is believed to enter into the catalysis of hydrogenation reactions, is most commonly ex-

plained in terms of a mechanism that involves homolytic splitting of the molecule on the catalyst surface with simultaneous formation of covalent bonds between the H atoms and two adjacent surface atoms (11). Application of the absolute reaction rate theory to this model has shown that the activation energy of the adsorption process should depend on the distance between adjacent surface sites (11,12). This interpretation implies a correlation between catalytic activity and the lattice parameter of the catalyst. Evidence for such a correlation has been observed experimentally for several hydrogenation reactions (13).

An alternative approach to the interpretation of hydrogenation catalysis relates the activity of solid catalysts to their electronic properties. Thus Couper and Eley (14) have proposed that d-band vacancies (i.e. unpaired d electrons) are essential for the catalytic activity of metals. This is helpful in explaining the high catalytic activities usually observed for the transition metals, and the decrease in catalytic activity which occurs when these metals are alloyed with elements such as Cu, Hg, Pb, Bi, etc., whose valence electrons enter into and fill the d-band of the transition metal (15). Thus the rate of parahydrogen conversion on Pd-Au alloys decreases markedly when the Au content reaches 60%, the concentration at which the d-band is just filled (14). Similar observations have been made for the hydrogenation of styrene and for the decomposition of formic acid and methanol on various alloys (16).

These results have been interpreted to imply the formation of covalent bonds between the metal catalyst and the adsorbed reactants, or, alternately, the entry of electrons from the latter into the unfilled electronic levels or bands of the catalyst. The latter view has received particular support from kinetic studies by Schwab (17) on the dehydrogenation of formic acid on silver alloys, where the activation energy was observed to increase

linearly with the square of the electron concentration of the Hume-Rothery α -phase. This has been interpreted to imply that catalytic activation involves the entry of two electrons from the formic acid molecule into the conduction band of the metal. Among the intermetallic Hume-Rothery phases, the γ -phase (in which the conduction band is nearly full) showed a maximum activation energy. Similar considerations have been applied to the interpretation of the catalytic activity of metal oxides, the most active of which are defect semi-conductors such as ZnCr_2O_4 , which can readily accept electrons (18).

Dowden (19,20) has attempted to provide a theoretical basis for the electronic interpretation of the catalytic activity of solids, and has shown how the catalytic activity may be related to the electronic work function, Θ , the energy density of electron levels at the Fermi surface $[g(E)]_{E = -\Theta}$, and the gradient of the latter $[dg(E) / dE]_{E = -\Theta} = G$. The energy density is a maximum when a d -band is partially filled, and the gradient, G , depends on the extent of filling of the whole Brillouin zone.

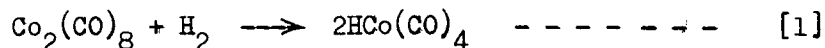
HOMOGENEOUS ACTIVATION OF HYDROGEN IN SOLUTION

By virtue of their much greater simplicity, the study of homogeneous hydrogenation catalysts should provide results which are more amenable to detailed interpretation and capable of discriminating more critically between alternative theories, than in the case of solid catalysts.

The first clear-cut example of the homogeneous activation of hydrogen in solution, observed by Calvin in 1938, was the hydrogenation of cupric acetate and cupric salicylaldehyde, dissolved in quinoline, to the corresponding cuprous salts (21, 22). The autocatalytic nature of the reactions suggested that the cuprous salt being produced was the effective catalyst, a view which was confirmed when it was demonstrated that other substrates such as quinone could also be hydrogenated homogeneously in the presence of dissolved cuprous acetate.

The kinetics of this reaction were found to be first order in dissolved hydrogen and between first and second order in the concentration of the cuprous salt. The latter result was originally interpreted as indicating that a dimer of cuprous acetate was the effective catalyst responsible for activating the hydrogen. Subsequent detailed studies of this system (23,24,25,26,27) substantiated the essential results and conclusions of the original work, demonstrating conclusively that hydrogen is activated homogeneously. However, in the light of recent work (27) it appears likely that the rate determining step, in which hydrogen is activated, involves the interaction of a hydrogen molecule with two cuprous acetate molecules (rather than with a dimer). An intermediate, hydrogen-carrying complex is thus formed which reacts rapidly with the reducible substrate, or which leads to parahydrogen conversion or hydrogen-deuterium exchange, but which decomposes only slowly to metallic copper.

Another system in which hydrogen is activated homogeneously and which has attracted much interest in recent years is the "OXO" or hydroformylation synthesis (28,29), in which an olefin reacts with hydrogen and carbon monoxide in the presence of metallic cobalt. Simple hydrogenation reactions have also been observed under these conditions (30,31,32). Studies in this system (32) have shown that H₂ is apparently activated by reaction with dicobalt octacarbonyl, i.e.



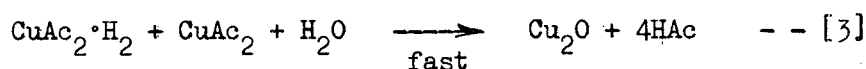
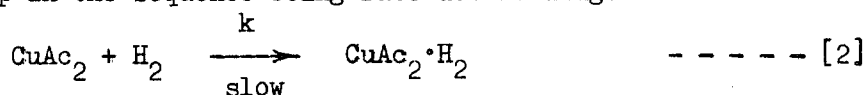
while the observed products result from the subsequent reaction of HCo(CO)₄ with the olefin. These reactions are homogeneous and proceed in a variety of organic solvents.

A number of further examples of homogeneous hydrogenation reactions in organic liquids, which have been reported recently, involve the activation of hydrogen by silver salts (33,34) and by ethylene platinumous chloride (35).

HOMOGENEOUS HYDROGENATION REACTIONS IN AQUEOUS SOLUTIONS

The first established homogeneous hydrogenation reaction in aqueous solution is the reduction by hydrogen of cupric acetate to cuprous oxide, reported in 1953 by Dakers and Halpern (36,37,38). This reaction was originally observed by Ipatieff and his co-workers (2) in their early metal displacement experiments. However, its homogeneous nature was not noted, although it was known to proceed rapidly under relatively mild conditions without the addition of any extraneous catalyst.

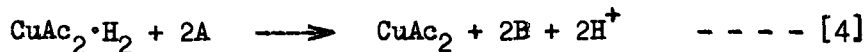
By kinetic studies, Dakers and Halpern showed this reaction to be first order in the concentrations of both dissolved hydrogen and of cupric acetate, and independent of solid surfaces in contact with the solution. The reaction was postulated to proceed through the following mechanism, the first step in the sequence being rate-determining:



The rate-controlling step is a bimolecular reaction between a cupric acetate molecule and a hydrogen molecule to form an intermediate complex whose subsequent fast reaction with cupric acetate and water yields the observed product, Cu_2O . Of special interest is the conclusion that only one metal atom is involved in the hydrogen activation process.

The reaction sequence implies that cupric acetate should also be capable of functioning as a homogeneous catalyst for reactions with hydrogen of other substrates which are thermodynamically more readily reducible than cupric acetate itself, but which do not react with hydrogen in the absence of a catalyst for kinetic reasons. By analogy with early observations on

cuprous acetate, such a substrate might be expected to react preferentially with the complex formed in the first step (equation [2]) to regenerate the cupric acetate molecule, i.e.



where A represents an equivalent of the substrate and B an equivalent of its reduction product.

Confirming this reasoning, it was demonstrated early in the research described in this thesis that substrates such as $\text{Cr}_2\text{O}_7^{=}$, IO_3^- , and Ce^{++++} were reduced by H_2 in the presence of cupric acetate according to this mechanism. The reduction of $\text{Cr}_2\text{O}_7^{=}$ (because of the low concentration which could be accurately determined) proved a particularly convenient reaction for studying the kinetics of the hydrogen activation process, and permitted the accurate determination of very low rates of activation.

The object of the research on which this thesis is based, was to investigate the kinetics of the homogeneous activation of hydrogen by a number of cupric salts. In particular, it was hoped to achieve some information on the following points:

1. Whether other cupric salts share with cupric acetate the ability to activate hydrogen homogeneously.
2. How the catalytic activities of different cupric salts and complexes are related to the structure and configuration of the catalyst species.
3. The detailed mechanism of the hydrogen activation process in these systems, and its relation to the mechanism of heterogeneous hydrogenation catalysis.

Since the work described in this thesis was undertaken, a number of other homogeneous hydrogenation reactions have come to light, partly as a result of this work. In particular, mercuric and mercurous salts have

been shown to activate hydrogen homogeneously (39,40,41), the kinetics of the activating process being analogous to that observed for cupric salts, i.e. first order in the concentration of hydrogen and first order in the concentration of Hg^{++} and Hg_2^{++} . On the other hand, the kinetics of the Ag^+ catalyzed hydrogenation of $\text{Cr}_2\text{O}_7^{=}$ in aqueous solution were found to be first order in hydrogen and second order in the concentration of Ag^+ (42,43). The homogeneous reduction of MnO_4^- by hydrogen in acid solutions is first order in MnO_4^- and H_2 , but in the presence of Ag^+ , a kinetic contribution of the form $k[\text{H}_2][\text{Ag}^+][\text{MnO}_4^-]$ was also noted (43).

EXPERIMENTAL

Glycine and ethylenediamine were of Eastman white label grade; all other chemicals were of reagent grade. Hydrogen and nitrogen gas were supplied in cylinders by the Canadian Liquid Air Company, and were used without further purification. Distilled water was used in the preparation of all solutions.

The reaction studies were conducted in a one-gallon stainless steel autoclave manufactured by Autoclave Engineers, Inc. The autoclave was equipped with a motor-driven propellor type stirrer mounted on a vertical shaft passing through a pressure gland. Auxiliary fittings included a thermo-couple well, a sampling tube, and gas connections through the lid. For solutions corrosive to stainless steel, a titanium liner and fittings were used. The autoclave was heated with a gas ring burner and the temperature was controlled to $\pm 0.3^{\circ}\text{C}$. by a Leeds and Northrop Micromax controlling recorder.

The experimental procedure comprised flushing the autoclave with nitrogen and heating to temperature. When the desired temperature was reached, a number of samples were taken while the solution (usually 3 liters) remained under steam or under a slight partial pressure of nitrogen. Then the desired pressure of hydrogen was introduced. Samples were taken periodically to follow the course of the reaction. When required, a sintered stainless steel filter was placed on the end of the sampling tube so that the samples of solution removed for analysis were free of precipitated products.

Samples of solution were analyzed either for the reactant or for the products of reaction. Most of the studies were concerned with the reduction of $\text{Cr}_2\text{O}_7^{=}$, the concentration of the latter usually being determined spectrophotometrically at its $350 \text{ m}\mu$ absorption peak with a Beckman DU

Spectrophotometer after suitable dilution*. Copper was determined either spectrophotometrically (as the ammine complex at $610\text{ m}\mu$ (36)) or electrolytically. When IO_3^- or Ce^{++++} were used as substrates, their concentrations were measured volumetrically. A known amount of ferrous sulphate was added to the sample and the excess was back titrated with a standard ceric sulphate or potassium permanganate solution. The same procedure was applied to determine $\text{Cr}_2\text{O}_7^{=}$ in chloride solutions, as the chloride complexes of copper, which absorb light at $350\text{ m}\mu$, interfered with the spectrophotometric method.

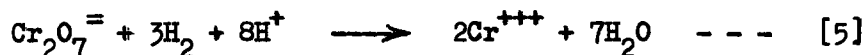
pH measurements were made with a Beckman Model H-2 A.C. pH meter.

* See Appendix A for details of absorption spectra of solutions.

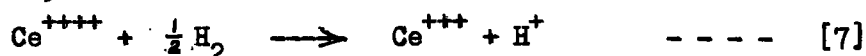
RESULTS AND DISCUSSION

A. CATALYTIC ACTIVATION OF MOLECULAR HYDROGEN BY CUPRIC PERCHLORATE

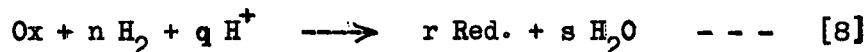
Among the cupric salts that were examined for homogeneous catalytic activity in hydrogenation reactions was cupric perchlorate, which is generally considered to be completely dissociated when dissolved in aqueous perchloric acid solution. Some typical rate plots for the reduction of dichromate by hydrogen in the presence of cupric perchlorate are shown in Fig. 1. At constant temperature and hydrogen pressure, the concentration of $\text{Cr}_2\text{O}_7^{=}$ is seen to decrease linearly with time, corresponding to zero order kinetic behaviour. The slopes of the zero order plots are independent of the initial $\text{Cr}_2\text{O}_7^{=}$ concentration. The stoichiometry of the reaction is represented by



Other substrates, including IO_3^- and Ce^{++++} , were also found to react with hydrogen in the presence of cupric perchlorate, as follows:



or in general



In each case the kinetics of the reduction were zero order with respect to the substrate. No change in the concentration of copper could be detected during the reactions.

The reaction rates were estimated from the slopes of rate plots such as those shown in Fig. 1, after introducing corrections for contributions due to side reactions not involving hydrogen. This contribution, which is

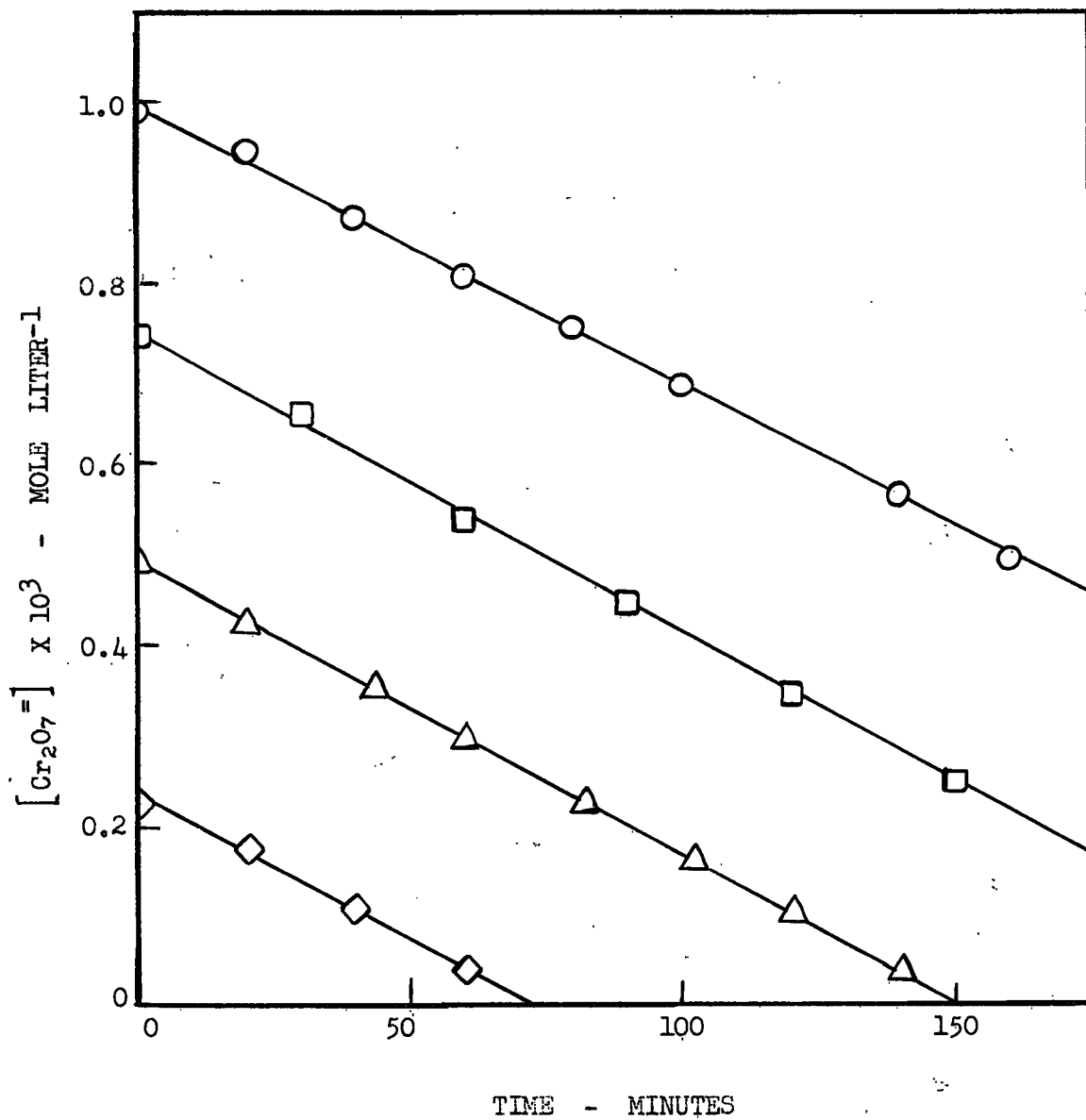


Fig. 1. Typical Rate Plots for the Cupric Perchlorate Catalyzed Reduction of Dichromate by Hydrogen. 0.10 M./L. $\text{Cu}(\text{ClO}_4)_2$; 110°C .; 20 atm. H_2 .

probably due to corrosion of the reaction vessel, was estimated from the rate of reduction of $\text{Cr}_2\text{O}_7^=$ while the reaction mixture was under nitrogen. This correction rarely exceeded 5% of the rate of reaction with hydrogen. Duplicate rate measurements generally reproduced to within $\pm 5\%$ in the case of $\text{Cr}_2\text{O}_7^=$ and IO_3^- and to within $\pm 10\%$ with Ce^{++++} . The rates for different substrates can best be compared by expressing them in terms of the equivalent rates of consumption of hydrogen, calculated from the stoichiometric relation of equation [8], i.e.

$$-d[\text{H}_2]/dt = -nd[\text{Ox}]/dt \quad \text{---} \quad [9]$$

Equivalent rate plots for the reaction of hydrogen with various substrates, i.e. $\text{Cr}_2\text{O}_7^=$, IO_3^- , and Ce^{++++} are shown in Fig. 2. At constant Cu^{++} concentration, the slopes of these plots are seen to be essentially independent of the nature of the substrate, within the limits of experimental uncertainties involved in their comparison. This observation, coupled with the zero order reaction kinetics, strongly suggests that the substrate species does not participate in the rate-determining step, and that this step is the same for all the substrates.

Further indication of this is provided by Fig. 3, in which the rates are plotted as functions of the cupric perchlorate concentration, and the points for $\text{Cr}_2\text{O}_7^=$, IO_3^- , and Ce^{++++} are all seen to lie on a single straight line. The fact that $-d[\text{H}_2]/dt$ is directly proportional to $[\text{Cu}^{++}]$ is consistent with the suggested catalytic role of the latter.

The reaction of $\text{Cr}_2\text{O}_7^=$ proved to be the most convenient one on experimental grounds, and to yield the most precise measurements of the rate of activation of hydrogen. It was therefore selected to elucidate the remaining kinetic variables. Figs. 4 and 5 depict the effect of H_2 on the rate of this reaction. In the range from 0 to 25 atm., $-d[\text{H}_2]/dt$ is seen to

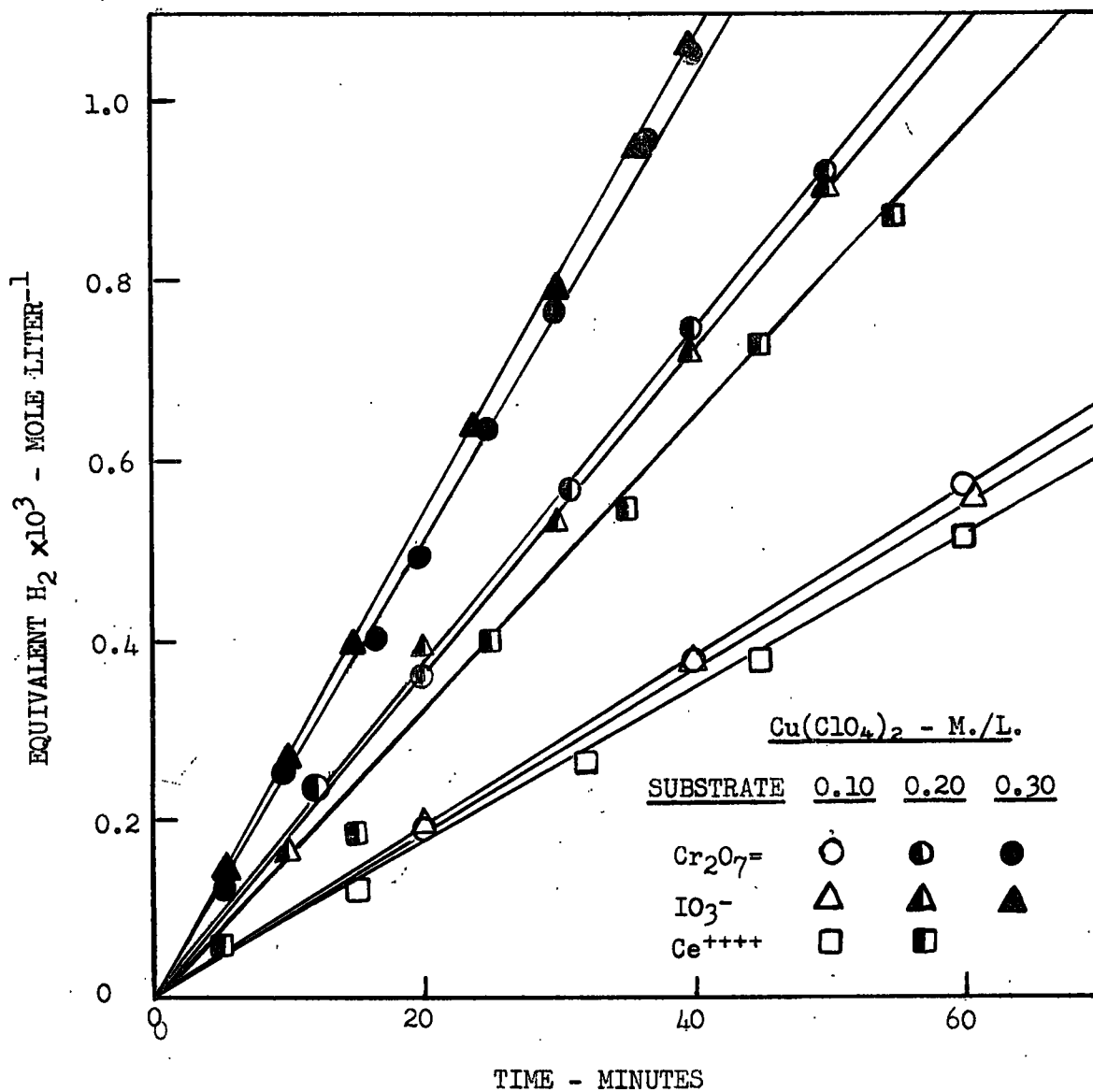


Figure 2.- Comparison of the Reaction Rates for Various Substrates. 110°C; 20 Atm. H₂.

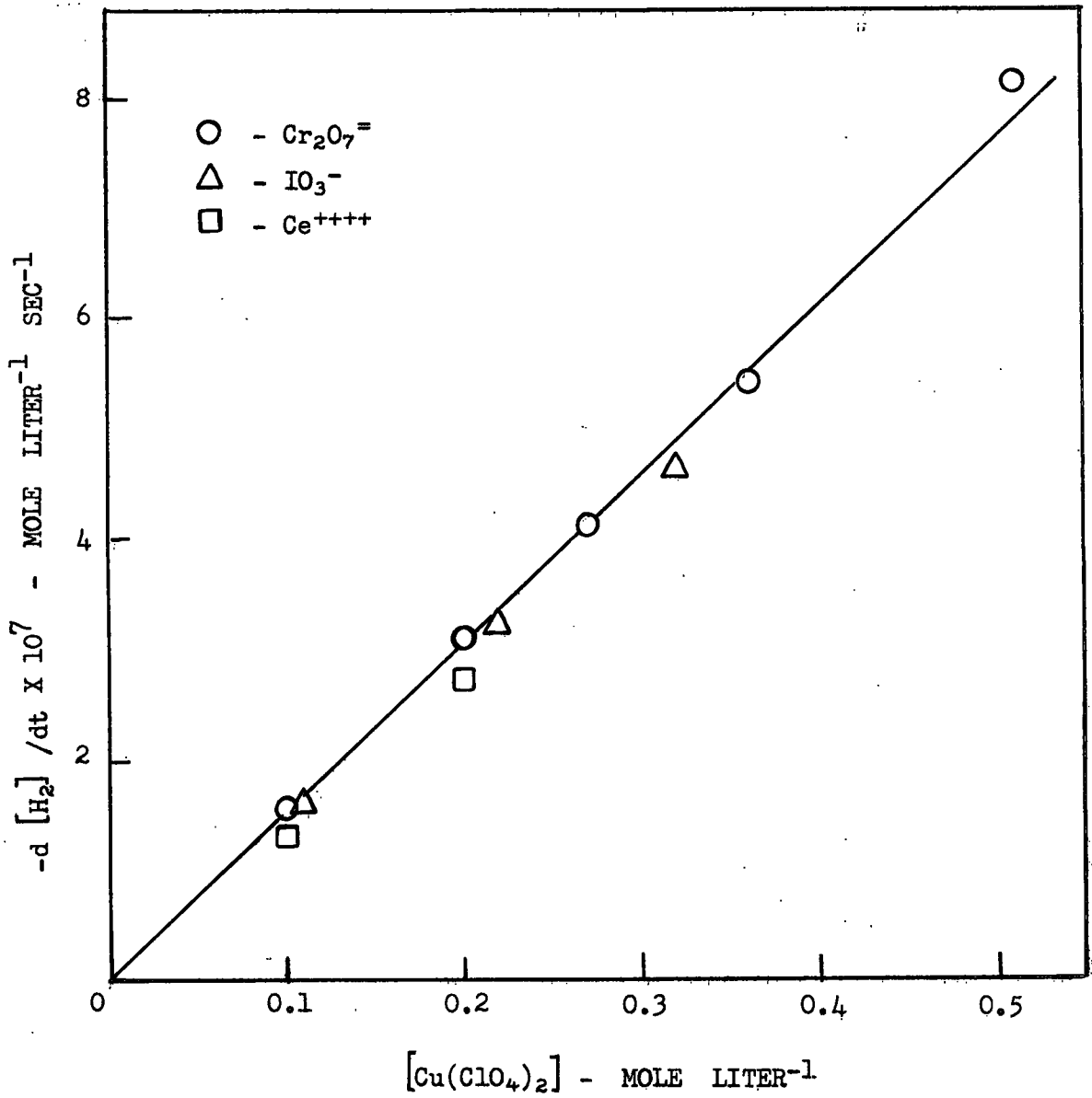


Fig. 3. Dependence of the Reaction Rate on Cupric Perchlorate Concentration; 110°C.; 20 atm. H₂.

