It thus appears as would be expected that the entropy of the glass at 0°K. increases with the complexity of the molecule.[14]

Summary

1. The specific heats from 16 to 298°K. of ethyl alcohol crystals, glass and liquid and of hexyl alcohol crystals and liquid have been measured.
2. The heats of fusion and the temperature of fusion have been determined.
3. The entropies and free energies of ethyl and hexyl alcohols at 298° K. and the entropy of ethyl alcohol glass at 0° K. have been calculated.
4. Regularities in the thermal data for the normal saturated aliphatic alcohols have been discussed.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 200]

CATALYTIC EFFECT OF RUTHENIUM SALTS ON THE REDUCTION OF PERCHLORIC ACID BY HYDROBROMIC ACID

BY WILLIAM R. CROWELL, DON M. YOST AND JAMES M. CARTER

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Introduction

It is well known that both dilute and moderately concentrated solutions of perchloric acid are remarkably unreactive with most reducing agents, although the thermodynamic tendency for the acid to act as an oxidizing agent is undoubtedly very great. Its great power as an oxidizing agent is shown only when the acid is hot and concentrated. Under such conditions the lower valence compounds of osmium and ruthenium are oxidized to the tetroxides.[1] In dilute solutions of perchloric acid the only reducing agents mentioned in the literature as reacting with it are trivalent titanium, trivalent molybdenum and bivalent chromium,[2] the reactions in all three cases being measurably slow. It is to be noted that these three reducing agents have not only a very high reduction potential but have also high reaction rates with most oxidizing agents.

It was found by Dr. Robert H. Dalton in this Laboratory that bromine is evolved on heating mixtures of perchloric and hydrobromic acids containing small amounts of ruthenium chloride, while in the absence of ruthenium no such effect is observed. Subsequent experiments showed that the

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[14] See Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, **1927**, pp. 137–138.

[1] Noyes and Bray, "Qualitative Analysis for the Rare Elements," Macmillan Co., New York, **1927**, p. 17.

[2] Bredig and Michel, *Z. physik. Chem.*, **100**, 124 (1922).

catalyzed reaction takes place both at room temperature and at 100°, but much more slowly at the lower temperature.

In this paper are described the results of a research on the nature of the catalysis involved in this reaction. We take this opportunity to express our appreciation of the many helpful suggestions made by Professor A. A. Noyes during the investigation. The work was aided by funds granted to him by the Carnegie Institution of Washington.

The resultant reaction under consideration is

$$ClO_4^- + 8Br^- + 8H^+ = Cl^- + 4Br_2 + 4H_2O \qquad (1)$$

The fact that eight equivalents of bromine are liberated in the catalyzed reaction per mole of perchlorate ion used up is of importance in discussing the results of rate experiments, since a considerable amount of bromine liberated may correspond to only a small change in the concentration of perchlorate ion.

Interpretation of the mechanism of the reaction involves a knowledge of the chemistry of ruthenium in its numerous oxidation states. Unfortunately this has not been completely investigated. It has been definitely established, however, that bi-, tri- and quadrivalent ruthenium compounds are capable of existing in acid solution. The bivalent compounds form deep blue solutions, which react slowly with atmospheric oxygen to form light yellow or pink solutions that are oxidized by chlorine and bromine, but not by iodine, to the dark orange-red solutions of the quadrivalent salts. The quadrivalent salts in acid solution are quantitatively reduced by iodide[3] or by sulfurous acid to the trivalent state.

The compounds of sexivalent and septivalent ruthenium, the ruthenates (M_2RuO_4) and perruthenates ($MRuO_4$), are rapidly reduced by the halogen acids to the trivalent and quadrivalent states,[4] while with non-reducing acids they are decomposed into the tetroxide and various forms of lower valence.[5]

Ruthenium tetroxide, not only in solution but also in the solid, liquid or gaseous form, is a very active and powerful oxidizing agent. It is not so powerful, however, as permanganic acid, as is shown by the fact that the tetroxide is formed by the action of permanganic acid on the compounds of lower valence. At ordinary temperatures ruthenium tetroxide reacts with hydrobromic acid with the formation of bromine and a mixture of trivalent and quadrivalent ruthenium,[3] the mixture resulting from the fact that trivalent compounds react with bromine to form the quadrivalent compounds.[6]

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[3] Ruff and Vidic, *Z. anorg. allgem. Chem.*, **136,** 49 (1924).