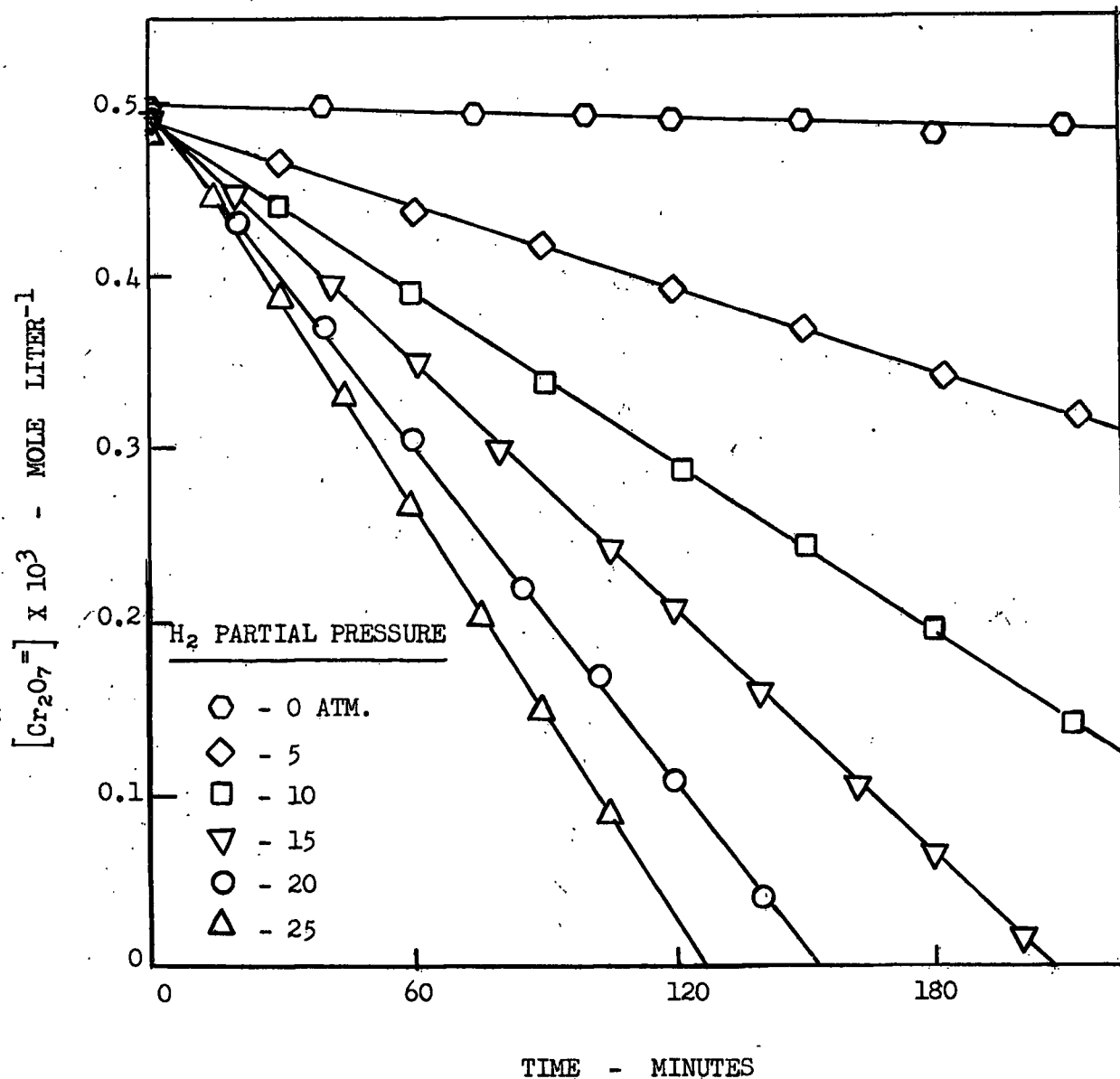


Fig. 4. Reduction of Dichromate in the Presence of Cupric Perchlorate at different Hydrogen Partial Pressures. 0.10 M./L. $\text{Cu}(\text{ClO}_4)_2$; 110°C .

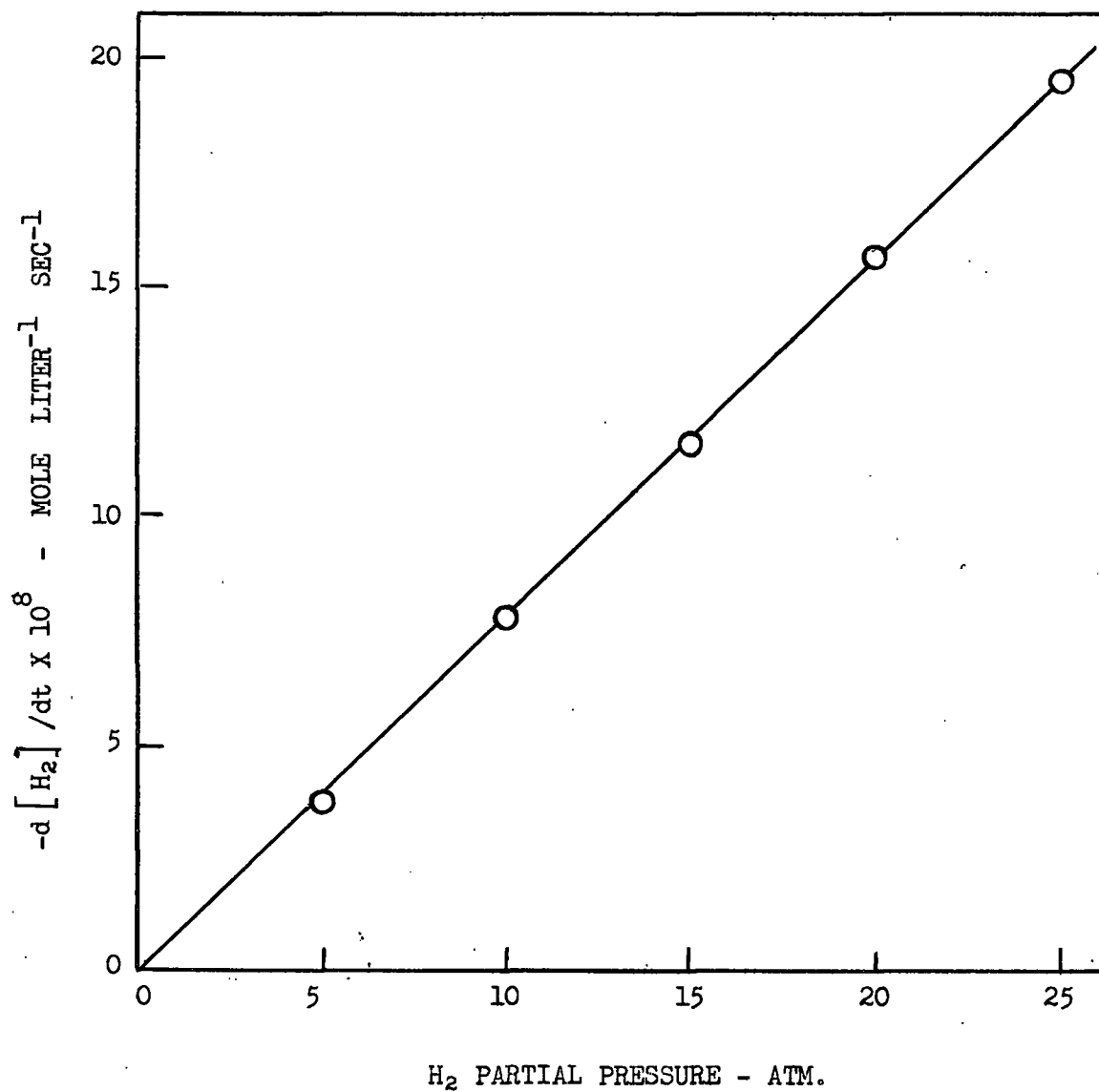


Fig. 5. Dependence of the Reaction Rate on the Hydrogen Partial Pressure. 0.10 M./L. $\text{Cu}(\text{ClO}_4)_2$; 110°C.

be directly proportional to the hydrogen partial pressure. The residual rate of disappearance of $\text{Cr}_2\text{O}_7^{=}$ in the absence of hydrogen, evident in Fig. 4, was subtracted from the slopes of the other rate plots to evaluate $-d[\text{H}_2]/dt$.

The rate of reaction can thus be represented by

$$-d[\text{H}_2]/dt = k'[\text{Cu}^{++}]P_{\text{H}_2} = k[\text{Cu}^{++}][\text{H}_2] \quad \text{---} \quad [10]$$

where $[\text{H}_2]$ is the concentration of hydrogen in solution, since the system obeys Henry's law (44,45) in the pressure range under consideration.

k' and k are related by Henry's constant, α , denoting the solubility of H_2 , i.e.

$$k' = \alpha k \quad \text{---} \quad [11]$$

The solubility of hydrogen in water varies with temperature, approximately as shown by the plot in Fig. 6, which is based on the data of Wiebe and Gaddy (44) and Pray, Schweichert, and Minnich (45). Values of α used in the calculation of k were taken from this plot, and are listed in the legend of Fig. 6.

At 100°C., the experimental value of k for the cupric perchlorate-catalyzed reaction between hydrogen and dichromate is 4.0×10^{-5} liter mole⁻¹ sec.⁻¹.

Rate measurements were made at seven different temperatures, ranging from 80 to 140°C. The slope of the resulting plot of $\log k/T$ vs. $1/T$, shown in Fig. 7, corresponds to an apparent enthalpy of activation, ΔH^\ddagger , of $24.6 \pm 1.5^*$ kilocalories per mole.

The rate constant for the cupric perchlorate catalyzed reaction is thus given by

* This large uncertainty in the enthalpy of activation is primarily due to an uncertainty in the variation of the hydrogen solubility with temperature. See Fig. 6.

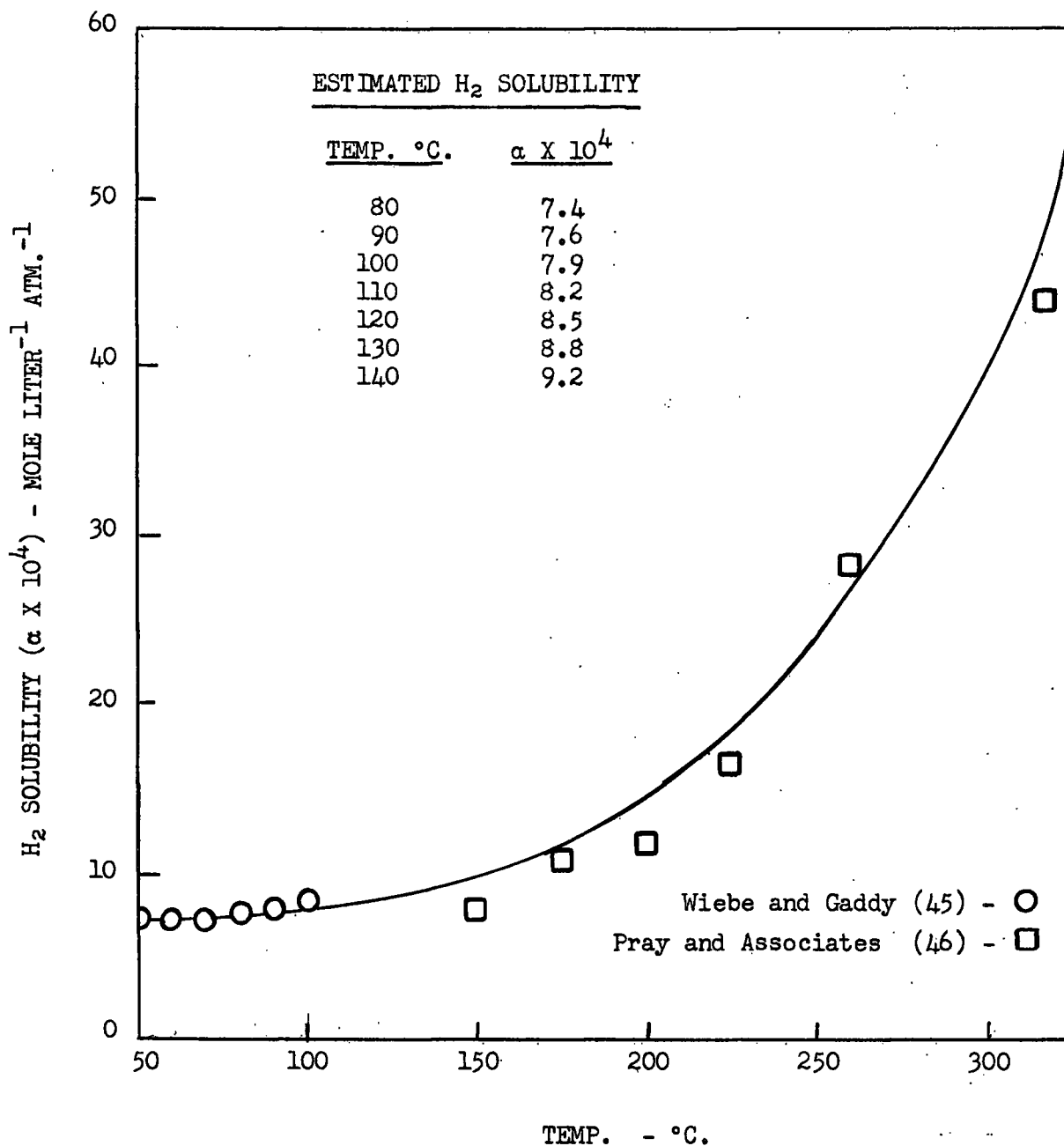


Fig. 6. The Solubility of Hydrogen in Water as a Function of Temperature. Based on Published Data (45,46).

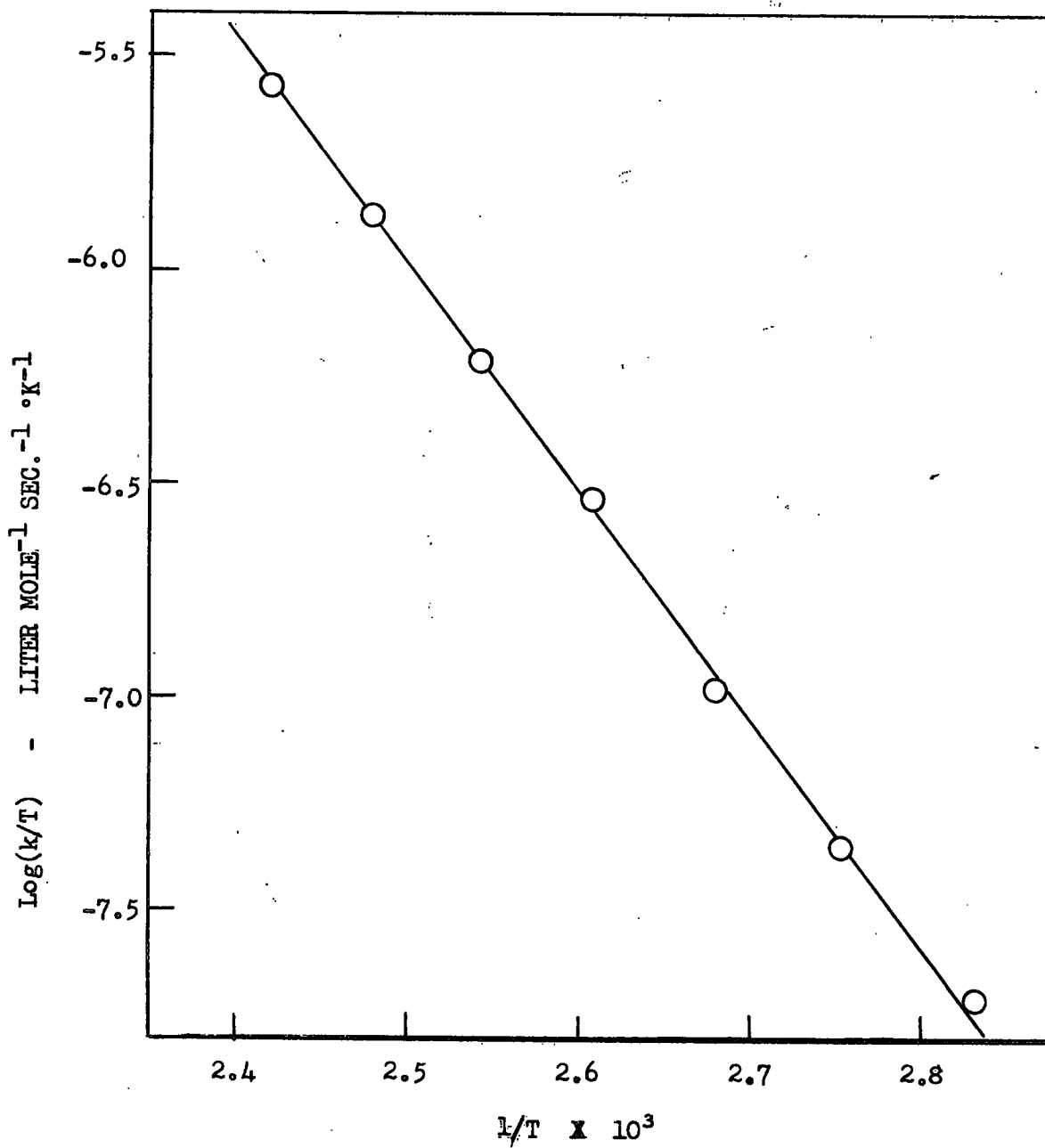


Fig. 7 . Plot of $\text{Log}(k/T)$ vs. $1/T$ for the Cupric Perchloric Catalyzed Reaction between Hydrogen and Dichromate. 0.10 M./L. $\text{Cu}(\text{ClO}_4)_2$; 20 atm. H_2 .

$$k = \frac{KT}{h} \cdot e^{-\frac{24,600}{RT}} \cdot e^{-\frac{13.1}{R}} \quad \text{---} \quad [12]$$

The entropy of activation, ΔS_c^\ddagger , i.e. -13.1 ± 4.0 e.u., is normal for a simple bimolecular reaction in solution (46,47).

In calculating the values of k , it was assumed that the solutions (which contained 0.1 M./L. $\text{Cu}(\text{ClO}_4)_2$, 0.01 M./L. HClO_4 , and 0.0005 M./L. $\text{Na}_2\text{Cr}_2\text{O}_7$) were sufficiently dilute so that α had the same value as that for pure water, i.e. that given in Fig. 6.

In Table I are listed the rates of $\text{Cr}_2\text{O}_7^{=}$ reduction in several solutions of differing salt concentration. The rate of reaction is seen to be essentially independent of NaClO_4 concentration from 0 to 1.0 M./L. Additions of 0.38 M./L. $\text{Ca}(\text{ClO}_4)_2$ or $\text{Zn}(\text{ClO}_4)_2$ were also without effect while 0.25 M./L. $\text{Al}(\text{ClO}_4)_3$ depressed the rate slightly. The general ionic strength effect, if any, is apparently small, consistent with the fact that one of the reactants, i.e., hydrogen, is uncharged. The absence of a specific perchlorate salt effect supports the conclusion that the catalytic activity, observed in this system, is due to the uncomplexed cupric ion.

Direct evidence for the homogeneous character of the reaction is provided by the results of an experiment (W-3, Table I) in which 30 g. of stainless steel powder, of similar composition to the autoclave itself, was added. Although the area of this powder was at least twice that of the autoclave surface normally exposed to the solution, no increase in the reaction rate could be detected.

Varying the stirring efficiency, either by reducing the impeller velocity to 600 r.p.m. from its normal value of 900 r.p.m. (expt. W-2) or by introducing a baffle into the autoclave (expt. W-1) also had no effect on the rate. This indicates, as do other features of the kinetics, that under the

TABLE I

RATES OF REACTION BETWEEN HYDROGEN AND DICHROMATE IN CUPRIC
PERCHLORATE SOLUTIONS OF VARYING COMPOSITION

0.1 M./L. $\text{Cu}(\text{ClO}_4)_2$; 0.010 M./L. HClO_4 ; 0.0005 M./L. $\text{Na}_2\text{Cr}_2\text{O}_7$; 20 atm. H_2 ;
110°C.

Expt. No.	Salt Concentration M./L.	$-\text{d}[\text{H}_2]/\text{dt} \times 10^7$ Mole liter ⁻¹ Sec. ⁻¹	$k \times 10^5$ L. Mole ⁻¹ Sec. ⁻¹
T-10	0.00	1.55	9.5
T-13	0.25 NaClO_4	1.55	9.5
T-14	0.50 "	1.50	9.2
T-15	0.75 "	1.53	9.3
T-12	1.00 "	1.48	9.0
T-16	0.38 $\text{Ca}(\text{ClO}_4)_2$	1.50	9.2
T-17	0.38 $\text{Zn}(\text{ClO}_4)_2$	1.53	9.3
T-18	0.25 $\text{Al}(\text{ClO}_4)_3$	1.39	8.5
W-1 ^a	0.00	1.56	9.5
W-2 ^b	0.00	1.53	9.3
W-3 ^c	0.00	1.49	9.1

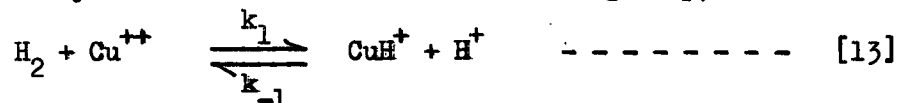
^a Baffle added to increase stirring efficiency.

^b Stirrer velocity decreased from 900 to 600 R.P.M.

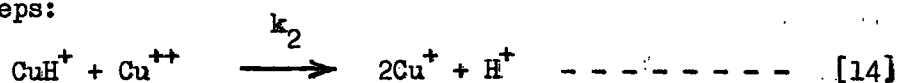
^c 30 g. of stainless steel powder added.

conditions of these experiments, the reaction was not limited by the rate of solution of hydrogen.

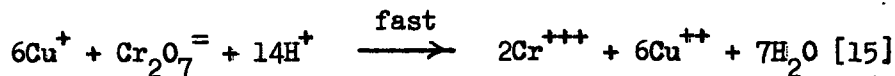
The dependence of the reaction on perchloric acid concentration is shown in Fig. 8. The observed decrease in the rate of reduction of dichromate with increasing acid concentration is believed to be due to a competing reaction involving activated hydrogen but not dichromate. The nature of this competing reaction was not definitely established. The absence of any chloride in the reduced solutions suggests that there is no reduction of perchlorate. The linear relation between $1/k$ and $HClO_4$ concentration, shown in Fig. 8, can be interpreted in terms of a competing reaction, involving H^+ , which is essentially a reversal of the rate-controlling step, i.e.