[4] (a) J. L. Howe, THIS JOURNAL, **49,** 3843 (1927); (b) Krauss and Kükenthal, *Z. anorg. allgem. Chem.*, **136,** 62 (1924).

[5] (a) A. Gutbier, *Z. anorg. allgem. Chem.*, **95,** 183 (1916); (b) F. Krauss, *ibid.*, **132,** 301 (1923).

[6] Crowell and Yost, THIS JOURNAL, **50,** 374 (1928).

Preparation of the Solutions

A stock solution of ruthenium chloride was prepared from material purchased as ruthenium trichloride, but containing also some tetrachloride. The solution was made by dissolving the salt in 0.5 *N* hydrochloric acid. The color of this mixture is dark orange-red. A measured portion of the stock solution was treated with chlorine; and, after boiling to expel the excess of chlorine, it was titrated with standard titanous sulfate solution, the end-point being determined electrometrically.[6] The stock solution was found to contain 2.09 g. of ruthenium per liter.

Another ruthenium solution was prepared by treating a definite volume of the stock solution with a small excess of sulfur dioxide, expelling the excess by boiling and adding just enough water to replace that lost by evaporation. The resulting solution had a light orange-red color and it was shown by an electrometric titration with titanous sulfate to contain substantially all of the ruthenium in the trivalent state.

Standard solutions of perchloric acid, hydrobromic acid, potassium iodide and sodium thiosulfate were made up and standardized by the usual well-known methods.

Non-Formation of Bromine from Hydrobromic Acid with Perchloric Acid Alone or with Ruthenium Tetrachloride Alone

To make sure that no bromine is formed by the action of perchloric acid alone on hydrobromic acid or by a reaction between quadrivalent ruthenium and hydrobromic acid, the following experiments were made.

Ten cc. of a mixture which was 0.2905 *M* in $HClO_4$ and 0.871 *M* in HBr was heated at 98° in a sealed glass tube for three and one-half hours. The mixture was then diluted three-fold and treated with potassium iodide; no iodine was liberated.

A mixture of 10 cc. of 9 *M* HBr and 1.00 cc. of 1 *M* $HClO_4$ was heated for seventy-five minutes in a distilling flask through which a stream of carbon dioxide was passed; after five minutes 0.05 milliequivalent of bromine (due to free bromine originally present in the hydrobromic acid) was found in the receiver by iodimetric analysis, but no more was formed afterward.

A solution which was 8 *M* in HBr and 0.0246 atomic in ruthenium, present as a mixture of the quadrivalent and trivalent chlorides, was heated in a sealed tube at 98° for one hour, and the resulting mixture was cooled and treated with carbon tetrachloride; no bromine was found to be present.

Effects of Perchloric, Hydrobromic and Hydrochloric Acids and Ruthenium Salt on the Reaction Rate

Experiments were next made to determine the effects of perchloric acid, hydrobromic acid, ruthenium salt and hydrogen ion on the rate of liberation of bromine. In these experiments definite volumes of the reaction mixtures were heated in a water-bath at 98° in sealed glass tubes. The tubes were removed at suitable intervals, broken under solutions of potassium iodide and the liberated iodine was titrated with standard thiosulfate. The stock solution containing both tri- and quadrivalent ruthenium was used, but the iodine liberated by the quadrivalent ruthenium present was so small compared to the total iodine that it could be neglected. The results of typical experiments are shown in Table I. The "bromine formed" is the number of milliequivalents produced per liter.