The simplest mechanism for the subsequent reaction of CuH^+ consistent with the observed zero order kinetics with respect to dichromate, involves the formation of Cu^+ as a further intermediate, through the following sequence of steps:



followed by



Application of the steady state treatment ($-d[CuH^+]/dt = 0$) to the above sequence leads to the following rate law:

$$-d[H_2]/dt = \frac{k_1 [Cu^{++}]^2 [H_2]}{[Cu^{++}] + (k_{-1}/k_2)[H^+]} \quad \text{-----} \quad [16]$$

This implies, in agreement with the results which have been reported, first order kinetics with respect to $[Cu^{++}]$ and $[H_2]$ at low H^+ concentrations, as well as a linear dependence of the reciprocal of the rate on $[H^+]$ at constant

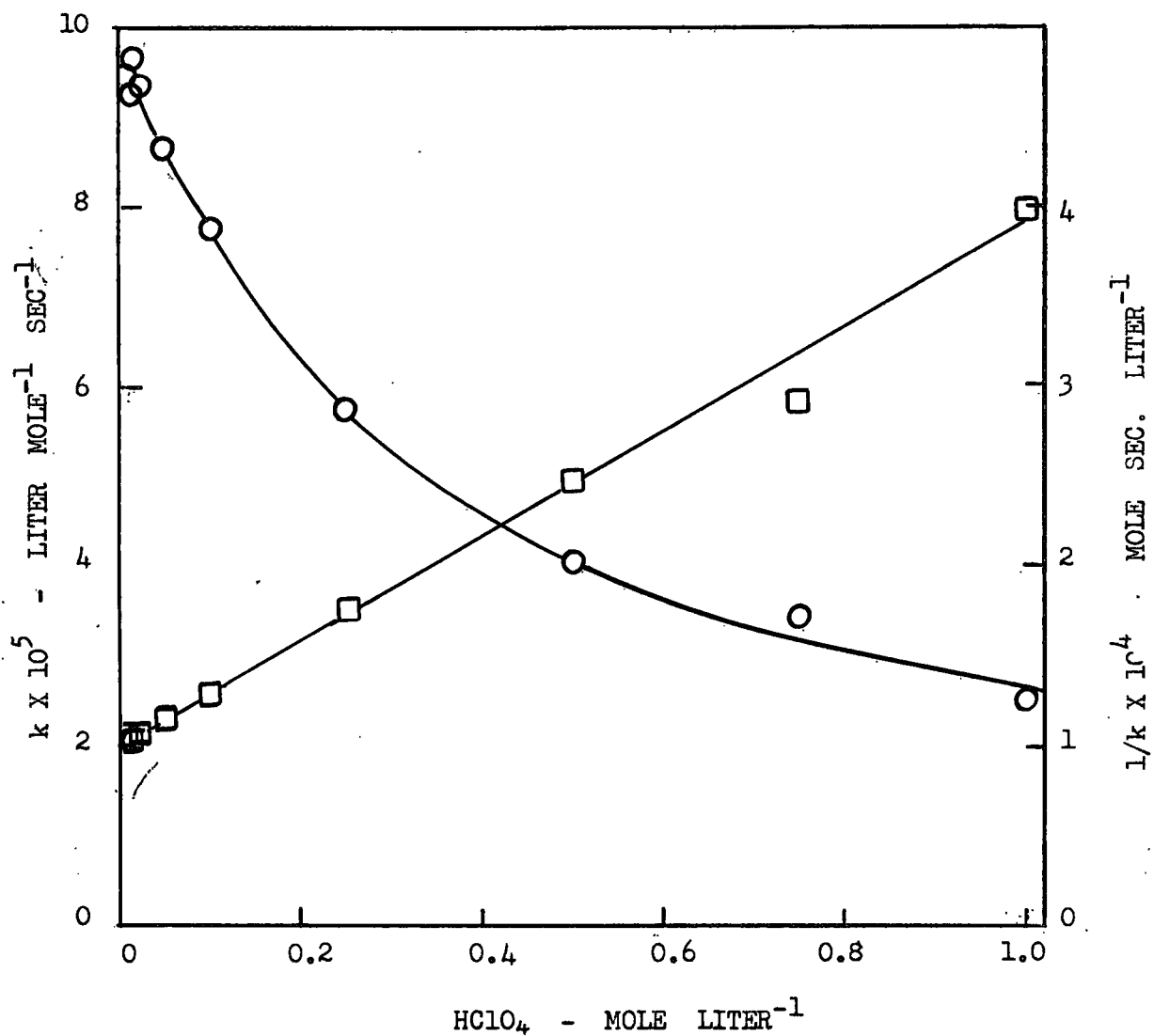
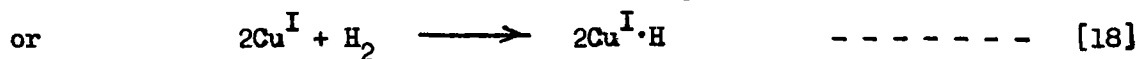
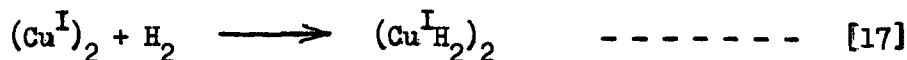


Fig. 8. Dependence of the Reaction Rate on the Perchloric Acid Concentration. 0.10 M./L. $\text{Cu}(\text{ClO}_4)_2$; 20 atm. H_2 .

[Cu⁺⁺] and [H₂]. The further suggestion that at high H⁺ concentrations the kinetic dependence on [Cu⁺⁺] would approach second order, has also recently received experimental support (48).

The intermediate proposed here, CuH⁺, is similar to that which has been postulated for the homogeneous activation of hydrogen by cuprous acetate in quinoline (21,22,24,27). In this system the kinetics demonstrate that two cuprous ions are involved in the rate-determining step which has been depicted as



Further evidence in support of the above mechanism will be presented later.

B. CATALYTIC ACTIVATION OF MOLECULAR HYDROGEN BY CUPRIC ACETATE

A similar kinetic study was made of the reduction of dichromate by hydrogen in the presence of dissolved cupric acetate, which, unlike cupric perchlorate, is known to be largely undissociated in aqueous solution (49). This was of particular interest in view of the earlier studies (36,37,38) on the kinetics of the hydrogenation of cupric acetate itself. As in the case of cupric perchlorate, the reaction was found to be zero order kinetically in Cr₂O₇⁼ (Fig. 9), first order in H₂ (Fig. 10) and nearly first order in CuAc₂ (Figs. 11 and 12). Thus the reaction rate is given by the expression

$$-3d[\text{Cr}_2\text{O}_7^=]/dt = -d[\text{H}_2]/dt = k[\text{CuAc}_2][\text{H}_2] \quad \text{---} \quad [19]$$

The relation between the reaction rate and the cupric acetate concentration is seen to be not quite linear (Fig. 11), k showing a tendency to fall off slightly with increasing cupric acetate. Thus at 100°C. the

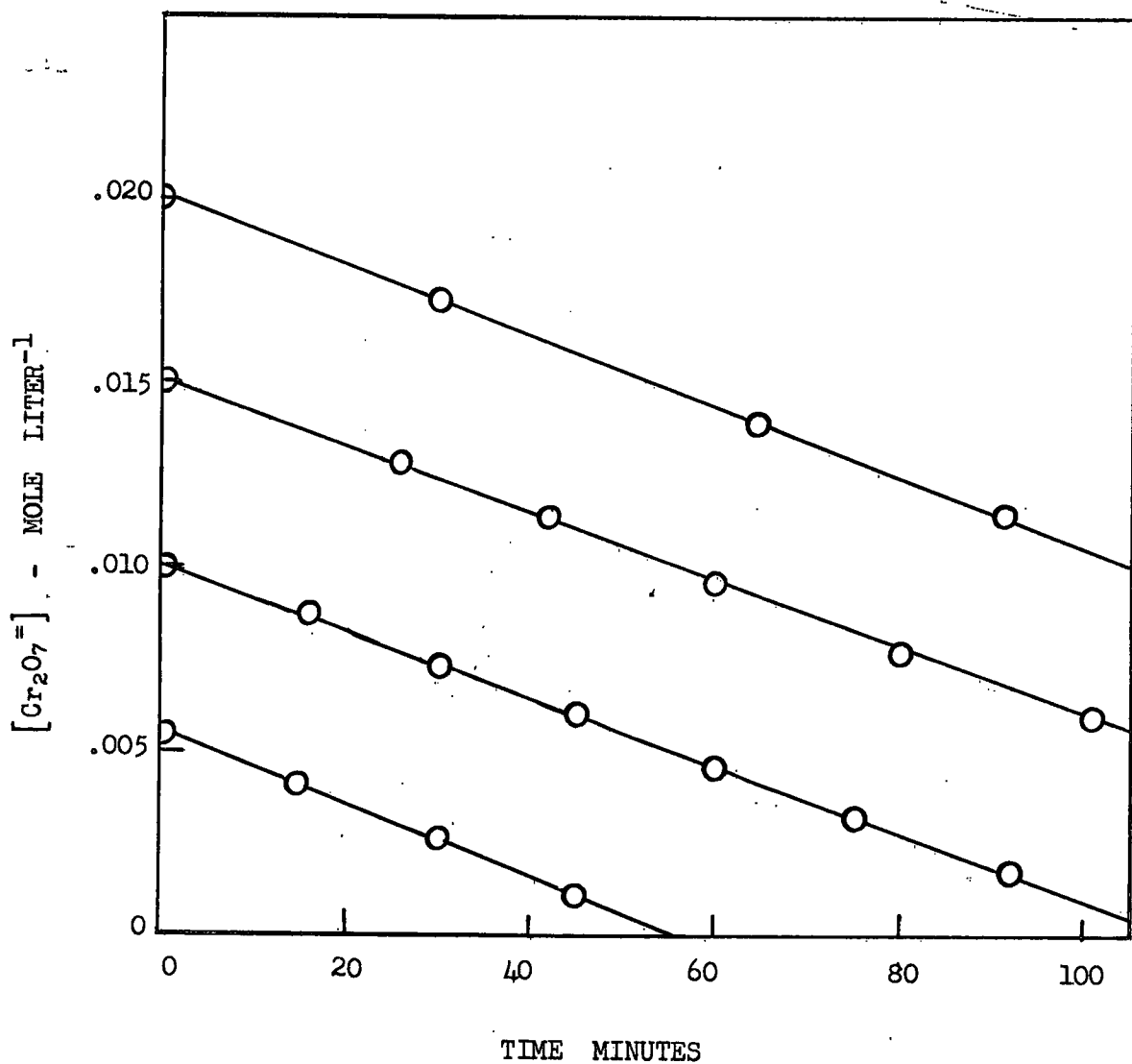


Fig. 9. Typical Rate Plots for the Cupric Acetate Catalyzed Reduction of Dichromate by Hydrogen. 0.10 M./L. $CuAc_2$; $100^\circ C.$; 13.6 atm. H_2 .

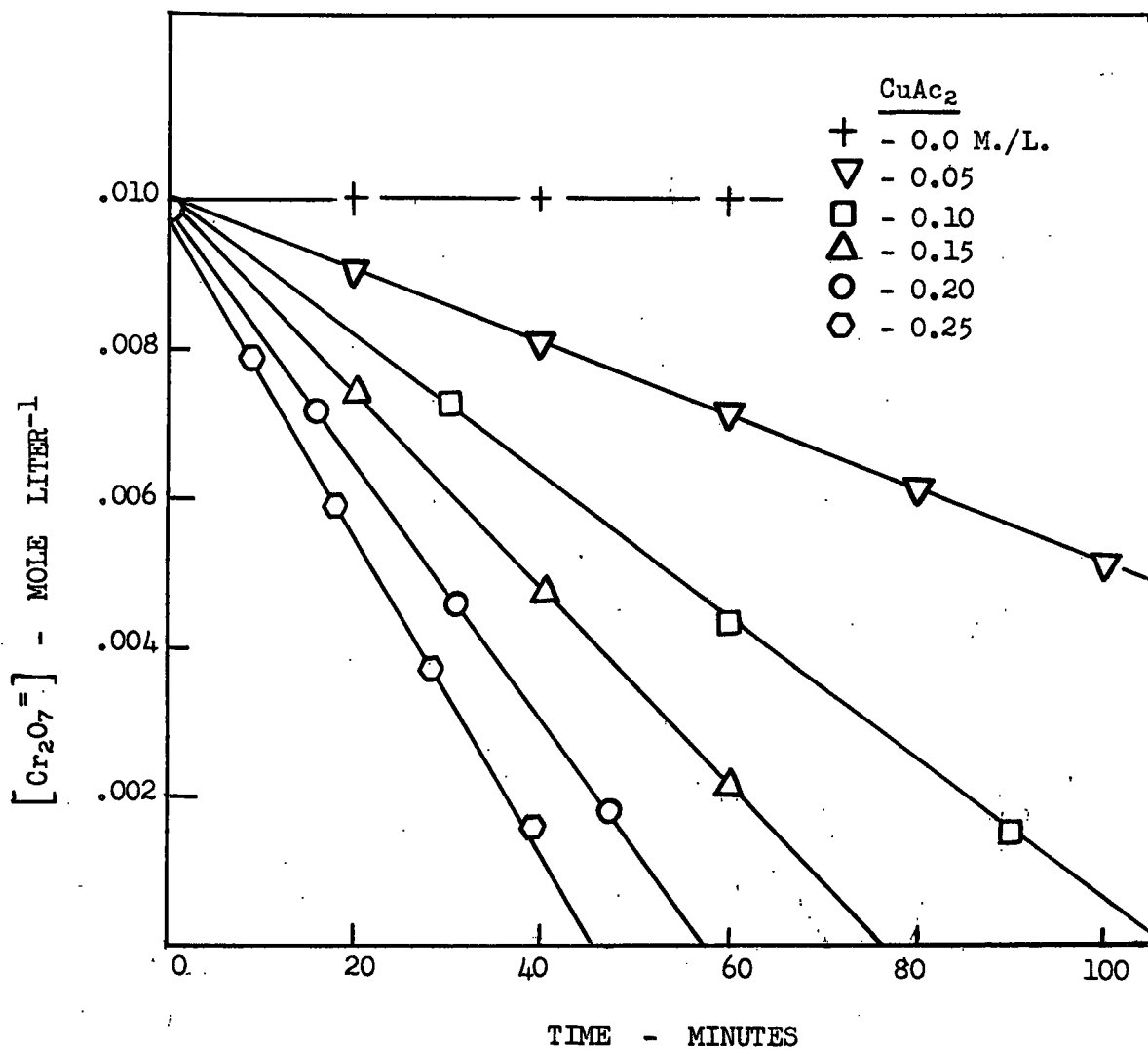


Fig. 10. Rate Plots for the Reduction of Dichromate at Different Cupric Acetate Concentrations. 0.25 M./L. NaAc; 0.50 M./L. HAc; 100°C.; 13.6 atm. H₂.

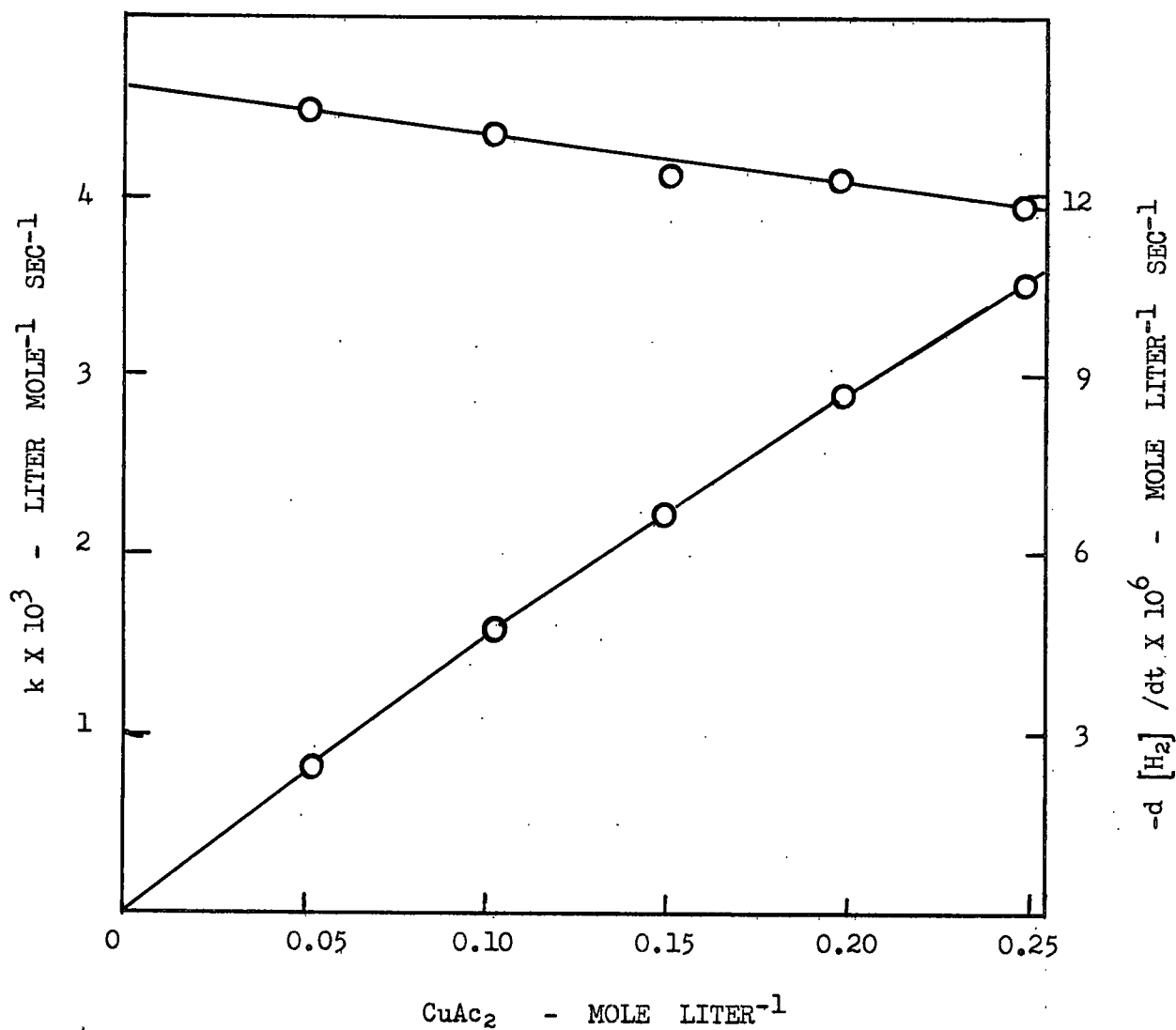


Fig. 11. Dependence of the Reaction Rate on the Cupric Acetate Concentration. 0.25 M./L. NaAc; 0.50 M./L. HAC; 100°C.; 13.6 atm. H₂.

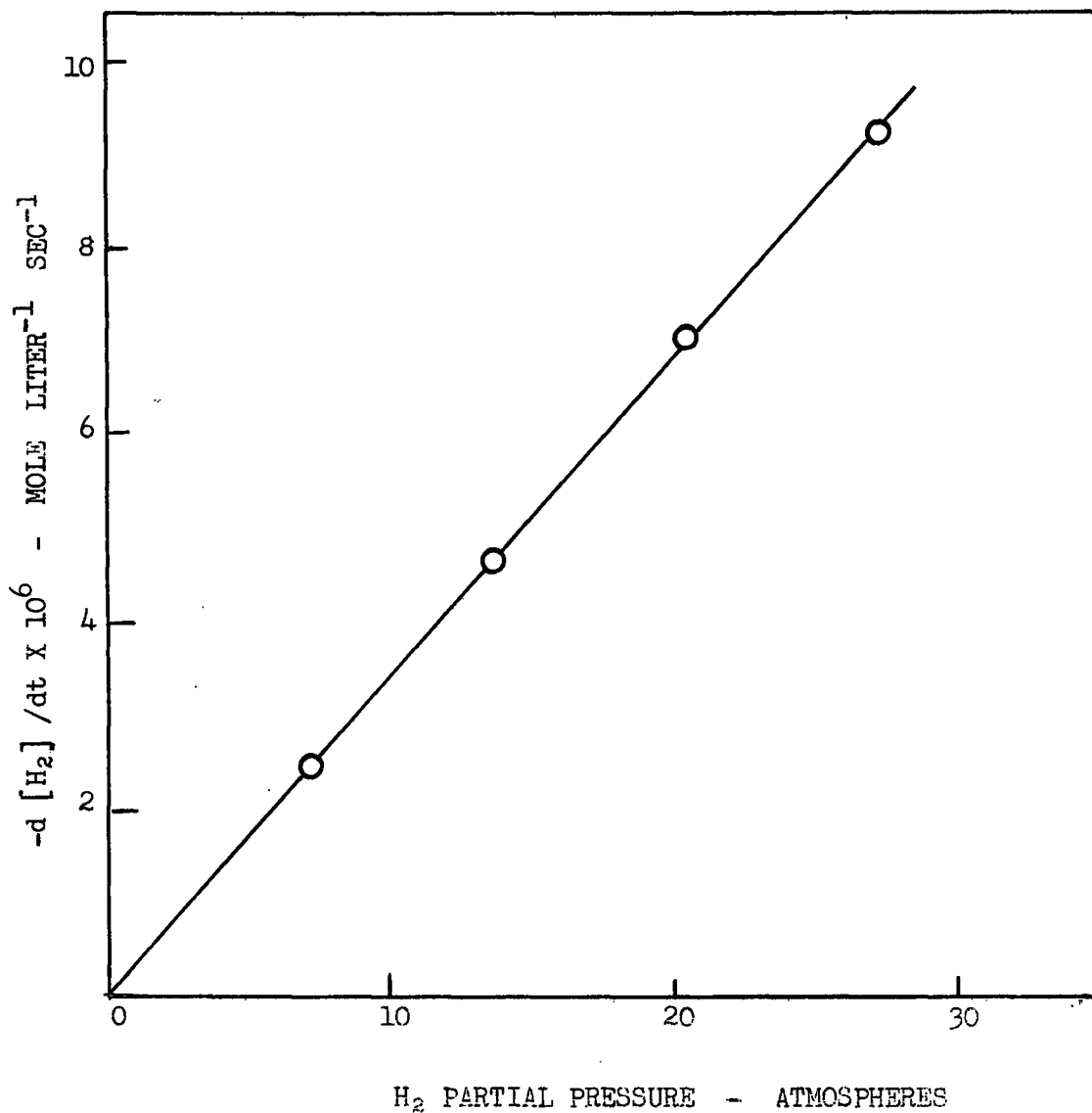


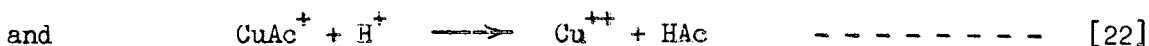
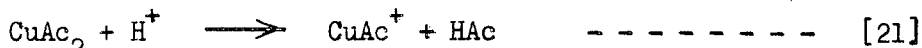
Fig. 12. Dependence of the Rate of the Cupric Acetate Catalyzed Reaction on the Hydrogen Partial Pressure. 0.10 M./L. CuAc₂; 0.25 M./L. NaAc; 0.50 M./L. HAc; 100°C.

value of k , extrapolated to zero $[\text{CuAc}_2]$ is 4.7×10^{-3} l. mole.⁻¹ sec.⁻¹, while at the highest cupric acetate concentration investigated, i.e. 0.25 M./L., it is only 4.05×10^{-3} or about 14% lower. The significance of this decrease will be discussed later.

The rate constant, k , for the cupric acetate catalyzed reduction of dichromate, is thus seen to be nearly 120 times that for the corresponding cupric perchlorate catalyzed reaction. This increased rate is reflected in the correspondingly lower value of ΔH^\ddagger (calculated from the linear plot of $\log (k/T)$ vs. $1/T$ in Fig. 13), i.e. 23.0 ± 1.5 kilocalories per mole. The corresponding entropy of activation, ΔS_e^\ddagger , i.e. -8.0 ± 4.0 e.u., is in reasonable agreement with that reported for the perchlorate system and may be considered normal for a simple bimolecular reaction in solution (46,47). Using the Eyring rate equation, the rate constant may be expressed as:

$$k = \frac{kT}{h} \cdot e^{-\frac{23,000}{RT}} \cdot e^{-\frac{8.0}{R}} \quad \text{-----} \quad [20]$$

In most of these experiments the solutions contained, in addition to sodium dichromate and cupric acetate, 0.25 M./L. of sodium acetate and 0.5 M./L. of acetic acid. The pH was thus buffered at a value of about 4.5 and changed very little during the course of the reaction. That these values are not critical is indicated by the results in Table II which show that wide variations in the acetate and acetic acid concentrations do not affect the rate significantly. However, where sufficient perchloric acid was added to lower the pH of the solution below 4, the rate decreased appreciably, as shown in Fig. 14, presumably as a result of the dissociation of the more active cupric acetate complexes, i.e.



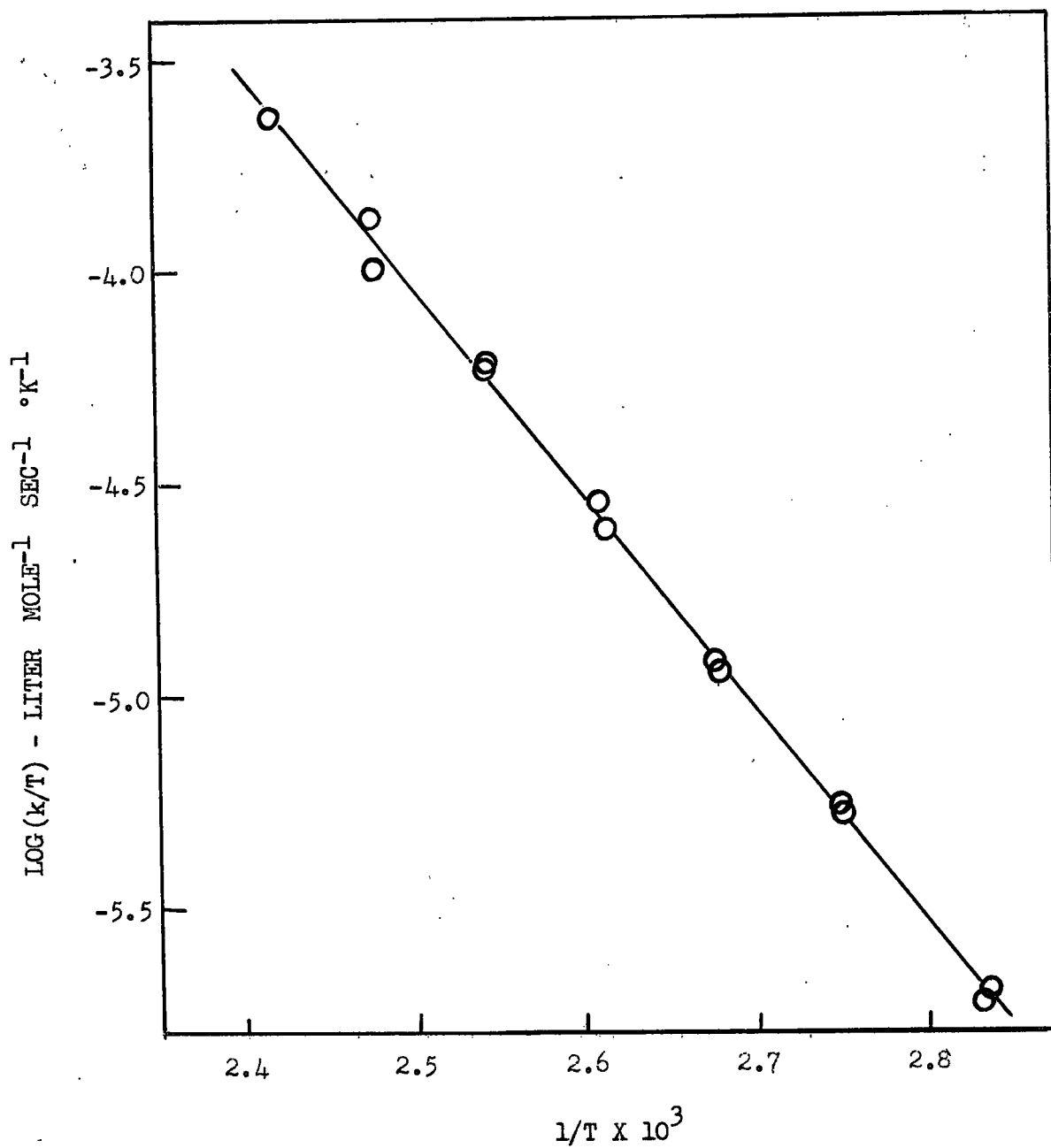


Fig. 13. Plot of $\text{Log}(k/T)$ vs. $1/T$ for the Cupric Acetate Catalyzed Reduction of Dichromate by Hydrogen. 0.05 M./L. CuAc_2 ; 13.6 atm. H_2 .

TABLE II

RATES OF REACTION BETWEEN HYDROGEN AND DICHROMATE IN CUPRIC

ACETATE SOLUTIONS OF VARYING COMPOSITION

0.10 M./L. CuAc_2 ; 100°C.; 13.6 atm. H_2

Solution Composition				Reaction Rate	
Expt. No.	$[\text{Na}_2\text{Cr}_2\text{O}_7]$ M./L.	$[\text{NaAc}]$ M./L.	$[\text{HAc}]$ M./L.	$-\frac{d[\text{H}_2]}{dt} \times 10^6$ mole l. ⁻¹ sec. ⁻¹	$k \times 10^3$ l. mole. ⁻¹ sec. ⁻¹
A-4	0.010	0.25	0.50	4.82	4.49
B-4	0.010	0.25	0.50	5.04	4.69
C-3	0.010	0.25	0.50	4.92	4.57
D-3	0.010	0.25	0.50	4.76	4.43
E-3	0.010	0.25	0.50	4.78	4.45
F-2	0.010	0.25	0.50	4.71	4.38
G-3	0.010	0.25	0.50	4.66	4.33
H-1*	0.010	0.25	0.50	4.66	4.34
C-4	0.005	0.25	0.50	5.13	4.77
C-3	0.010	0.25	0.50	4.92	4.57
C-2	0.015	0.25	0.50	4.62	4.30
C-5	0.020	0.25	0.50	4.76	4.43
F-5	0.010	0.00	0.50	4.61	4.29
F-4	0.010	0.05	0.50	4.71	4.39
F-3	0.010	0.15	0.50	4.74	4.42
F-2	0.010	0.25	0.50	4.71	4.39
F-1	0.010	0.50	0.50	4.79	4.46
G-2	0.010	0.25	0.50	4.66	4.33
G-3	0.010	0.25	0.75	4.75	4.42
G-4	0.010	0.25	1.00	4.63	4.30

* Stirring velocity reduced to 600 r.p.m. In all other experiments stirring velocity was 900 r.p.m.

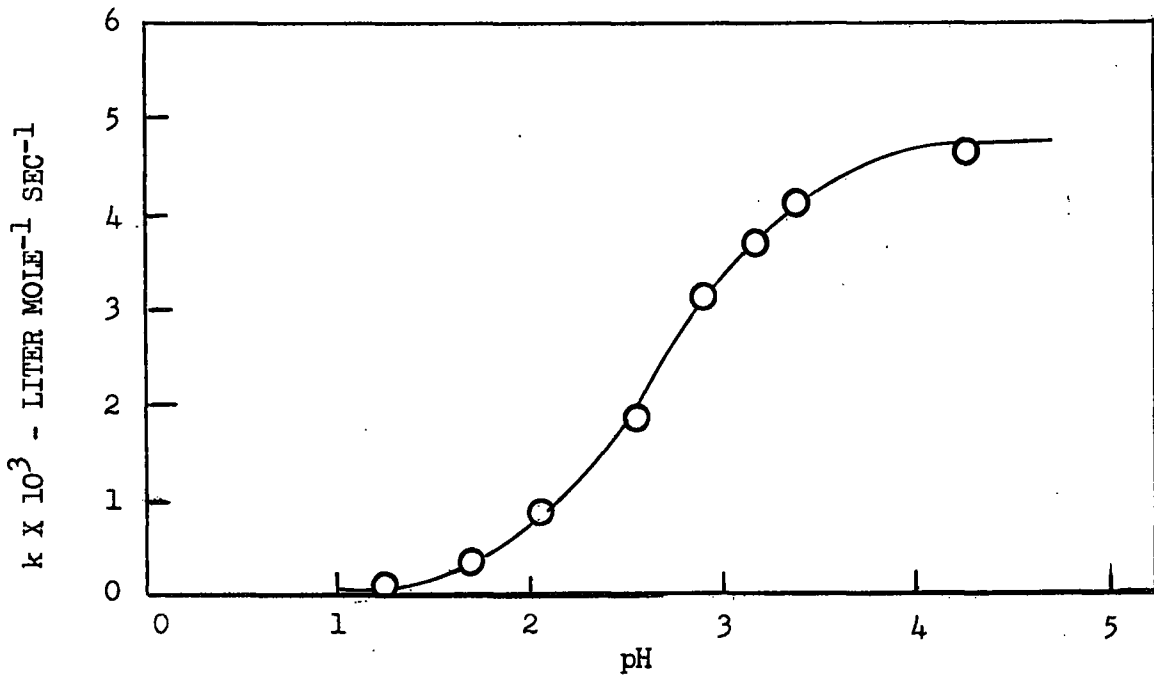


Fig. 14. Dependence of the Reaction Rate in Acetate Solutions on pH. 0.05 M./L. Cu(II); 1.0 M./L. Total Acetate; 100°C.; 20 atm. H₂. pH measured at Room Temperature.

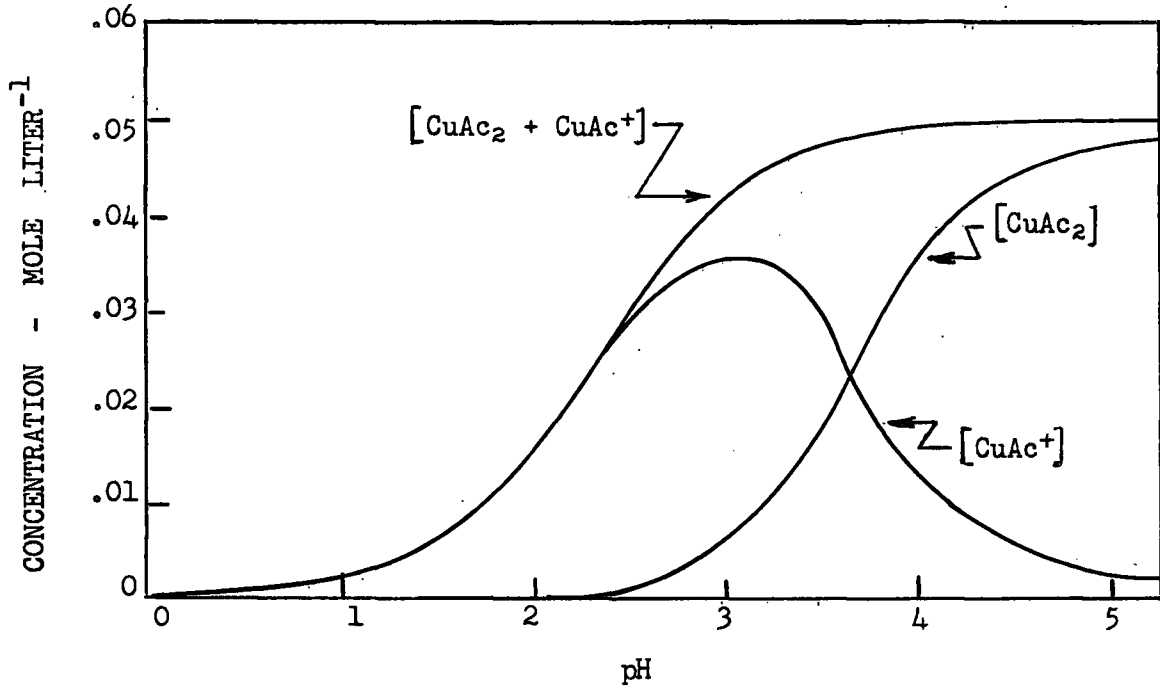


Fig. 15. Effect of pH on the Relative Concentrations of Cupric Species in Acetate Solutions at Room Temperature. 0.05 M./L. Cu(II); 1.0 M./L. Total Acetate. Based on Published Complexity Constants (49,50,51,52).

The shape of the curve, depicting pH dependence of the reaction rate (Fig. 14), is qualitatively similar to that for the variation of total concentration of complexed Cu(II) (i.e., $\text{CuAc}_2 + \text{CuAc}^+$) plotted in Fig. 15, utilizing the known room temperature complexity constants for cupric acetate (49,50,51,52). This supports the view that the catalytic activity of cupric acetate solutions is primarily due to complexes such as CuAc_2 and CuAc^+ . A comparison of the curves in Figs. 14 and 15 suggests that the two complexes have similar catalytic activities.

It is probable that the observed slight decrease in k with increasing cupric acetate concentration arises from a secondary effect such as the lowering of the solubility of hydrogen. Similar decreases in rate were observed when inert salts were added to the solution, as shown in Fig. 16. In most cases for which data are available, the variation of k with salt concentration was found to be in fair agreement with the lowering of the solubility of hydrogen (53). The anomalous increase in reaction rate due to sodium perchlorate may be due to a slight salting-in effect, i.e. an increased hydrogen solubility, sometimes observed for large negative ions (54).

The kinetics of the cupric acetate-catalyzed reduction of dichromate by hydrogen, reported above, are in good quantitative agreement with those found earlier for the reduction by hydrogen of cupric acetate itself to cuprous oxide (37,38,39). A similar reduction of cupric acetate was observed if the reduction of dichromate was allowed to proceed to completion, as shown in Fig. 17. The first order rate constant for this reduction agreed with the value obtained previously for this reaction (39) and with the rate constant for the activation of hydrogen calculated from the rate of the preceding dichromate reduction.

As in the case of the perchlorate system, the pattern of kinetic

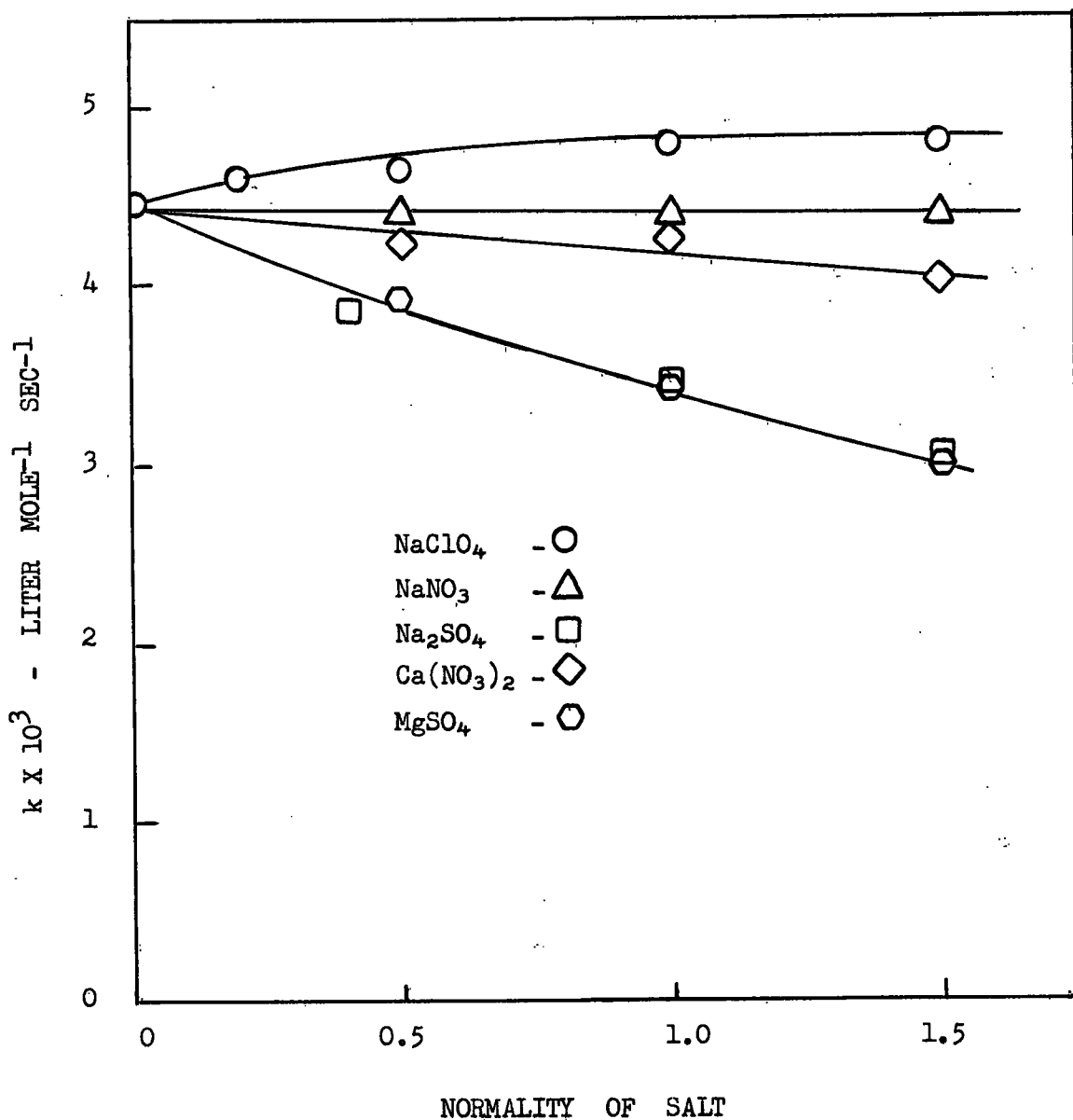


Fig. 16. Effect of Various Salts on the Rate of the Cupric Acetate Catalyzed Reaction. 0.10 M./L. CuAc₂; 0.25 M./L. NaAc; 0.50 M./L. HAc; 100°C.; 13.6 atm. H₂.

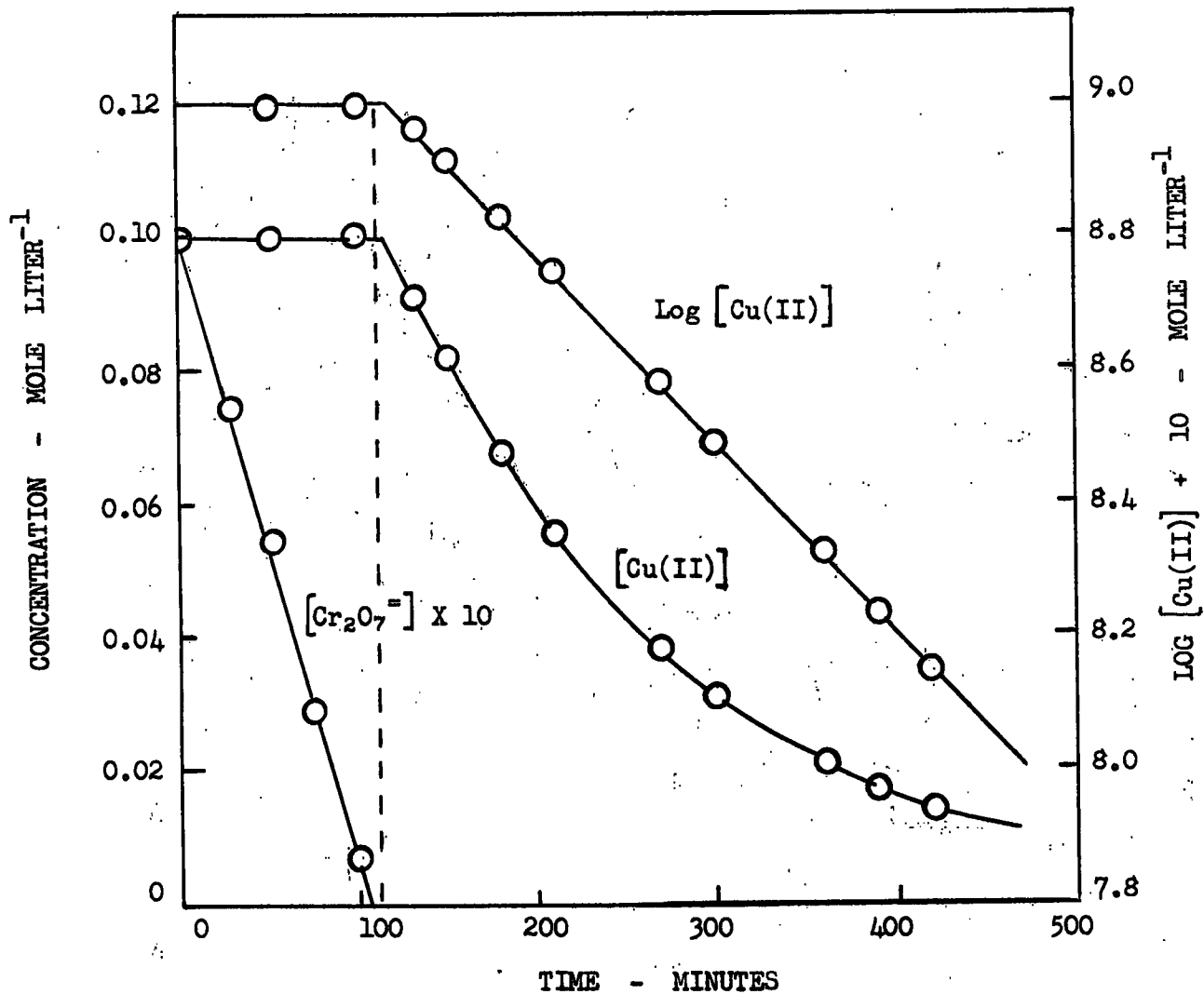
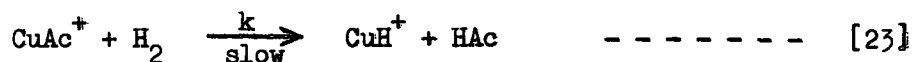


Fig. 17. Typical Rate Plots for the Consecutive Reduction of Dichromate and Cupric Acetate by Hydrogen. 100°C; 13.6 atm. H₂.

behaviour suggests that the rate is determined by a bimolecular process involving one cupric acetate complex and one hydrogen molecule. The large difference in the rate constants for the two systems, (i.e. a factor of 120) reflecting the higher catalytic activity of the cupric acetate, may be explained by assigning to the acetate ligand the role of a proton acceptor in the rate determining step, i.e.



Some measure of further support would thus appear to be provided for the suggestion that CuH^+ is the activated intermediate in these systems.

C. EFFECT OF COMPLEXING ON THE HOMOGENEOUS ACTIVATION OF MOLECULAR HYDROGEN BY CUPRIC SALTS

In view of the fact that the catalytic activity of the undissociated cupric acetate complex was found to be about 120 times greater than that of the uncomplexed cupric ion, it seemed of interest to examine the effect of other complexing ligands. Therefore, kinetic studies on the catalytic activation of hydrogen by a number of organic and inorganic cupric complexes were made. In each case, the reduction of dichromate was used as a measure of the rate.

Cupric Carboxylate Complexes

Measurements of the rate of reduction of dichromate by hydrogen in the presence of various cupric carboxylate salts are reported in Table III. As with cupric acetate, the kinetics were found to be zero order in dichromate. The reaction rates could generally be estimated to within $\pm 5\%$, except in solutions containing formate, where the uncertainty was much greater, because the rate of reaction of dichromate with formate was of the same order

TABLE III

RATES OF REACTION BETWEEN HYDROGEN AND DICHROMATE IN SOLUTIONS

OF VARIOUS CUPRIC CARBOXYLATE SALTS

0.0005 M./L. $\text{Na}_2\text{Cr}_2\text{O}_7$; 20 atm. H_2 ; 100°C.

Expt. No.	Solution Composition *			$-\frac{d[\text{H}_2]}{dt} \times 10^6$ Mole Liter ⁻¹ Sec. ⁻¹	$k \times 10^3$ L.Mole ⁻¹ Sec. ⁻¹
	M./L.				
Pr-3	0.05 CuPr	0.0 NaPr	0.5 HPr	4.38	5.75
Pr-8	0.05 " 2	0.25 "	0.5 "	4.38	5.83
Pr-5	0.05 " 2	0.50 "	0.5 "	4.83	6.33
Pr-4	0.05 " 2	1.00 "	0.5 "	4.50	5.94
Pr-6	0.05 " 2	0.25 "	0.2 "	4.44	5.90
Pr-7	0.05 " 2	0.25 "	2.0 "	5.49	7.13
Bu-1	0.026 CuBu	0.25 NaBu	0.5 HBu	2.31	5.82
Bu-2	0.052 " 2	0.25 "	0.5 "	4.59	5.86
Fo-1	0.10 CuFo	0.25 NaFo	0.25 HFo	2.94	1.8
Fo-2	0.10 " 2	0.25 "	0.25 "	2.88	1.8
Su-4	0.01 CuSu	0.025 Na ₂ Su	0.25 H ₂ Su	0.39	2.8
Su-10	0.01 " 2	0.05 " 2	0.60 "	0.33	2.2
Ma-2	0.01 CuMa	0.13 Na ₂ Ma	0.015 H ₂ Ma	0.16	1.1
Fu-1	0.002 CuFu	0.03 Na ₂ Fu	0.13 H ₂ Fu	0.08	2.5

* The following abbreviations are used in this thesis: Ac - acetate;

Pr - propionate; Bu - butyrate; Fo - formate; Su - succinate;

Fu - fumarate; Ma - maleate; Gl - glycine or glycinatate; EDA - ethylenediamine.

as that with hydrogen.

The results for cupric propionate (CuPr_2) parallel those obtained earlier for cupric acetate, suggesting that the mechanism of activation of hydrogen in the two systems is essentially the same. Fig. 18 shows that the rate is nearly proportional to the cupric propionate concentration, a slight tendency being apparent for the rate constant, k , to decrease at higher cupric propionate concentrations. A similar effect in the cupric acetate system was attributed to a lowering of the solubility of hydrogen. The rate is seen to be essentially independent of sodium propionate or propionic acid over a wide range. By analogy with the cupric acetate system it is concluded that the active species in the present case are probably CuPr_2 and CuPr^+ .

At 100°C ., the catalytic activity of cupric propionate in propionate-buffered solutions ($k \approx 6.0 \times 10^{-3}$ liter mole $^{-1}$ sec. $^{-1}$) was found to be about 25% higher than that determined for cupric acetate ($k \approx 4.7 \times 10^{-5}$ liter mole $^{-1}$ sec. $^{-1}$). Rate measurements for cupric propionate at temperatures between 80° and 120°C . gave a good linear plot of $\log(k/T)$ vs. $1/T$ (Fig. 19) from whose slope an apparent activation enthalpy, ΔH^\ddagger , of 23.0 ± 1.5 kilocalories per mole and an activation entropy, ΔS_c^\ddagger , of -7.5 ± 4.0 e.u. were calculated. These values are in excellent agreement with those for cupric acetate.

Two experiments with cupric butyrate in butyrate-buffered solutions yielded rates identical with those for cupric propionate (see Table III).