In Expts. 1 and 2 the composition of the reaction mixtures differed

Table I

Effect of Perchloric Acid, Hydrobromic Acid, Total Acid and Ruthenium Salt on the Reaction Rate

Experiment no.	1	2	3	11	12
Milli-atoms of Ru per liter	2.06	2.06	1.03	1.03	1.03
Molality of HBr	0.5	0.5	0.5	1.0	0.5
Molality of $HClO_4$	.3	.6	.3	0.3	.3
Molality of HCl	.7	.4	.7	.2	2.2
Molality of total acid	1.5	1.5	1.5	1.5	3.0
Bromine formed in 15 min.	8.9	14.8	4.5	6.9	6.8
Bromine formed in 30 min.	17.3	30.6	8.5	11.1	13.3
Bromine formed in 45 min.	23.5	43.1	11.8	15.3	18.5
Bromine formed in 60 min.	29.7	54.0	15.7	20.2	24.9
Bromine formed in 75 min.	34.8	62.4	20.5	23.7	29.2
Bromine formed in 90 min.	41.1	65.8	22.2	25.1	33.5
Bromine formed in 120 min.	47.3	76.8	27.3	33.1	43.6
Bromine formed in 150 min.	56.5	83.3	32.2	36.0	56.3
Bromine formed in 24 hours	131.9	168.0	100.6	77.4	99.5
Bromine formed in 72 hours	188.9	...	159.7	141.2	178.7

initially only in the concentration of perchlorate, that in Expt. 2 being twice that in Expt. 1. Since the concentration of perchlorate decreased only 2% after two hours, the amounts of bromine liberated within this interval may be compared directly in determining the order of the reaction with respect to the perchlorate. It will be seen that in Expt. 2 the amount of bromine liberated was at first approximately twice that liberated in Expt. 1 in the same interval of time, but that this ratio decreases appreciably as the reaction proceeds. Therefore, at the beginning of the experiments the rate is directly proportional to the concentration of perchlorate.

By comparing in the same way the results of Expts. 1 and 3, the effect of the concentration of ruthenium may be determined. At first the rate of the reaction is directly proportional to the concentration of ruthenium, but as the reaction proceeds, this is no longer true. Thus after twenty-four hours the ratio of the amounts of bromine liberated is 1.3, although the initial ratio of the ruthenium concentrations was 2.0 and that of the perchlorate had decreased by less than 5%.

A comparison of the results of Expt. 3 with those of Expts. 11 and 12 shows that both the bromide and total acid influence the rate appreciably, but in neither case is the rate directly proportional to their concentrations. It is difficult to say whether their action is of a specific nature or is due to activity effects. It is also possible that the total acid and bromide govern to some extent the nature of the complex ions of ruthenium which are present in the solutions and in this way influence the reaction rate.

The Catalytically Active Form of Ruthenium

The fact that the rate does not remain directly proportional to the concentration of perchlorate and of the ruthenium indicates that the catalytically active form of the latter is decreasing in concentration as the reaction proceeds.

If trivalent ruthenium were more active catalytically than the quadrivalent form, the liberation of bromine would decrease the concentration of the former by oxidizing it to the quadrivalent state. The two experiments presented in Table II were made to determine whether this was true. In Expt. 4 the ruthenium was present initially in the trivalent form, while in Expt. 5 it was present in the quadrivalent state. The quadrivalent ruthenium was prepared by treating a definite volume of the stock solution at 98° with a large excess of bromine for forty-eight hours. The excess of bromine was expelled by boiling.

TABLE II

CATALYTIC EFFECTS OF TRIVALENT AND QUADRIVALENT RUTHENIUM

Initial concentrations: ruthenium, 0.00103 atomic; $HClO_4$, 0.3 molal; HBr, 0.5 molal; total acid, 1.5 molal.