Measurements of the rate of activation of hydrogen in formate-buffered solutions were subject to large uncertainties because of complications arising from side reactions between formate and dichromate. The rate at 100°C . ($k = 1.8 \times 10^{-3}$ liter mole $^{-1}$ sec. $^{-1}$) was about one-third that for cupric acetate and the higher carboxylate complexes. This may reflect the

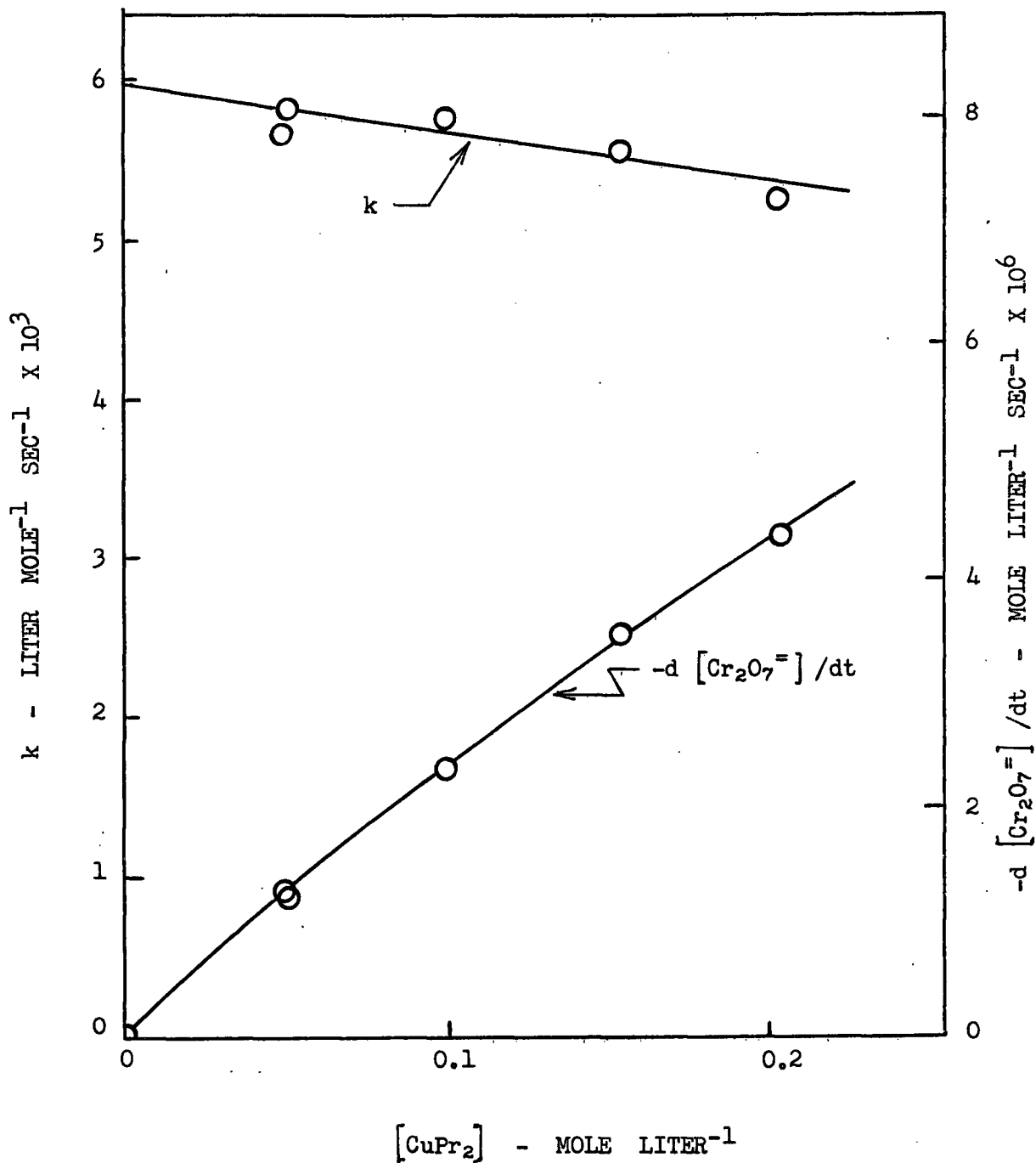


Fig. 18. Dependence of the Reaction Rate on the Cupric Propionate Concentration. 0.25 M./L. NaPr; 0.50 M./L. HPr; 100°C.; 20 atm. H₂.

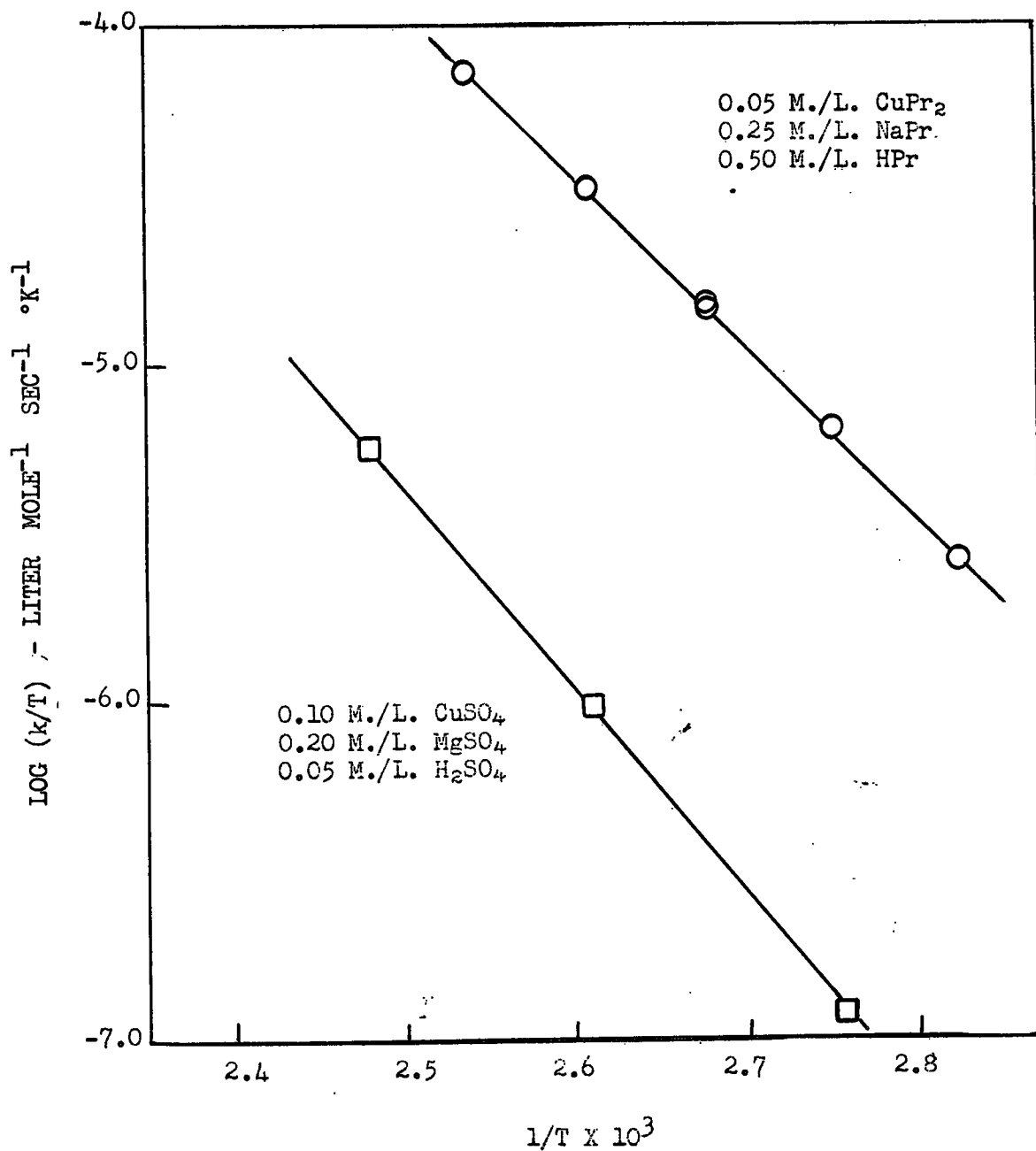


Fig. 19. Plots of Log (k/T) vs. 1/T for the Cupric Propionate and Cupric Sulphate Catalyzed Reactions Between Dichromate and Hydrogen. 20 atm. H₂.

fact that complexing between Fo^- and Cu^{++} is incomplete, consistent with the higher dissociation constant of formic acid. Similar considerations apply to cupric fumarate and cupric maleate.

The catalytic activity of succinate-buffered cupric solutions ($k \approx 2.5 \times 10^{-3}$ liter mole⁻¹ sec.⁻¹ at 100°C.) was about one half that for cupric acetate. It is probable that the cupric succinate complex has a chelate structure.

Cupric Sulphate

A typical rate plot for the reduction of dichromate in the presence of cupric sulphate is shown in Fig. 20. The results for cupric sulphate are summarized in Figs. 21 and 22. It is seen that the addition of Na_2SO_4 was found to increase the catalytic activity of Cu^{++} , presumably as a result of complex formation. It has been suggested that only the first stage of association, i.e.



is important (55,56), and that higher cupric sulphate complexes are not formed to an appreciable extent. The failure of the curve in Fig. 21 to level off suggests that complexing is incomplete at $\text{SO}_4^{=}$ concentrations as high as 0.5 M./L.

Consistent with the above interpretation, it was found that the experimental results could be fitted by a relation of the form:

$$k = \frac{k_1[\text{Cu}^{++}] + k_2[\text{CuSO}_4]}{[\text{Cu(II)}]} \quad \text{---} \quad [25]$$

where k_1 and k_2 represent the specific rate constants for the activation of H_2 by Cu^{++} and CuSO_4 respectively; k_1 is known from measurements in perchlorate solutions and has a value of 0.93×10^{-4} liter mole⁻¹ sec.⁻¹ at

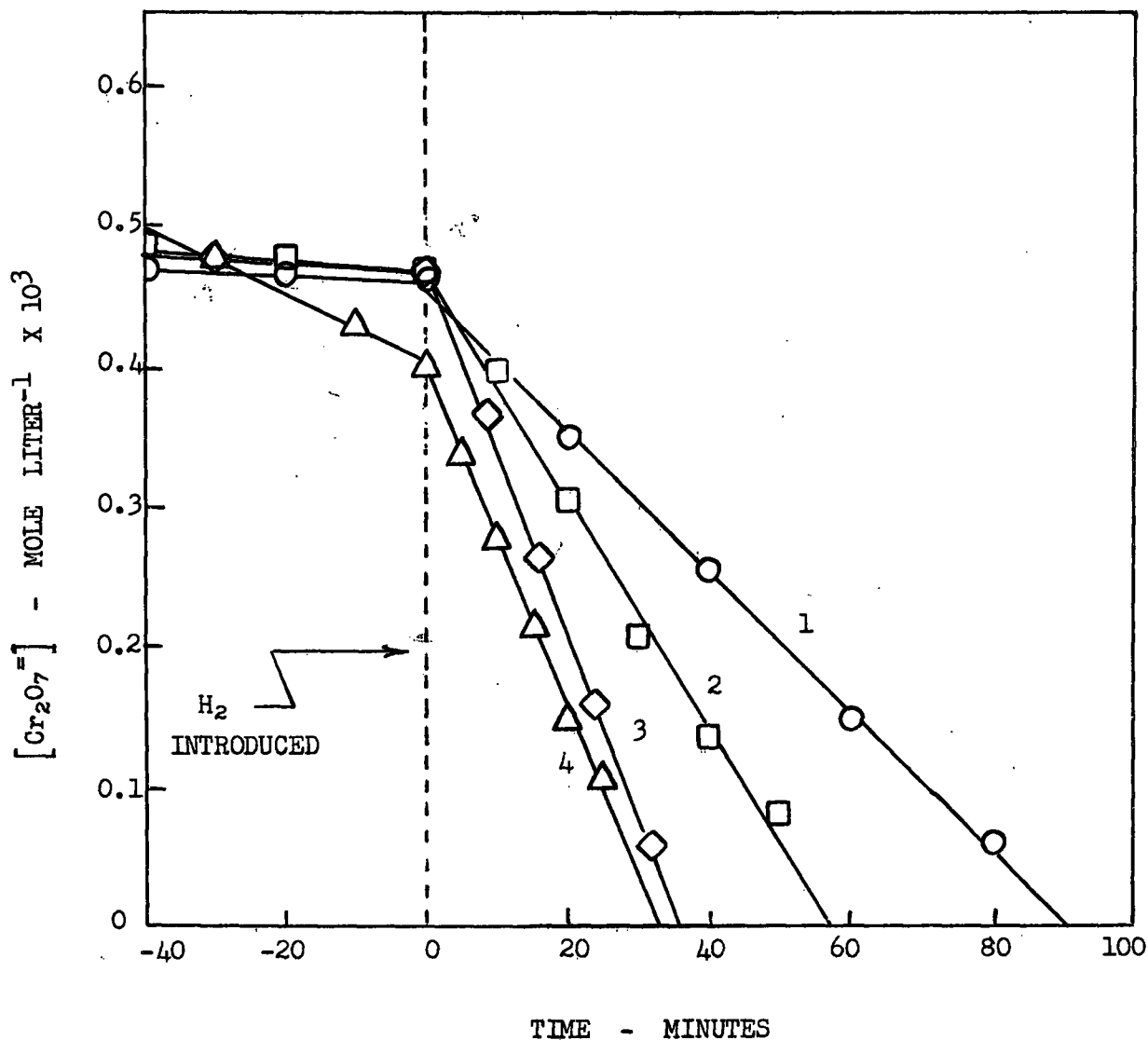


Fig. 20. Typical Rate Plots for the Reduction of $Cr_2O_7^{2-}$ by H_2 in the Presence of Various Cupric Complexes. 20 atm. H_2 .

1. Ethylenediamine (0.05 M./L. Cu(II), 0.20 M./L. EDA, pH 4.0, 130°C.
2. Chloride (0.10 M./L. Cu(II); 1.0 M./L. Cl^- ; 110°C.
3. Sulphate (0.10 M./L. Cu(II); 0.10 M./L. SO_4^{2-} ; 110°C.
4. Glycine (0.05 M./L. Cu(II); 0.05 M./L. Gl; pH 3.5; 130°C.

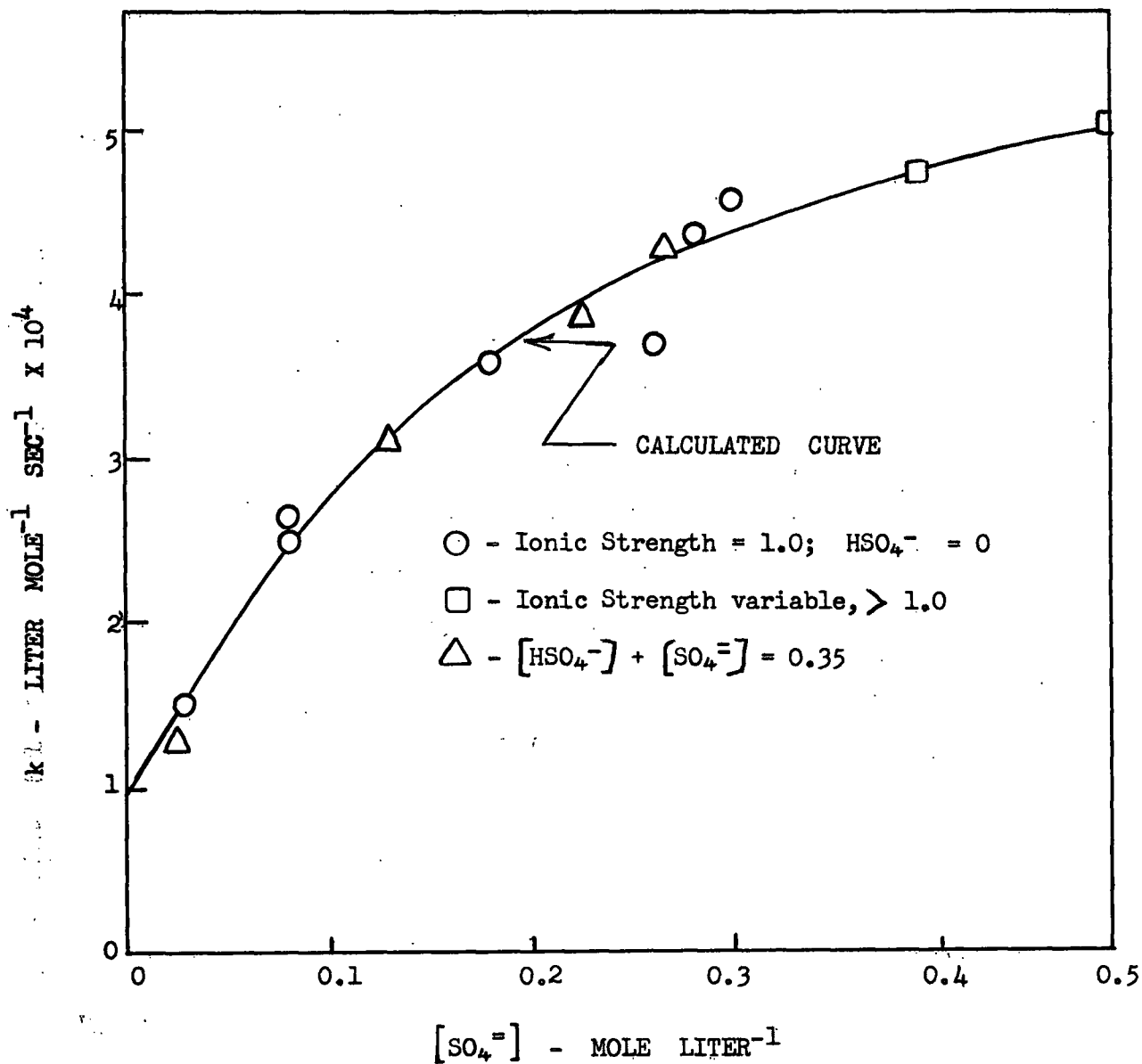


Fig. 21. Dependence of the Reaction Rate on SO₄⁼ Concentration. 0.10 M. Cu(II); 20 atm. H₂; 110°C.

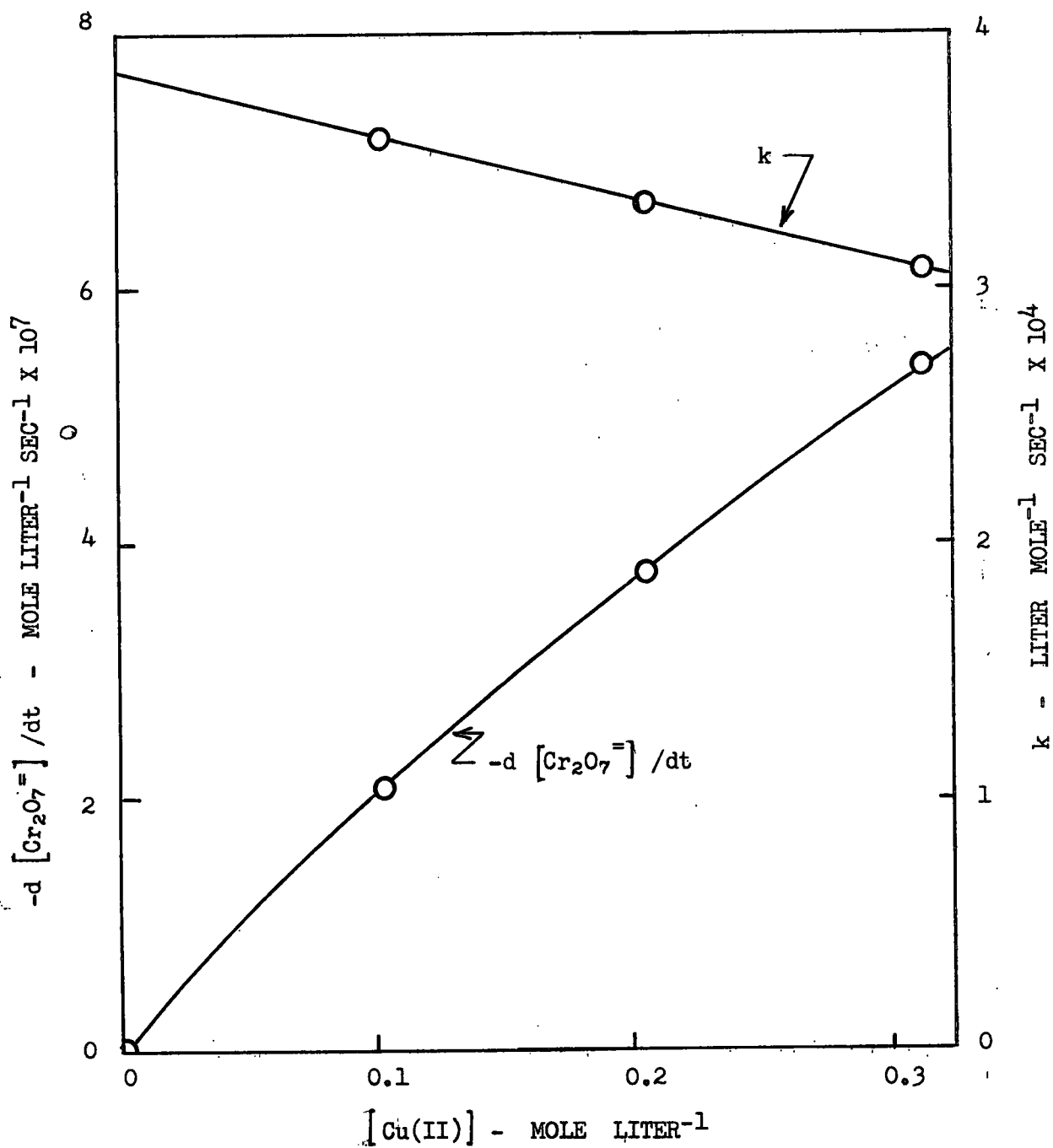


Fig. 22. Dependence of the Reaction Rate in Sulphate Solution on Cu(II) Concentration. 0.25 M./L. $SO_4^{=}$; 0.10 M./L. HSO_4^{-} ; 20 atm. H_2 ; 110°C.

110°C. (Table I).

From equation [24], $[Cu^{++}]$ and $[CuSO_4]$ are related by

$$\frac{[CuSO_4]}{[Cu^{++}][SO_4^{=}] } = K \quad \text{-----} \quad [26]$$

while $[Cu^{++}] + [CuSO_4] = [Cu(II)] \quad \text{-----} \quad [27]$

The best correspondence between a curve for k , calculated from equations [25], [26], and [27], and the experimental points (shown in Fig. 21) was obtained using the following values: $k_2 = 6.5 \times 10^{-4}$ liter mole⁻¹ sec.⁻¹ at 110°C. (i.e. about 7 times as great as k_1) and $K = 6.7$ liter mole⁻¹. The excellent fit lends support to these values. However, some uncertainty arises through neglect of activity coefficients and of the effect of variable salt concentration on the solubility of hydrogen. It is of interest that the above value of K , derived from the kinetic results at 110°C., is of the same order as the room temperature value (≈ 4.5 liter mole⁻¹ for ionic strength of unity) estimated by a spectrophotometric method (56).

A plot of $\log (k/T)$ vs. $1/T$ for $CuSO_4$ based on reaction rate measurements at temperatures between 90° and 130° is shown in Fig. 18. The apparent activation enthalpy of 27.3 kilocalories per mole, obtained from the slope of this plot, presumably reflects the effect of temperature on the relative proportions of the cupric sulphate complex and the cupric ion present, as well as on their specific rate constants.

Cupric Chloride Complexes

A typical rate plot for the reduction of dichromate by hydrogen in the presence of cupric chloride is shown in Fig. 20. The results for cupric chloride solutions, summarized in Fig. 23, indicate that Cl^-

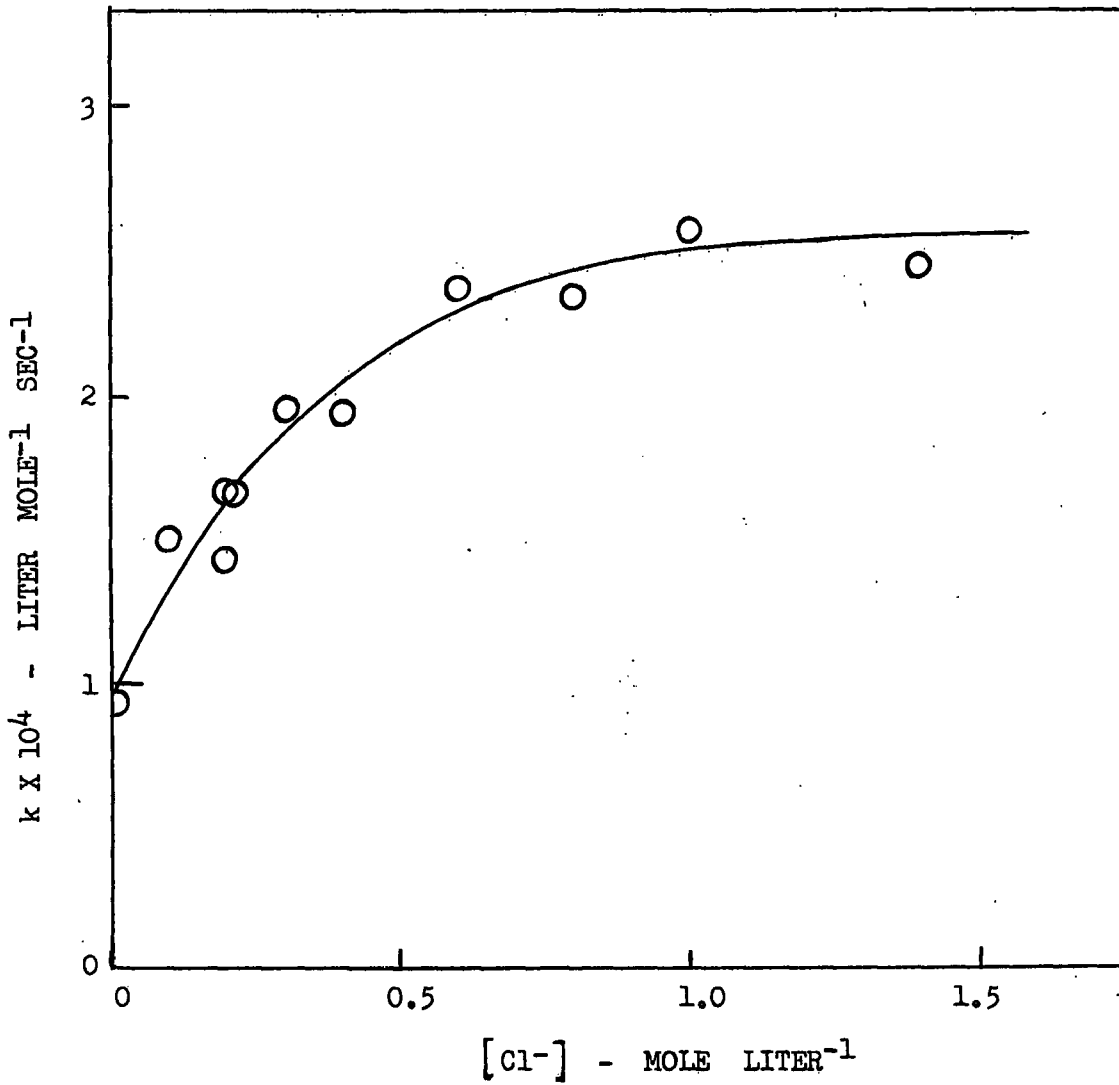


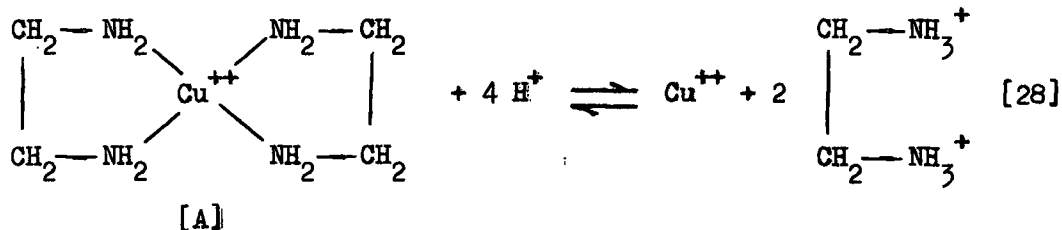
Fig. 23. Dependence of the Rate of the Cupric Chloride Catalyzed Reaction on the Chloride Concentration. 0.10 M./L. $\text{Cu}(\text{ClO}_4)_2$; 20 atm. H_2 ; 110°C .

increases the catalytic activity in a manner attributable to the formation of cupric chloride complexes. It is probable that in the region above 1 M./L. Cl^- , where the rate levels off, the cupric ion is fully complexed, i.e. exists as CuCl_4^{2-} . Hence it seems reasonable to attribute the measured value of k in this region to this complex.* This value (2.5×10^{-4} liter mole $^{-1}$ sec. $^{-1}$) is about 2.7 times as great as for the uncomplexed Cu^{++} ion.

At constant Cl^- concentrations the rate was found to be directly proportional to the total cupric concentration (Fig. 24) confirming that the catalytic activity is associated with the cupric species.

Cupric Ethylenediamine Complexes

The extent of complexing between Cu^{++} and EDA is a function of the H^+ concentration, i.e.



The variation of k with pH, shown in Fig. 25, thus probably reflects a variation in the extent of complexing of the cupric ion.

At low pH (< 3 , measured at room temperature) dissociation of the complex is apparently complete and the observed value of k approaches that for

* Spectrophotometrically determined values of the complexity constants of cupric chloride at room temperature (57) suggest that higher Cl^- concentrations would be required to achieve complete complexing. However, it has been pointed out that these values probably increase with temperature (58).

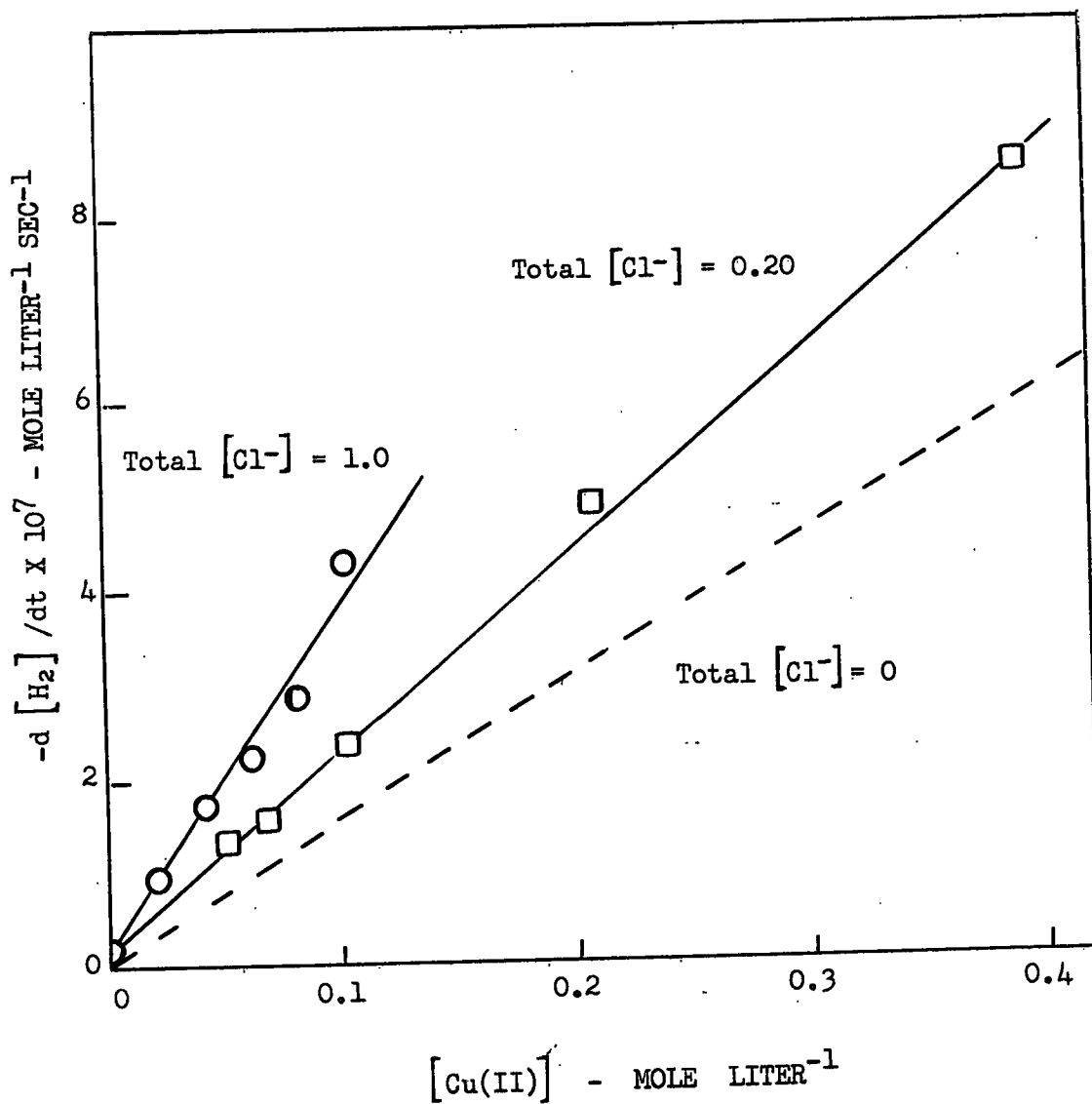


Fig. 24. Dependence of the Reaction Rate in Chloride Solutions on the Cupric Salt Concentration. 20 Atm. H₂; 110°C.

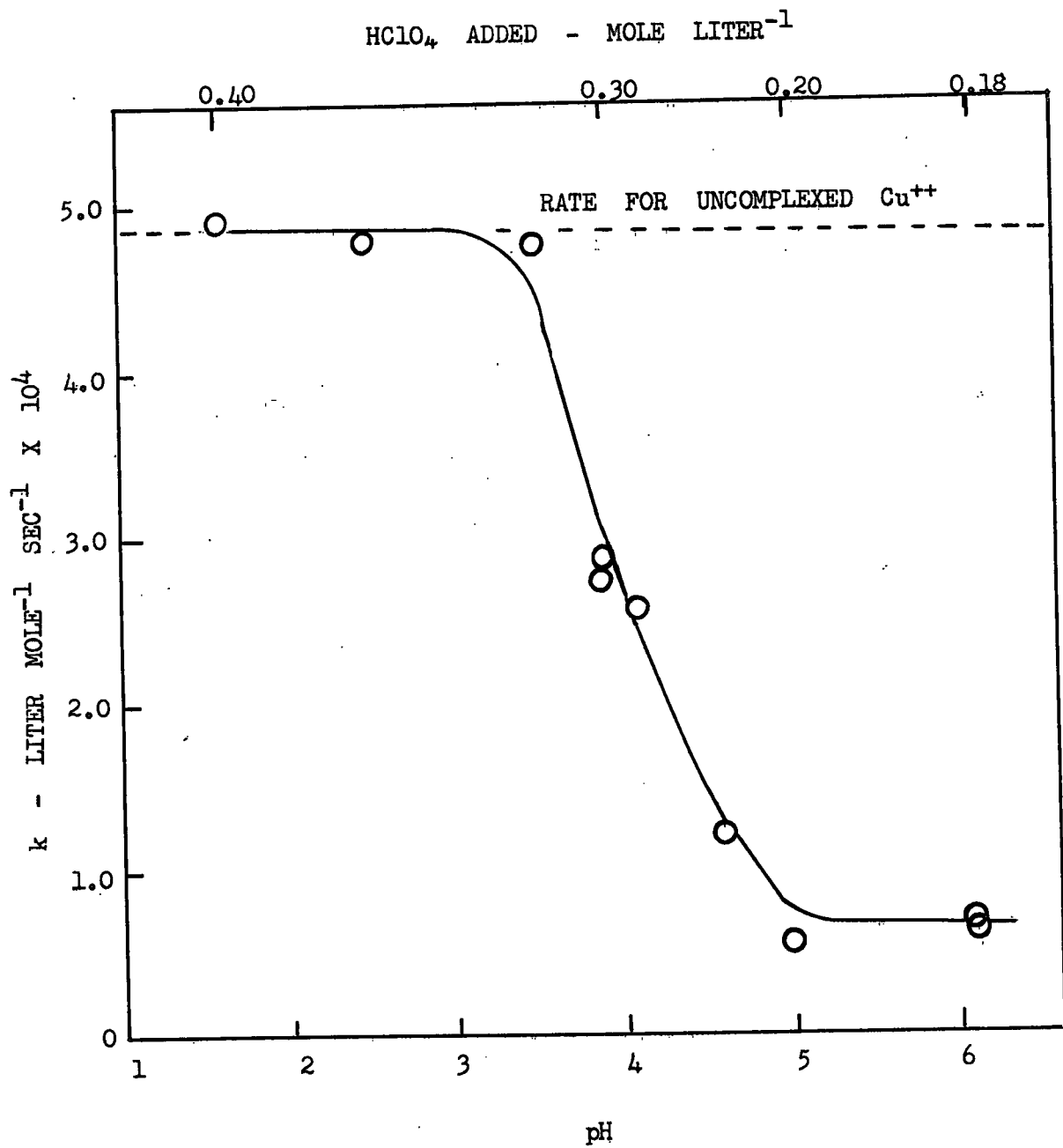


Fig. 25. Effect of pH on the Reaction Rate in Cupric Ethylenediamine Solutions.

the uncomplexed Cu^{++} ion. Increasing the pH (by decreasing the amount of added HClO_4) results in a lowering of the rate, presumably reflecting the lower catalytic activity of the $\text{Cu}(\text{EDA})_2^{++}$ complex [A]. At high pH (> 5) the rate levels off at a value ($k \approx 0.6 \times 10^{-4}$ liter mole $^{-1}$ sec. $^{-1}$ at 130°C .) which is about one-eighth that for the uncomplexed cupric ion at the same temperature. Room temperature values of the complexity constants (59) suggest that in this region complexing is essentially complete, all the $\text{Cu}(\text{II})$ being present as the $\text{Cu}(\text{EDA})_2^{++}$ complex; hence it seems reasonable to associate the measured value of k with this complex.

This interpretation is consistent with the results shown in Fig. 26. In a series of experiments in which the $\text{Cu}(\text{II})$ concentration was increased while the total EDA concentration was held constant, the rate (and the apparent value of k) rose sharply as the ratio $[\text{Cu}(\text{II})]/[\text{EDA}]$ approached the value 0.5.

Cupric Glycinate Complexes

Figs. 27 and 28 depict the effect of glycine on the rate of catalytic activation of hydrogen by $\text{Cu}(\text{II})$ in solutions of different pH.

In basic solutions complexing of Cu^{++} with glycine (involving formation of the CuGl_2 chelate complex) is essentially complete (59). However, with decreasing pH it is probable that the complex undergoes dissociation, passing through a number of intermediate stages including the following:

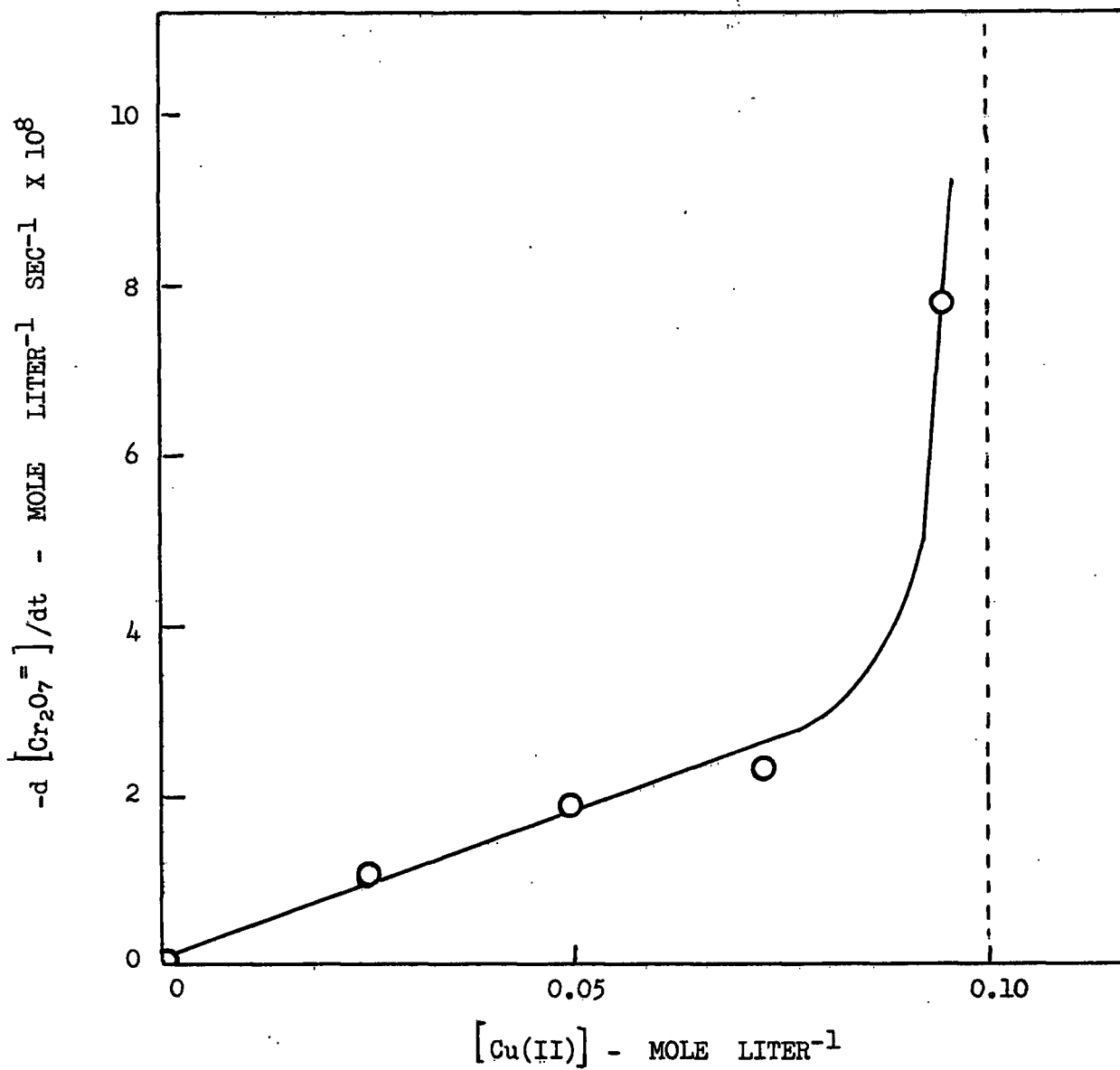


Fig. 26. Dependence of the Reaction Rate in Ethylenediamine Solutions on the Cupric Salt Concentration. 0.20 M./L. EDA; 20 Atm. H₂; 130°C.; pH 6 (Room Temperature).

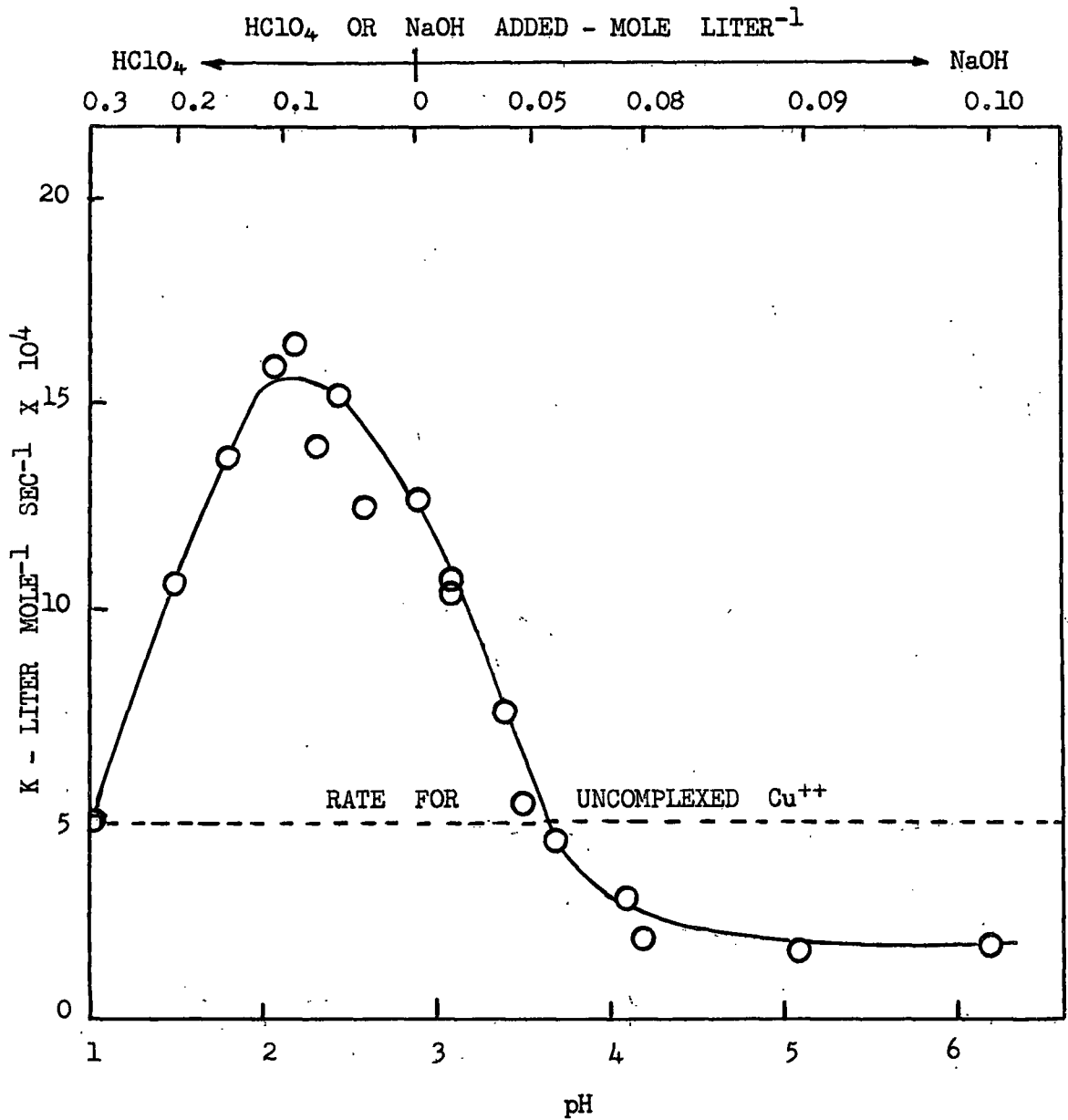


Fig. 27. Effect of pH on the Reaction Rate in Cupric Glycinate Solutions. 0.05 M./L. $\text{Cu}(\text{ClO}_4)_2$; 0.20 M./L. Gl; 20 Atm. H_2 ; 130°C .

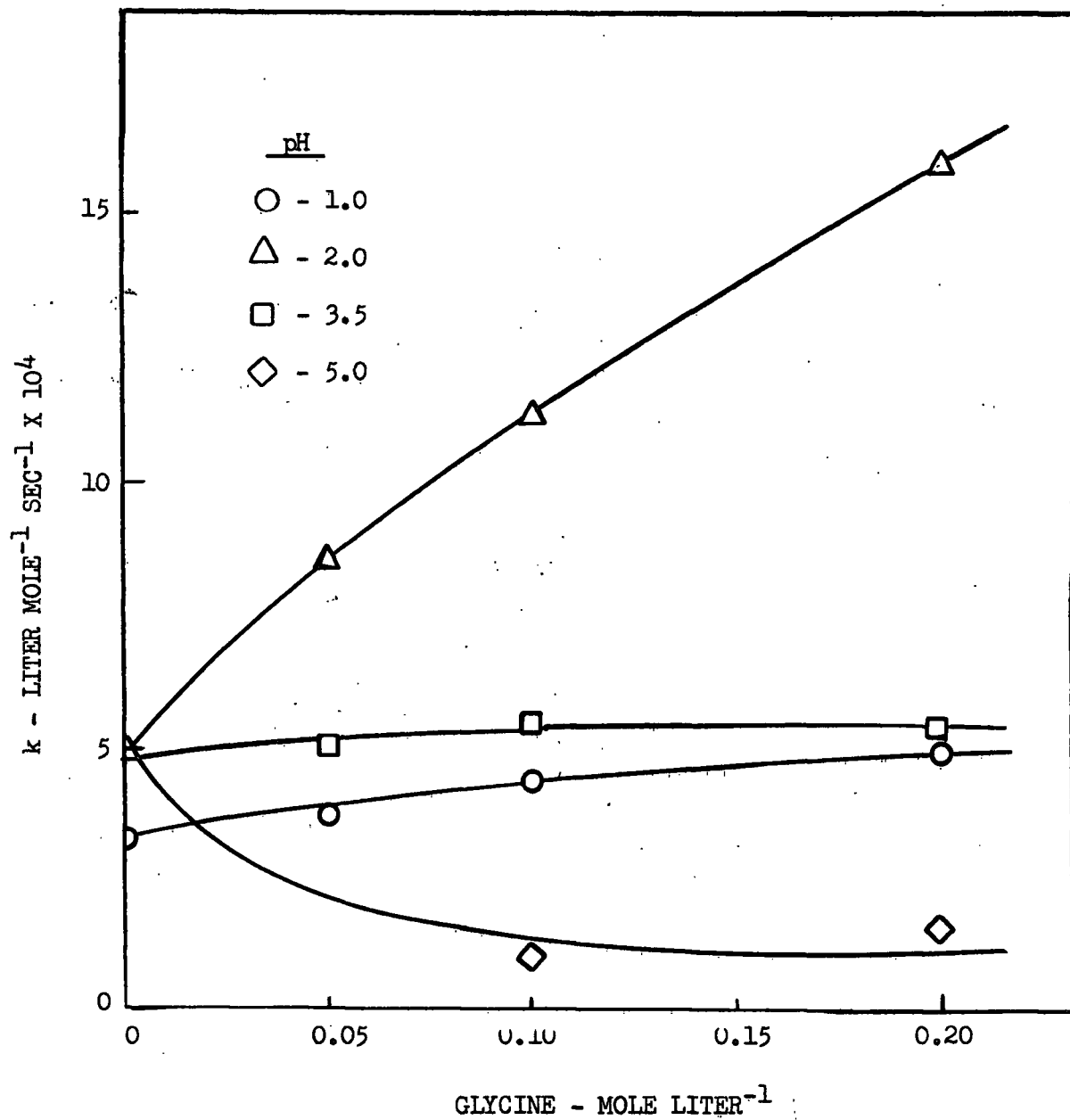
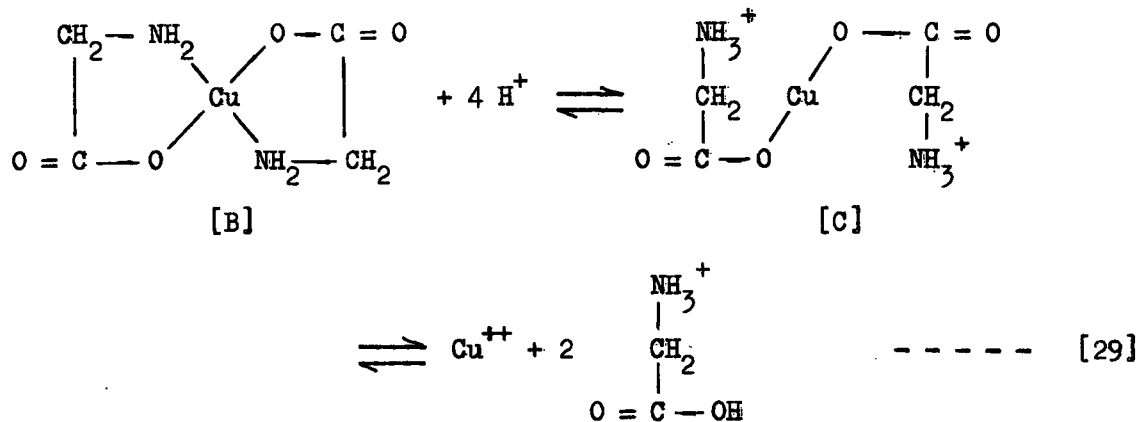


Fig. 28. Dependence of the Rate of the Cupric Glycinate Catalyzed Reaction on the Glycine Concentration at Several pH's. 0.05 M./L. $\text{Cu}(\text{ClO}_4)_2$; 20 Atm. H_2 ; 130°C.