	Bromine liberated, milli-equivalents per liter			Bromine liberated, milli-equivalents per liter	
Time, min.	Expt. 4 Ru^{III}	Expt. 5 Ru^{IV}	Time, min.	Expt. 4 Ru^{III}	Expt. 5 Ru^{IV}
15	22.6	1.08	90	79.8	7.55
30	41.0	2.20	120	88.1	8.65
45	52.1	5.18	150	95.5	9.90
60	62.0	6.28	24 (hours)	154.2	62.10
75	72.1	7.10	72 (hours)	201.5	132.4

The results show definitely that the quadrivalent form is much less active as a catalyst than the trivalent.

Two other types of experiments were made to obtain further evidence regarding the active form of the ruthenium. In the first type the reaction was carried out in a special distilling flask provided with a short reflux condenser bent at an angle with the exit tube and having an inlet tube which could be used to introduce a current of carbon dioxide. The bromine was caught in an acidified potassium iodide solution, which was replaced by a fresh one at measured intervals of time. The liberated iodine was titrated with standard thiosulfate. The results of an experiment of this type and of a similar experiment carried out in sealed glass tubes are given in Table III.

TABLE III

EFFECT OF REMOVAL OF BROMINE ON THE REACTION RATE

Initial concn.: $HClO_4$, 0.3 *N;* HCl, 0.33 *N;* HBr, 1.0 *N;* Ru, 0.00103 at.

Time, hours		0	1	2	3	4	5	6
Bromine lib., milli-equiv. per liter	Dist. expt.	0	51.6	92.2	122.2	147.2	169.5	191.1
	Closed-tube expt.	0	60.7	86.8	103.2	114.5	121.5	130.0

In the distillation experiment the bromine formed was removed fairly rapidly by the stream of carbon dioxide and was thereby prevented from reacting with the trivalent ruthenium to form the less active quadrivalent form, for it is shown later that this reaction is a slow one. The result showed that the rate of formation of bromine is less rapid in the sealed-tube experiments and therefore less rapid with quadrivalent than with trivalent ruthenium.

In the second type of experiments potassium iodide was added to the reaction mixtures and these were heated in sealed tubes. The iodide by its rapid reducing action prevents the formation of much bromine and quadrivalent ruthenium and, consequently, the concentrations of trivalent ruthenium and of bromide are held constant so long as iodide is present. The results of four such experiments are given in Table IV and are shown graphically in Fig. 1. The quantities of iodide added and of bromine formed are expressed in milli-equivalents per liter, both in the table and on the chart.

TABLE IV

EFFECT OF IODIDE ON THE REACTION RATE

	Expt. 4	Expt. 8	Expt. 9	Expt. 10
Ru, at. wts. per liter	0.00103	0.00103	0.00103	0.00103
HBr, mole per liter	.5	.5	.5	.5
$HClO_4$, mole per liter	.3	.3	.3	.3
HCl, mole per liter	.7	.7	.7	.7
KI, millimoles per liter	.0	12.0	30.0	60.0
Bromine formed in 15 minutes	22.6	27.5	27.9	29.5
Bromine formed in 30 minutes	41.0	50.6	52.4	55.5
Bromine formed in 45 minutes	52.1	66.6	73.8	79.0
Bromine formed in 60 minutes	62.0	79.2	91.9	99.0
Bromine formed in 75 minutes	72.1	91.0	104.2	118.5
Bromine formed in 90 minutes	79.8	98.5	114.6	132.4
Bromine formed in 120 minutes	88.1	104.0	131.0	158.0
Bromine formed in 150 minutes	95.5	119.7	140.7	173.2
Bromine formed in 24 hours	154.2	192.1	211.6	251.4
Bromine formed in 72 hours	201.5	228.8	258.0	283.0

The curves in Fig. 1 are straight lines and are nearly coincident until the bromine formed equals the iodide added. This shows that the rate of the reaction is maintained practically constant until the iodide is used up. After this point is reached the rate falls off. This is probably due to the oxidation of the trivalent form by the bromine, which begins to accumulate as soon as all of the iodine has been oxidized to iodine.

The results of all of the experiments described in this section show conclusively that the active form of the catalyst is the trivalent ruthenium, and that this active form reacts with the bromine to produce quadrivalent ruthenium, which is much less active catalytically. If, however, bromine reacted very rapidly with the trivalent ruthenium, a much greater decrease in the rate with time would result than was actually observed. It may be inferred, therefore, that trivalent ruthenium and bromine react at a slow but measurable rate to form the quadrivalent ruthenium. To determine whether this was really the case, experiments were carried out as described in the next section.

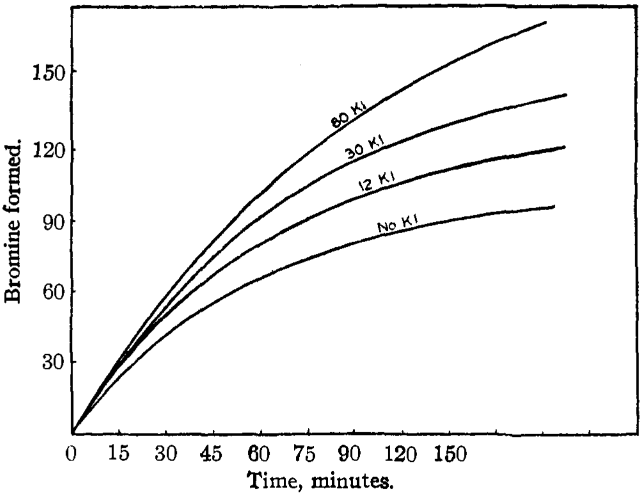

Fig. 1.—Effect of iodide on the reaction rate.

The Rate of the Reaction between Trivalent Ruthenium and Bromine

Stock solutions of bromine water, hydrobromic acid, hydrochloric acid and ruthenium trichloride were mixed and 20-cc. portions sealed in glass tubes. The tubes were placed in a water-bath whose temperature was maintained at 98°. The tubes were removed, one at a time, after measured intervals, cooled rapidly and emptied into a separating funnel. The bromine was extracted with ten 5-cc. portions of carbon tetrachloride. The carbon tetrachloride layer was treated with potassium iodide and the liberated iodine titrated with standard thiosulfate. The results of a typical experiment are shown in Table V.

Table V

Rate of the Reaction between Trivalent Ruthenium and Bromine

Initial concn.: Ru^{III}, 0.00206 *M*; HBr, 0.5 *N*; HCl, 1.0 *N*; Br_2, 0.00850 *N*

Time	0 min.	30 min.	1 hr.	3 hrs.	5 hrs.	7 hrs.
Br_2 in CCl_4 layer (milliequiv. per l.)	8.5	7.6	7.1	6.8	6.6	6.3

The results, though not very accurate, show that the rate of the reaction between bromine and trivalent ruthenium is slow, as was inferred from the catalytic experiments. It was not practicable to make a complete investigation of this rate, since rather large quantities of ruthenium would have been required.

The Mechanism of the Catalyzed Reaction

Since hydrogen ion and bromide ion exert only secondary effects, the first step determining the rate of the catalyzed reaction might be that expressed by either of the equations

$$ClO_4^- + RuBr_5^{=} + 2H_2O = RuO_4^- + HClO_2 + 5Br^- + 3H^+ \qquad (2)$$

$$ClO_4^- + RuBr_5^{=} + 2H_2O = RuO_4^{=} + 5Br^- + ClO_2 + 4H^+ \qquad (3)$$

Either of these reactions would be in agreement with the experimentally established fact that the rate is directly proportional to the concentration of perchlorate ion and of trivalent ruthenium.