Consistent with this it was found that at low pH (≈ 1) the value of k approaches that for the undissociated Cu^{++} ion (Fig. 27) and is essentially independent of the Gl concentration (Fig. 28).

In the region of high pH (> 3.5), k decreases with increasing pH (Fig. 27) and with increasing glycine concentration (Fig. 28) approaching a value ($\approx 1.6 \times 10^{-4}$ liter mole $^{-1}$ sec. $^{-1}$ at 130°C.) about one-third that of the uncomplexed Cu^{++} ion at the same temperature. This value, which presumably reflects the catalytic activity of the CuGl_2 complex [B], (equation [29]) is subject to considerable uncertainty because of the competing side reactions between dichromate and glycine (see Fig. 20).

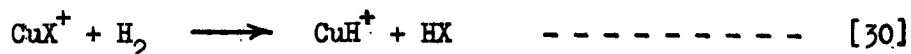
In the region of intermediate pH (1 - 3.5) the measured value of k is greater than that for Cu^{++} and increases with the Gl concentration, presumably reflecting the presence of cupric carboxylate complexes such as [C] (equation [29]). In common with the other cupric carboxylate complexes discussed earlier, the catalytic activity of this complex is apparently greater than that of the uncomplexed cupric ion.

Summary of the Effect of Complexing

Complex forms of copper in aqueous solutions apparently activate

hydrogen by essentially the same mechanism as the simple hydrated cupric ion, but with widely differing activities. The data obtained in these studies have been used to compile Table IV in which the various complexes, for which values of k have been determined, are arranged in order of decreasing catalytic activity. The listed values of the relative catalytic activities (that of the uncomplexed cupric ion being taken as unity) are only approximate since they are based on rate measurements at different temperatures (ranging from 100° to 130°C.) and of varying precision.

Of particular interest is the fact that the negative ions enhance the catalytic activity of Cu^{++} in order of increasing basicity, i.e. Bu^- , $\text{Pr}^- > \text{Ac}^- > \text{SO}_4^{=} > \text{Cl}^- > \text{ClO}_4^-$. This supports the suggestion, made previously for Ac^- , that their promoting action results from their role as proton acceptors in the rate determining step, i.e.



The depressing effect of chelating reagents containing ammine groups is not clearly understood. The effect is thought to be primarily due to co-ordination of the cupric ion with nitrogen, which is less electro-negative than oxygen or chlorine and, therefore, through electron donation to the Cu^{++} ion decreases the electron accepting power of the latter. The role of the electron accepting power (i.e. electron affinity) of the Cu^{++} ion in the hydrogen activation process will be discussed later.

D. HOMOGENEOUS ACTIVATION OF HYDROGEN BY SALTS OF OTHER METALS

In addition to the cupric salts, salts of certain other metals were tested for their ability to activate molecular hydrogen homogeneously in aqueous solutions. In most cases, dichromate was used as an indicator. The following salts were tested:

TABLE IV

RELATIVE CATALYTIC ACTIVITIES OF VARIOUS
CUPRIC COMPLEXES

<u>Complex</u>	<u>k - liter mole⁻¹ sec.⁻¹</u>	<u>Catalytic Activity</u> *
CuBu ₂	5.84 x 10 ⁻³ at 100°C.	150
CuPr ₂	5.95 x 10 ⁻³ " "	150
CuAc ₂	4.70 x 10 ⁻³ " "	120
Cu ⁺⁺	3.88 x 10 ⁻⁵ " "	1
CuSO ₄	6.5 x 10 ⁻⁴ at 110°C.	7
CuCl ₄ ⁼	2.5 x 10 ⁻⁴ " "	2.7
Cu ⁺⁺	9.55 x 10 ⁻⁵ " "	1
Cu ⁺⁺	5.35 x 10 ⁻⁴ at 130°C.	1
CuGl ₂	1.6 ± 1.0 x 10 ⁻⁴ " "	< 0.5
Cu(EDA) ₂ ⁺⁺	6 x 10 ⁻⁵ " "	0.1

*Relative to that of Cu⁺⁺ which is taken as unity at each temperature.

MgAc ₂	NiAc ₂	ZnAc ₂	HgAc ₂
MgSO ₄	Ni(ClO ₄) ₂	Zn(ClO ₄) ₂	HgSO ₄
Mg(ClO ₄) ₂	NiSO ₄	ZnSO ₄	AgAc
CaAc ₂	CoAc ₂	CdAc ₂	Al(ClO ₄) ₃
Ca(ClO ₄) ₂	MnAc ₂	UO ₂ Ac ₂	Cr(ClO ₄) ₃

Of these, only the mercuric and silver salts showed measurable reactivity towards hydrogen at temperatures up to 140°C. and pressures of 13.6 atmospheres.*

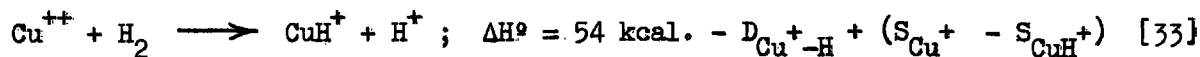
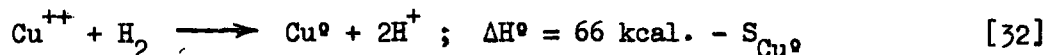
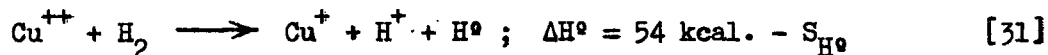
E. MECHANISM OF HYDROGEN ACTIVATION

In the above discussions of the experimental results, repeated references have been made to the occurrence of an "activated intermediate". While the nature of this intermediate complex has not been determined by direct observation, the kinetic evidence for its formation is considered fairly conclusive. Of the various possible intermediates for which reasonable 'classical' structures can be written, the most likely is believed to be CuH⁺, whose formation is depicted by equation [30]. This suggestion is supported by a consideration of the energetics of the processes leading to the formation of the possible alternative intermediates.

The available thermochemical data** lead to the following expressions for the endothermicities of the alternative rate-determining processes:

* Reference has already been made to the results of subsequent kinetic studies of these reactions. See pages 7 and 8.

** The following standard enthalpies of formation (ΔH_f°) have been used: H⁺ (aq.), 0; H^o (g), 52.1 kilocal.; He (g), 0; Cu^o (g), 81.5 kilocal.; Cu⁺⁺ (aq.), 15.4 kilocal. (60); Cu⁺ (aq.), 17.1 kilocal. (61).



where S_x represents the hydration energy of the gaseous species, x, and $\text{D}_{\text{A-B}}$ represents the dissociation energy of the gaseous molecule, AB.

Of these possibilities, reactions [31] and [32] appear to be energetically inconsistent with the observed activation energy of 24 kcal. since S_{H^0} and S_{Cu^0} , corresponding to the hydration energies of the gaseous atoms, can hardly be very large. The energetics of reaction [33] cannot be evaluated very accurately. While CuH^+ appears to have been detected spectroscopically (62) its dissociation energy is not known; however, the value is not likely to be smaller than that of the isoelectronic molecule NiH , i.e. 60 kcal. (9). At the same time, while S_{Cu^+} is probably larger than S_{CuH^+} , the difference is not likely to exceed the 30-40 kcal. which would be required to make the endothermicity of the process greater than the observed activation energy. Thus, on energetic grounds, the occurrence of CuH^+ as the activated intermediate as a result of the process represented by equation [33] appears the most probable.

It is unlikely that the formation of H_2^+ (in place of $\text{H}^0 + \text{H}^+$ in equation [31]), or of CuH_2^{++} (in place of $\text{CuH}^+ + \text{H}^+$ in equation [33]) in aqueous solution would be energetically favoured, because of the high solvation energy of the proton.

The reaction represented by equation [33] can be depicted schematically by means of a potential energy diagram such as that shown in Fig. 29. Repulsion between the reacting species, Cu^{++} and H_2 , is reflected in the increasing potential energy as the Cu - H distance decreases. The activated complex corresponding to the cross-over point of the two curves

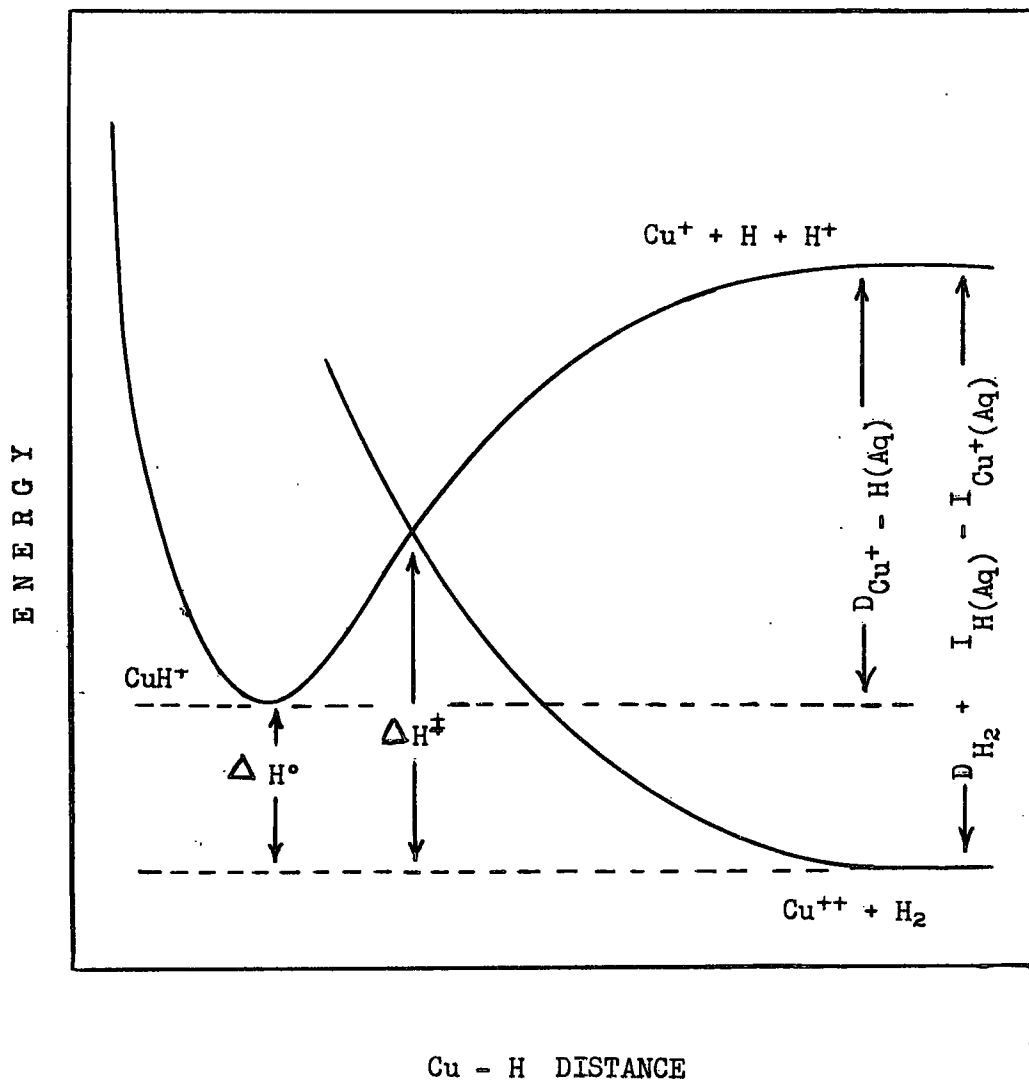
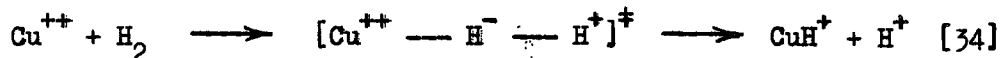


Fig. 29. Schematic Potential Energy Diagram for the Reaction $Cu^{++} + H_2 \rightarrow CuH^+ + H^+$.

probably has a configuration approximating $[\text{Cu}^{++} \text{ --- } \text{H}^- \text{ --- } \text{H}^+]$. A further decrease in the Cu - H distance from this point results in the formation of a CuH^+ molecule, accompanied by a decrease in potential energy, the resulting proton being released to an adjacent base. The entire process of hydrogen activation can therefore be represented by the expression



This mechanism implies that a H^- displacement or, essentially, an electron displacement from the hydrogen molecule to the cupric ion, occurs during the activation process. A prerequisite requirement for this is presumably that the catalyst species, i.e. Cu^{++} , must have a high electron affinity.

Certain electron displacement phenomena that occur in solution, such as the formation of co-ordinated complex molecules, have been related to the electron affinities of the corresponding gaseous ions. Thus in a series of metal chelate complexes, a linear relation was observed between the log of the stability constants and the ionization potential for the removal of the last electron in the formation of the corresponding gaseous ion (63). Where an electron displacement mechanism is responsible for the homogeneous activation of hydrogen, some degree of correlation might similarly be expected between catalytic activity and the corresponding gaseous electron affinities of the active metal ions. In support of this view, it might be pointed out that Cu^{++} and other metal ions such as Cu^+ , Hg^{++} , Hg^+ , and Ag^+ which have been found to activate hydrogen homogeneously in solution are characterized by high electron affinities in the gaseous state, compared with analogous inactive ions.

Also consistent with the suggestion that the activation process involves electron transfer from the hydrogen molecule to the catalyst, is

the observation that other electron transfer reactions of the catalytically active ions are also notably fast, as indicated by studies of the isotopic electron exchange between Hg_2^{++} and Hg^{++} (64) and of the catalytic influence of Cu^{++} on various oxidation reactions (65,66). The promoting influence of negative ions on the catalytic activity of Cu^{++} also parallels the well known general catalytic influence of complexing negative ions such as OH^- and Cl^- on the $\text{Fe}^{++} - \text{Fe}^{+++}$ and other isotopic electron exchange reactions (68), an effect that has been attributed to their bridging action, or effectiveness in lowering the electrostatic repulsion which constitutes a barrier to the mutual approach of two exchanging ions (68,69). This may be an alternative interpretation of the influence of these ions, to that which has already been considered.

Eyring and Smith (70) have pointed out that the fusion of more than one electronically saturated molecule into an activated complex normally involves electron promotion; hence a lowering of the activation energy is to be expected when the activated complex is co-ordinated with a suitable electron acceptor. The mechanism proposed here, which attributes the catalytic activation of hydrogen to the electron accepting properties of the metal ion catalysts, reflects the same principle.

The interpretation proposed here has some important features in common with that originally suggested by Dowden (20,21,71) for the ordinary heterogeneous catalytic activity of metals, in which the electronic work function of the metal was introduced in a manner analogous to the electron affinity of the metal ion in the present case.

CONCLUSIONS

The ability to activate molecular hydrogen homogeneously in aqueous solutions was found to be a general property of the dissolved cupric salts that were studied. The catalytic activity of the cupric ion was found to be strongly affected by complexing, the activities of the cupric complexes decreasing in the order: butyrate, propionate > acetate sulphate > chloride > water (i.e. the uncomplexed cupric ion) > glycine, ethylenediamine).

The species CuH^+ is postulated to occur as the reactive intermediate in the stepwise process leading to the overall reduction of the substrate. This suggestion is supported by the following considerations:

(1) The dependence of the dichromate reduction rate on the H^+ concentration can be explained most readily in terms of competition from a back reaction, if CuH^+ and H^+ are the immediate products of the rate controlling step.

(2) The promoting influence of complexing anions which follows the same order as their basicities finds explanation if they are assigned the role of proton acceptors in the rate determining step.

(3) Within the limits of endothermicity consistent with the observed activation energy of the reaction, CuH^+ appears energetically more plausible than the other intermediates which have been suggested.

(4) A similar intermediate, i.e. $\text{Cu}^{\text{I}}\cdot\text{H}$, has been postulated to explain the homogeneous activation of hydrogen by cuprous acetate in quinoline (21,22,24,27).

The mechanism proposed here, entails the displacement of a hydride ion from H_2 to the Cu^{++} ion, both electrons in the $\text{Cu}^+ - \text{H}$ bond being con-

tributed by the hydrogen molecule. In this context, the role of Cu^{++} appears to be that of an electron-acceptor suggesting that its catalytic activity may be related to the presence of low-lying unoccupied orbitals into which the H_2 electrons can enter. The lowering of the catalytic activity of Cu^{++} on chelation with glycine and ethylenediamine (Table IV) may reflect the fact that in the complex these orbitals are used in bonding.

The heterolytic splitting of the H_2 molecule in the activation process requires only one metal atom 'site', as evidenced by the first order kinetics with respect to the cupric salt. The 'dual site' requirement of the process applies only in the sense that a base molecule such as H_2O or Ac^- may be necessary as a second site to absorb the proton.

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APPENDIX A

ABSORPTION SPECTRA OF SODIUM DICHROMATE AND
CHROMIC ACETATE IN AQUEOUS SOLUTIONS

Dichromate was normally determined in solution samples by a spectrophotometric method based on the absorption peak at $350\text{ m}\mu$ shown in Fig. 30. Except in chloride solutions where another method was used, cupric salts do not generally absorb light in this region. Beer's law is obeyed at all concentrations up to 5×10^{-4} moles per liter $\text{Cr}_2\text{O}_7^{=}$, the maximum that was determined without further dilution. Dichromate concentrations as low as 5×10^{-6} moles per liter were detectable by this method.

The absorption spectrum of dissolved chromic acetate, shown in Fig. 30, was found to be identical with that of reduced dichromate solutions of similar total chromium concentration, allowance being made for absorption by cupric acetate in the red region of the spectrum. This was accepted as evidence that the reduction product of $\text{Cr}_2\text{O}_7^{=}$ in these solutions was Cr(III).

From Fig. 30, CrAc_3 is seen to absorb light in the $350\text{ m}\mu$ region of the spectrum. This absorption was found to be general for chromic salts in aqueous solution, their optical density averaging about 1.7% of that for similar concentrations of dichromate. A small correction was made to eliminate systematic errors from this source.

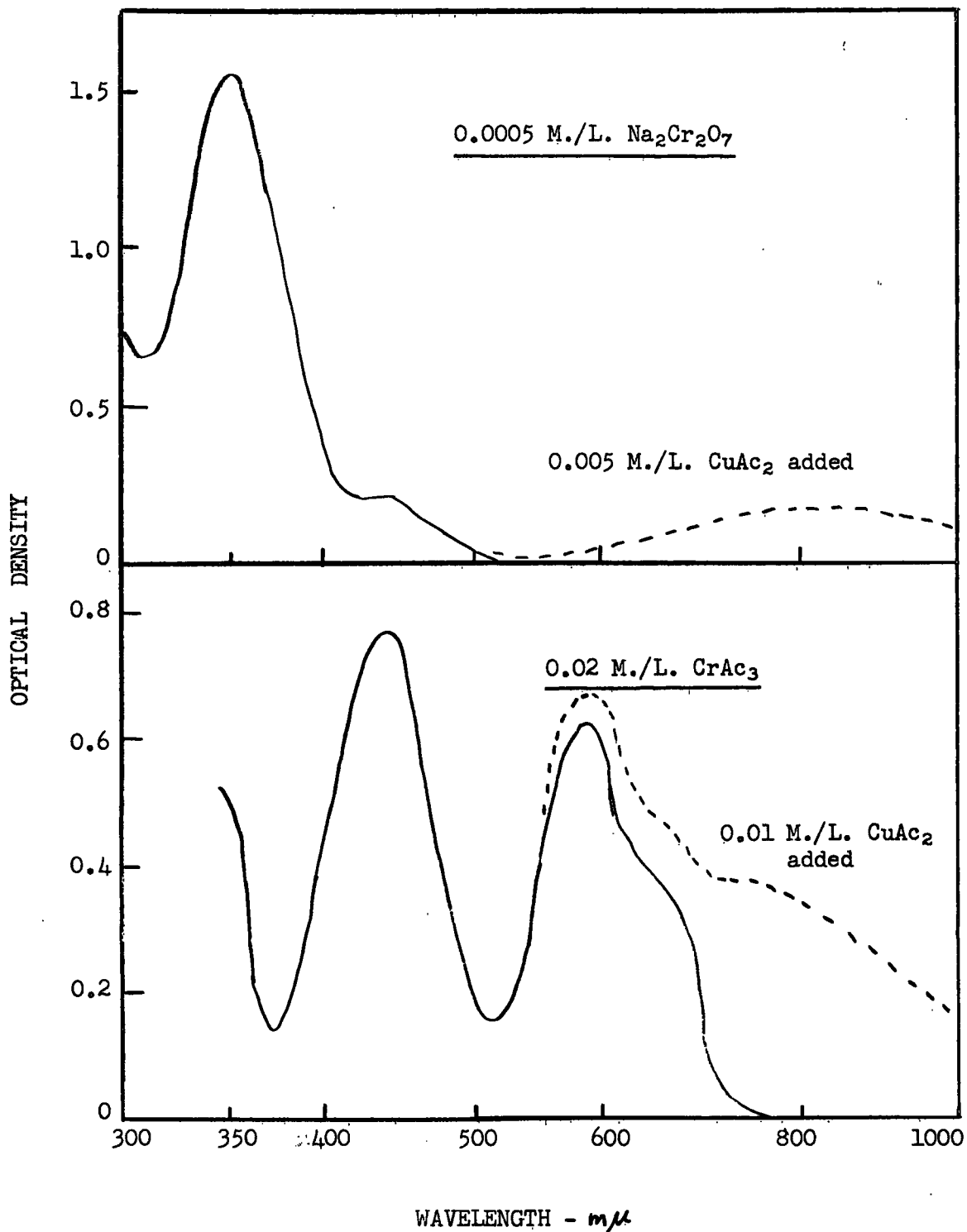


Figure 30. Absorption Spectra of Sodium Dichromate and Chromic Acetate Solutions. (Determined with a Beckman DU Spectrophotometer).

APPENDIX B

SUMMARY OF SELECTED EXPERIMENTAL DATA

(a) Effect of Initial Dichromate Concentration on the Rate of the Cupric Perchlorate Catalyzed Reduction of Dichromate by Hydrogen (Fig. 1).

0.10 M./L. $\text{Cu}(\text{ClO}_4)_2$, 0.01 M./L. HClO_4 ; 110°C.; 20 atm. H_2

Expt. No.	Initial $[\text{Cr}_2\text{O}_7^{=}]$ M./L.	$-\text{d}[\text{Cr}_2\text{O}_7^{=}]/\text{dt} \times 10^8$ mole liter ⁻¹ sec. ⁻¹	$-\text{d}[\text{H}_2]/\text{dt} \times 10^8$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^5$ liter mole ⁻¹ sec. ⁻¹
S-7-R	0.0010	5.25	15.7	9.48
S-5	0.00025	5.37	16.1	9.63
S-6	0.00075	5.30	15.9	9.55
S-8	0.00050	5.37	16.1	9.75

(b) Comparison of the Reaction Rates for Various Substrates; Effect of Cupric Perchlorate Concentration (Figs. 2 and 3). 0.01 M./L.

HClO_4 ; 110°C.; 20 atm. H_2

Expt. No.	$[\text{Cu}(\text{ClO}_4)_2]$ M./L.	Substrate (X)	$-\text{d}[X]/\text{dt}$ $\times 10^8$ -mole liter ⁻¹ sec. ⁻¹	$-\text{d}[\text{H}_2]/\text{dt}$ $\times 10^7$ -mole liter ⁻¹ sec. ⁻¹	$k \times 10^5$ liter mole ⁻¹ sec. ⁻¹
U-1	0.20	$\text{Cr}_2\text{O}_7^{=}$	10.3	3.10	9.43
U-2	0.27	$\text{Cr}_2\text{O}_7^{=}$	13.8	4.13	9.32
U-3	0.36	$\text{Cr}_2\text{O}_7^{=}$	18.0	5.41	9.07
U-4	0.51	$\text{Cr}_2\text{O}_7^{=}$	27.2	8.15	9.80
U-5	0.10	$\text{Cr}_2\text{O}_7^{=}$	5.23	1.57	9.60

(b) contd.

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X-1	0.11	IO_3^-	6.37	1.59	8.80
X-2	0.22	IO_3^-	12.9	3.22	8.90
X-3	0.32	IO_3^-	18.6	4.64	8.78
X-4	0.20	Ce^{++++}	54.5	2.72	8.18
X-5	0.10	Ce^{++++}	26.2	1.31	7.77

(c) Effect of Hydrogen Pressure on the Reaction Rate (Figs. 4 and 5).

0.10 M./L. $\text{Cu}(\text{ClO}_4)_2$, 0.01 M./L. HClO_4 ; 110°C.

Expt. No.	P_{H_2} Atm.	$-\text{d}[\text{Cr}_2\text{O}_7^{=}] / \text{dt} \times 10^8$ mole liter ⁻¹ sec. ⁻¹	$-\text{d}[\text{H}_2] / \text{dt} \times 10^8$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^5$ liter mole ⁻¹ sec. ⁻¹
U-5	20	5.23	15.7	9.60
U-6	25	6.50	19.5	9.48
U-7	15	3.87	11.6	9.43
U-8	10	2.60	7.8	9.48
U-9	5	1.23	3.7	8.88

(d) Effect of Temperature on the Reaction Rate (Fig. 7). 0.10 M./L.

 $\text{Cu}(\text{ClO}_4)_2$, 0.01 M./L. HClO_4 ; 20 atm. H_2

Expt. No.	Temp. °C.	$-\text{d}[\text{Cr}_2\text{O}_7^{=}] / \text{dt}$ $\times 10^8$ -mole liter ⁻¹ sec. ⁻¹	$-\text{d}[\text{H}_2] / \text{dt}$ $\times 10^8$ -mole liter ⁻¹ sec. ⁻¹	$k \times 10^5$ liter mole ⁻¹ sec. ⁻¹	$\log(k/T)$ liter mole ⁻¹ sec. ⁻¹ °K ⁻¹
V-1	130	31.6	94.8	53.5	$\bar{6}.123$
V-2	140	73.3	220	111	$\bar{6}.430$
V-3	120	13.3	40.0	23.8	$\bar{7}.783$

(d) contd.

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V-4	110	5.08	15.3	9.18	$\bar{7}.452$
V-5	100	2.05	6.15	3.88	$\bar{7}.017$
V-6	90	0.83	2.47	1.61	$\bar{8}.648$
V-7	80	0.33	1.00	0.67	$\bar{8}.289$

(e) Effect of Perchloric Acid on the Reaction Rate (Fig. 8).

0.10 M./L. $\text{Cu}(\text{ClO}_4)_2$; 20 atm. H_2

Expt. No.	HClO_4 M./L.	$-\text{d}[\text{Cr}_2\text{O}_7^{=}] / \text{dt} \times 10^8$ mole liter ⁻¹ sec. ⁻¹	$-\text{d}[\text{H}_2] / \text{dt} \times 10^8$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^5$ liter mole ⁻¹ sec. ⁻¹
S-16	0.25	3.10	9.30	5.72
S-17	0.50	2.22	6.66	4.07
S-18	0.75	1.88	5.65	3.44
S-19	1.00	1.37	4.10	2.51
T-5	0.10	4.28	12.8	7.76
T-6	0.05	4.72	14.2	8.67
T-7	0.025	5.13	15.4	9.33
T-8	0.017	5.32	16.0	9.64
T-9	0.013	5.15	15.4	9.25
T-10	0.010	5.17	15.5	9.45
T-11	0.004	5.23	15.7	9.42

(f) Effect of Initial Dichromate Concentration on the Rate of the Cupric Acetate Catalyzed Reduction of Dichromate by Hydrogen (Fig. 9).

0.10 M./L. CuAc_2 ; 0.25 M./L. NaAc; 0.50 M./L. HAc; 13.6 atm. H_2 ; 100°C.

Expt. No.	Initial $[\text{Cr}_2\text{O}_7^{=}]$ M./L.	$-\text{d}[\text{Cr}_2\text{O}_7^{=}]/\text{dt} \times 10^6$ mole liter ⁻¹ sec. ⁻¹	$-\text{d}[\text{H}_2]/\text{dt} \times 10^6$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^3$ liter mole ⁻¹ sec. ⁻¹
C-4	0.005	1.67	5.00	4.65
C-5	0.020	1.55	4.64	4.34
C-6	0.015	1.52	4.55	4.20
C-7	0.010	1.56	4.67	4.34

(g) Effect of Cupric Acetate Concentration on the Reaction Rate (Figs.

10 and 11). 0.25 M./L. NaAc; 0.50 M./L. HAc; 13.6 atm. H_2 ; 100°C.

Expt. No.	$[\text{CuAc}_2]$ M./L.	$-\text{d}[\text{Cr}_2\text{O}_7^{=}]/\text{dt} \times 10^6$ mole liter ⁻¹ sec. ⁻¹	$-\text{d}[\text{H}_2]/\text{dt} \times 10^6$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^3$ liter mole ⁻¹ sec. ⁻¹
E-1	0.198	2.89	8.66	4.08
E-2	0.150	2.20	6.60	4.10
E-3	0.102	1.58	4.74	4.34
E-4	0.051	0.81	2.44	4.47
K-2	0.248	3.50	10.5	3.94

(h) Effect of Hydrogen Pressure on the Cupric Acetate Catalyzed Reaction Rate (Fig. 12). 0.25 M./L. NaAc; 0.50 M./L. HAC; 0.10 M./L. CuAc₂; 100°C.

Expt. No.	P _{H₂}	$-d[\text{Cr}_2\text{O}_7^{=}] / dt \times 10^6$ mole liter ⁻¹ sec. ⁻¹	$-d[\text{H}_2] / dt \times 10^6$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^3$ liter mole ⁻¹ sec. ⁻¹
D-1	27.2	3.08	9.24	4.27
D-2	20.4	2.34	7.03	4.35
D-3	13.6	1.54	4.64	4.31
D-4	7.1	0.81	2.44	4.30

(i) Effect of Temperature on the Cupric Acetate Catalyzed Reaction Rate (Fig. 13). 0.10 M./L. CuAc₂; 0.25 M./L. NaAc; 0.50 M./L. HAC; 13.6 atm. H₂

Expt. No.	Temp. °C.	$-d[\text{Cr}_2\text{O}_7^{=}] / dt \times 10^2$ mole liter ⁻¹ sec. ⁻¹	$-d[\text{H}_2] / dt \times 10^5$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^3$ liter mole ⁻¹ sec. ⁻¹	log (k/T) liter mole ⁻¹ sec. ⁻¹ °K ⁻¹
A-1	130.5	22.2	66.7	54.2	$\bar{4}.129$
A-2	120.0	8.78	26.3	22.8	$\bar{5}.763$
A-3	110.2	4.03	12.1	10.8	$\bar{5}.452$
A-4	100.5	1.57	4.70	4.38	$\bar{5}.070$
A-5	90.3	0.65	1.93	1.87	$\bar{6}.712$
A-6	80.0	0.22	0.66	0.65	$\bar{6}.266$
B-1	140	39.8	119	95.3	$\bar{4}.364$
B-2	130	16.4	49.2	41.1	$\bar{4}.008$
B-3	120.0	8.95	26.8	23.2	$\bar{5}.771$
B-4	100.0	1.53	4.59	4.27	$\bar{5}.057$

(i) contd.

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B-5	80.3	0.23	0.70	0.69	$\bar{6}.292$
B-6	90.5	0.67	2.00	1.94	$\bar{6}.728$
B-7	109.5	3.42	10.3	9.2	$\bar{5}.380$

(j) Effect of pH on the Reaction Rate in Acetate Solutions (Fig. 14).

0.05 M./L. CuAc_2 ; 0.90 HAC; 20 atm. H_2 ; 100°C.

Expt. No.	$[\text{HClO}_4]$ or $[\text{NaOH}]$ M./L.	pH	$-\text{d}[\text{Cr}_2\text{O}_7^{=}] / \text{dt} \times 10^7$ mole liter ⁻¹ sec. ⁻¹	$-\text{d}[\text{H}_2] / \text{dt} \times 10^7$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^3$ liter mole ⁻¹ sec. ⁻¹
Ac-1	0.25 NaOH	4.25	13.0	38.9	4.68
Ac-2	-	3.39	11.3	34.0	4.11
Ac-3	0.10 HClO_4	2.05	2.32	6.96	0.88
Ac-4	0.05 HClO_4	2.90	8.03	24.1	3.12
Ac-5	0.15 HClO_4	1.25	0.28	0.84	0.10
Ac-6	0.11 HClO_4	1.70	0.90	2.68	0.34
Ac-7	0.025 HClO_4	3.17	10.31	30.9	3.70
Ac-8	0.075 HClO_4	2.55	5.00	15.0	1.86

(k) Effect of Various Salts on the Rate of the Cupric Acetate Catalyzed

Reaction (Fig. 16). 0.05 M./L. CuAc_2 (M,N Series); 0.10 M./L. CuAc_2 (Q series); 0.25 M./L. NaAc; 0.50 M./L. HAC; 13.6 atm. H_2 ;

100°C.

Expt. No.	Salt M./L.	$-\text{d}[\text{Cr}_2\text{O}_7^{=}] / \text{dt} \times 10^6$ mole liter ⁻¹ sec. ⁻¹	$-\text{d}[\text{H}_2] / \text{dt} \times 10^6$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^3$ liter mole ⁻¹ sec. ⁻¹
M-1	0.20 CaAc_2	0.822	2.47	4.33
M-2	-	0.857	2.57	4.67

(k) contd.

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N-2-B	0.20 CrAc ₃	0.773	2.32	4.29
N-3-B	0.20 NiAc ₂	0.755	2.26	4.20
N-4	0.20 NaClO ₄	0.836	2.51	4.60
N-5	0.20 Na ₂ SO ₄	0.690	2.07	3.87
N-6	0.75 NaAc	0.772	2.31	4.31
Q-1	1.50 NaClO ₄	1.77	5.30	4.81
Q-2	1.00 NaClO ₄	1.77	5.30	4.81
Q-3	0.50 NaClO ₄	1.70	5.10	4.64
Q-4	-	1.64	4.93	4.45
Q-5	0.25 Na ₂ SO ₄	1.44	4.33	3.93
Q-6	0.50 Na ₂ SO ₄	1.27	3.80	3.45
Q-7	0.75 Na ₂ SO ₄	1.13	3.39	3.06
Q-8	1.50 NaNO ₃	1.58	4.75	4.40
Q-9	1.00 NaNO ₃	1.58	4.74	4.39
Q-10	0.50 NaNO ₃	1.59	4.77	4.40
Q-11	-	1.60	4.81	4.38
Q-12	0.75 Ca(NO ₃) ₂	1.45	4.35	4.04
Q-13	0.50 Ca(NO ₃) ₂	1.55	4.67	4.28
Q-14	0.25 Ca(NO ₃) ₂	1.53	4.60	4.26
Q-15	-	1.60	4.81	4.45
Q-16	0.75 MgSO ₄	1.09	3.25	3.00
Q-17	0.50 MgSO ₄	1.24	3.72	3.41
Q-18	0.25 MgSO ₄	1.42	4.26	3.94
Q-19	1.00 KNO ₃	1.59	4.78	4.40
Q-20	0.90 NH ₄ NO ₃	1.30	3.90	3.85
Q-21	0.33 Cr(NO ₃) ₃	negligible	-	-
Q-22	0.50 Mg(NO ₃) ₂	1.60	4.80	4.32

(k) contd.

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Q-23	0.50 Ca(ClO ₄) ₂	1.52	4.58	4.17
Q-24	0.50 Mg(ClO ₄) ₂	1.62	4.85	4.44
Q-25	0.25 Ni(ClO ₄) ₂	1.56	4.69	4.29
Q-26	0.50 (NH ₄) ₂ SO ₄	1.10	3.30	3.05
Q-27	0.50 NiSO ₄	1.09	3.29	2.98
Q-28	0.50 ZnSO ₄	0.99	2.96	2.72
Q-29	0.50 NH ₄ Ac	1.17	3.52	3.28
Q-30	0.50 CaAc ₂	1.42	4.25	3.85

(1) Reaction Rate Measurements from a Typical Experiment Involving the Consecutive Reduction of Dichromate and Cupric Acetate by Hydrogen (Expt. H-2, Fig. 17). 0.01 M./L. Initial Na₂Cr₂O₇; 0.10 M./L. Initial CuAc₂; 0.25 M./L. NaAc; 0.50 M./L. HAC; 13.6 atm. H₂; 100°C.

	<u>Substrate</u>	
	<u>Cr₂O₇⁼</u>	<u>CuAc₂</u>
$-d[\text{Cr}_2\text{O}_7^=]/dt$ - mole liter ⁻¹ sec ⁻¹	1.60×10^{-6}	-
$-d[\text{CuAc}_2]/[\text{CuAc}_2]dt$ - sec. ⁻¹	-	1.07×10^{-4}
$-d[\text{H}_2]/[\text{CuAc}_2]dt$ - sec. ⁻¹	4.77×10^{-5}	5.35×10^{-5}
k - liter mole ⁻¹ sec. ⁻¹	4.44×10^{-3}	4.98×10^{-3}

(m) Effect of Cupric Propionate Concentration on the Reaction Rate.

0.25 M./L. NaPr; 0.50 HPr; 20 atm. H₂; 100°C.

Expt. No.	[CuPr ₂] M./L.	$-d[Cr_2O_7^{=}] / dt \times 10^{-6}$ mole liter ⁻¹ sec. ⁻¹	$-d[H_2] / dt \times 10^6$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^3$ liter mole ⁻¹ sec. ⁻¹
Pr-1	0.10	2.80	8.40	5.38
Pr-8	0.05	1.46	4.39	5.45
Pr-9	0.15	4.22	12.6	5.18
Pr-10	0.20	5.24	15.7	4.88
Pr-13	0.05	1.50	4.51	5.30

(n) Effect of Temperature on the Rate of the Cupric Propionate Catalyzed

Reaction (Fig. 19). 0.05 M./L. CuPr₂; 0.25 M./L. NaPr; 0.50 M./L.

HPr; 20 atm. H₂.

Expt. No.	Temp. °C.	$-d[Cr_2O_7^{=}] / dt \times 10^6$ mole liter ⁻¹ sec. ⁻¹	$-d[H_2] / dt \times 10^6$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^3$ liter mole ⁻¹ sec. ⁻¹	log (k/T) liter mole ⁻¹ sec. ⁻¹ °K ⁻¹
Pr-8	100.0	1.46	4.39	5.45	$\bar{5}.164$
Pr-11	120.6	8.58	25.7	28.1	$\bar{5}.854$
Pr-12	110.0	3.51	10.6	12.5	$\bar{5}.513$
Pr-13	100.0	1.50	4.51	5.30	$\bar{5}.153$
Pr-14	90.2	0.60	1.78	2.28	$\bar{6}.799$
Pr-15	80.5	0.23	0.69	0.92	$\bar{6}.415$

(o) Effect of Sulphate Concentration on the Reaction Rate (Fig. 21).

0.10 M./L. Cu(II); 20 atm. H₂; 110°C.

Expt. No.	[SO ₄ ²⁻] M./L.	-d[Cr ₂ O ₇ ²⁻]/dt x 10 ⁷ mole liter ⁻¹ sec. ⁻¹	-d[H ₂]/dt x 10 ⁷ mole liter ⁻¹ sec. ⁻¹	k x 10 ⁴ liter mole ⁻¹ sec. ⁻¹
SO ₄ -1 ^a	0.30	2.55	7.65	4.58
SO ₄ -2 ^a	0.30	2.56	7.68	4.58
SO ₄ -3 ^a	0.28	2.43	7.32	4.36
SO ₄ -4 ^a	0.18	2.00	6.00	3.58
SO ₄ -5 ^a	0.08	1.38	4.14	2.47
SO ₄ -6 ^a	0.03	0.85	2.54	1.52
SO ₄ -7 ^a	0.0	0.50	1.48	0.95
SO ₄ -9 ^b	0.27	2.38	7.15	4.27
SO ₄ -10 ^b	0.23	2.15	6.45	3.85
SO ₄ -11 ^b	0.13	1.73	5.20	3.11
SO ₄ -12 ^b	0.026	0.77	2.31	1.29
SO ₄ -13 ^a	0.08	1.50	4.50	2.66
SO ₄ -14 ^c	0.49	2.83	8.51	5.03
SO ₄ -15 ^c	0.39	2.67	8.00	4.76
SO ₄ -18 ^a	0.26	2.09	6.25	3.70

a - Ionic Strength Constant at 1.0; b - [SO₄²⁻] + [HSO₄⁻] = 0.35;

c - Ionic Strength > 1.0.

(p) Effect of Temperature on the Rate of the Cupric Sulphate Catalyzed Reaction (Fig. 19). 0.10 M./L. CuSO_4 ; 0.20 M./L. MgSO_4 ; 0.05 M./L. H_2SO_4 ; 20 atm. H_2 .

Expt. No.	Temp. °C.	$-\frac{d[\text{Cr}_2\text{O}_7^{=}]}{dt} \times 10^7$ mole liter ⁻¹ sec. ⁻¹	$-\frac{d[\text{H}_2]}{dt} \times 10^7$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^4$ liter mole ⁻¹ sec. ⁻¹	$\log (k/T)$ liter mole ⁻¹ sec. ⁻¹ °K ⁻¹
SO ₄ -18	110.0	2.09	6.25	3.70	7.985
SO ₄ -19	130.0	13.45	40.4	22.6	6.750
SO ₄ -20	89.8	0.23	0.69	0.44	7.083

(q) Effect of Cu(II) Concentration on the Rate of the Cupric Sulphate Catalyzed Reaction (Fig. 22). 0.25 M./L. $\text{SO}_4^{=}$; 0.10 M./L. HSO_4^- ; 20 atm. H_2 ; 110°C.

Expt. No.	[Cu(II)] M./L.	$-\frac{d[\text{Cr}_2\text{O}_7^{=}]}{dt} \times 10^7$ mole liter ⁻¹ sec. ⁻¹	$-\frac{d[\text{H}_2]}{dt} \times 10^7$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^4$ liter mole ⁻¹ sec. ⁻¹
SO ₄ -16	0.314	5.40	16.2	3.14
SO ₄ -17	0.207	3.78	11.3	3.48
SO ₄ -18	0.103	2.09	6.25	3.70

(r) Effect of Chloride Concentration on the Reaction Rate (Fig. 23). 0.10 M./L. Cu(II); 20 atm. H_2 ; 110°C.

Expt. No.	[Cl ⁻] M./L.	$-\frac{d[\text{Cr}_2\text{O}_7^{=}]}{dt} \times 10^7$ mole liter ⁻¹ sec. ⁻¹	$-\frac{d[\text{H}_2]}{dt} \times 10^7$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^4$ liter mole ⁻¹ sec. ⁻¹
Cl-30	1.00	1.44	4.32	2.57
Cl-31	0.80	1.31	3.93	2.33

(r) contd.

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Cl-32	0.60	1.33	3.99	2.37
Cl-33	0.40	1.06	3.18	1.93
Cl-34	0.20	0.93	2.78	1.66
Cl-35	0.21	0.95	2.84	1.67
Cl-39	0.30	1.12	3.36	1.96
Cl-40	0.10	0.83	2.49	1.50
Cl-44	0.20	0.79	2.37	1.42
Cl-47	1.40	1.36	4.08	2.45

(s) Effect of Cu(II) Concentration on the Cupric Chloride Catalyzed

Reaction Rate (Fig. 24). 20 atm. H₂; 110°C.

Expt. No.	[Cl ⁻] M./L.	[Cu(II)] M./L.	$-d[\text{Cr}_2\text{O}_7^{2-}]/dt$ $\times 10^7$ mole liter ⁻¹ sec. ⁻¹	$-d[\text{H}_2]/dt \times 10^7$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^4$ liter mole ⁻¹ sec. ⁻¹
Cl-25	1.00	0	0.07	0.20	-
Cl-26	"	0.020	0.31	0.93	2.80
Cl-27	"	0.041	0.58	1.75	2.62
Cl-28	"	0.062	0.74	2.23	2.20
Cl-29	"	0.080	0.96	2.87	2.18
Cl-30	"	0.103	1.44	4.32	2.57
Cl-42	0.20	0.390	2.83	8.50	1.33
Cl-43	"	0.209	1.63	4.90	1.43
Cl-44	"	0.102	0.79	2.37	1.42
Cl-45	"	0.067	0.53	1.60	1.46
Cl-46	"	0.051	0.46	1.38	1.67
Cl-35	0.21	0.104	0.95	2.84	1.67

(s) contd.

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Cl-36	0.42	0.205	1.94	5.82	1.73
Cl-37	0.63	0.306	2.78	8.35	1.67
Cl-38	0.84	0.408	3.79	11.37	1.70

(t) Effect of pH on the Reaction Rate in Cupric Ethylenediamine Solutions

(Fig. 25). 0.05 M./L. $\text{Cu}(\text{ClO}_4)_2$; 0.20 M./L. EDA; 20 atm. H_2 ;

130°C.

Expt. No.	$[\text{HClO}_4]$ M./L.	pH	$-\frac{d[\text{Cr}_2\text{O}_7^{2-}]}{dt}$ $\times 10^7$ -mole liter ⁻¹ sec. ⁻¹	$-\frac{d[\text{H}_2]}{dt} \times 10^7$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^4$ liter mole ⁻¹ sec. ⁻¹
ED-2	0.38	2.5	1.37	4.11	4.79
ED-3	0.36	3.5	1.35	4.05	4.76
ED-4	0.26	4.1	0.72	2.17	2.56
ED-5	0.20	5.0	0.15	0.45	0.54
ED-6	0.19	6.1	0.16	0.49	0.59
ED-7	0.31	3.9	0.82	2.45	2.87
ED-7-R	0.31	3.9	0.78	2.35	2.72
ED-8	0.23	4.6	0.34	1.02	1.20
ED-9	0.40	1.6	1.39	4.17	4.91
ED-13	0.18	6.1	0.19	0.57	0.66

(u) Effect of Cu(II) Concentration on the Reaction Rate in Ethylenediamine Solutions (Fig. 26). 0.20 M./L. EDA; pH 6 (Room Temp.); 20 atm. H₂; 130°C.

Expt. No.	[Cu(ClO ₄) ₂] M./L.	[HClO ₄] M./L.	-d(Cr ₂ O ₇ ⁼)/dt x 10 ⁷ mole liter ⁻¹ sec. ⁻¹	-d[H ₂]/dt x 10 ⁷ mole liter ⁻¹ sec. ⁻¹	k x 10 ⁴ liter mole ⁻¹ sec. ⁻¹
ED-10	0.025	0.27	0.105	0.315	0.72
ED-11	0.095	0.00	0.781	2.34	1.33
ED-12	0.073	0.08	0.232	0.696	0.54
ED-13	0.049	0.18	0.189	0.567	0.66
ED-17	0.000	0.36	0.008	0.024	-

(v) Effect of pH on the Reaction Rate in Cupric Glycinate Solutions (Fig. 27). 0.05 M./L. Cu(ClO₄)₂; 0.20 M./L. Gl; 20 atm. H₂; 130°C.

Expt. No.	[NaOH] or [HClO ₄] M./L.	pH	-d(Cr ₂ O ₇ ⁼)/dt x 10 ⁷ mole liter ⁻¹ sec. ⁻¹	-d[H ₂]/dt x 10 ⁷ mole liter ⁻¹ sec.	k x 10 ⁴ liter mole ⁻¹ sec. ⁻¹
G1-14	0.10 NaOH	5.1	0.50	1.49	1.66
G1-15	0.08 "	4.1	0.89	2.68	2.97
G1-17	0.02 "	3.1	3.17	9.51	10.6
G1-20	0.08 "	4.2	0.56	1.69	1.92
G1-21	0.06 "	3.7	1.25	3.75	4.31
G1-22	0.04 "	3.4	2.28	6.84	7.55
G1-23	0.02 "	3.1	3.21	9.63	10.5
G1-24	-	2.9	3.90	11.7	12.7
G1-26	0.10 HClO ₄	2.2	4.98	14.9	16.4

(v) contd.

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G1-27	0.15	HClO ₄	1.8	4.18	12.5	13.7
G1-28	0.10	"	2.1	4.98	14.9	15.9
G1-29	0.20	"	1.5	3.23	9.7	10.7
G1-30	0.30	"	1.0	1.47	4.41	4.9
G1-31	0.50	"	0.55	0.68	2.04	2.26
G1-32	0.03	"	2.6	3.90	11.7	12.5
G1-33	0.05	"	2.45	4.57	13.7	15.1
G1-41	0.05	NaOH	3.5	1.56	4.68	5.4
G1-46	0.10	"	6.2	0.51	1.53	1.8

(w) Effect of Glycine Concentration on the Reaction Rate at Several pH's
(Fig. 28). 0.05 M./L. Cu(ClO₄)₂; 20 atm. H₂; 130°C.

Expt. No.	[G1] M./L.	[HClO ₄] or [NaOH] M./L.	pH	$-d[Cr_2O_7^{=}] / dt \times 10^7$ mole liter ⁻¹ sec. ⁻¹	$-d[H_2] / dt \times 10^7$ mole liter ⁻¹ sec. ⁻¹	$k \times 10^4$ liter mole ⁻¹ sec. ⁻¹
G1-4	0.05	0.04 HClO ₄	2.0	2.47	7.41	8.51
G1-12	0.10	0.05 "	2.2	3.40	10.2	11.2
G1-13	0.10	0.09 NaOH	5.1	0.33	0.98	1.09
G1-14	0.20	0.10 "	5.1	0.50	1.49	1.66
G1-28	0.20	0.10 HClO ₄	2.1	4.98	14.9	15.9
G1-30	0.20	0.30 "	1.0	1.47	4.41	4.89
G1-35	0	0.10 "	1.2	1.04	3.12	3.49
G1-37	0.05	0.15 "	1.1	1.07	3.21	3.78
G1-38	0.10	0.20 "	1.1	1.21	3.63	4.39
G1-39	0.05	0.03 NaOH	3.5	1.49	4.47	5.10
G1-40	0.10	0.04 "	3.6	1.56	4.68	5.42

(w) contd)

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GI-41	0.20	0.05 NaOH	3.5	1.56	4.68	5.36
V-1 ^a	0	0.01 HClO ₄	2.0	3.16	9.48	5.35

a- Earlier Experiment. See page 72.