This first slow step might then be followed by the rapid reactions

$$RuO_4^- + 9Br^- + 8H^+ = RuBr_5^{=} + 2Br_2 + 4H_2O \qquad (4)$$

$$RuO_4^{=} + 8Br^- + 8H^+ = RuBr_5^{=} + 1^1/_2Br_2 + 4H_2O \qquad (5)$$

$$HClO_2 + 4Br^- + 3H^+ = Cl^- + 2Br_2 + 2H_2O \qquad (6)$$

$$ClO_2 + 5Br^- + 4H^+ = Cl^- + 2^1/_2Br_2 + 2H_2O \qquad (7)$$

The bromine that is thus formed would then slowly convert the trivalent ruthenium to the quadrivalent state. The fact that ruthenium tetroxide is formed by the action of hot concentrated perchloric acid on trivalent ruthenium compounds is not in disagreement with Reactions 2 and 3, since the ruthenates and perruthenates are decomposed by non-reducing acids into ruthenium tetroxide and ruthenium salts of lower valence. A detailed study of the very slow reaction between perchlorate ion and quadrivalent ruthenium was not made and therefore no data are available for determining its mechanism.

Summary

The reaction $ClO_4^- + 8Br^- + 8H^+ = Cl^- + 4Br_2 + 4H_2O$ is shown to be catalyzed by the presence of ruthenium salts. Its rate is found to be roughly proportional to the concentrations of perchlorate ion and of trivalent ruthenium salt, and to be considerably increased by increasing the concentrations of the bromide and of the acid.

It is shown that the bromine liberated by the reaction slowly converts the trivalent into the quadrivalent form and that removal of the free bromine by a current of carbon dioxide or by addition of an iodide maintains a larger reaction rate. These results, as well as those of comparative experiments in which the ruthenium salt was initially introduced in the trivalent and quadrivalent forms, respectively, show that trivalent ruthenium has a much greater catalytic effect on the reaction than quadrivalent ruthenium.

To explain the observed facts the following mechanism is suggested: the perchloric acid first slowly oxidizes the ruthenium from the trivalent to the sexivalent or septivalent state; the latter is then almost instantaneously reduced by the bromide to the trivalent state. The production of quadrivalent ruthenium by oxidation of trivalent ruthenium by the liberated bromine accounts for the secondary effect produced by free bromine.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE HEATS OF DILUTION AND SPECIFIC HEATS OF BARIUM AND CALCIUM CHLORIDE SOLUTIONS[1]

BY THEODORE W. RICHARDS AND MALCOLM DOLE

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Introduction

The recent accurate and systematic investigations of the heats of dilution of various electrolytes carried out by Richards,[2] Lange[3] and their coworkers have been practically entirely limited to uni-univalent salts. The rise of the Debye and Hückel theory of complete dissociation has focused attention, however, on compounds with unsymmetrical valences, because, according to their ideas, the deviations of solutions from those predicted by the perfect gas laws are due partly to the electrical charges on the ions and when these are different the deviations are more marked. Hence a study of the heats of dilution of barium and calcium chloride solutions should prove of particular interest to the modern theories of solutions. Furthermore, one of us[4] had just completed electrochemical and viscosity experiments on barium chloride solutions and was therefore interested in this salt.

Determination of Specific Heats by the Direct Method

Introduction.—As in the previous papers of this series, the procedure in measuring the heats of dilution consisted in diluting a concentrated solution in several successive steps until the experimental errors became greater than the heat effect of the dilution. In addition to observing the rise in temperature of the calorimetric system, in order to calculate the amount of heat energy evolved it was necessary to know the heat capacity of the factors involved. The heat capacity of water and of the apparatus having been determined previously, the only factors remaining unknown were the heat capacities of the salt solutions. If the heat capacity at one

[1] On account of the death of Professor Richards on April 2, 1928, the work here described was completed and the manuscript was prepared by the junior author under the general direction of Dr. Lawrence P. Hall.

[2] Theodore W. Richards and Allan Winter Rowe, THIS JOURNAL, **43**, 770 (1921).

[3] J. Wüst and E. Lange, *Z. physik. Chem.*, **116**, 161 (1925); E. Lange and F. Dürr, *ibid.*, **121**, 361 (1926); E. Lange and A. Eichler, *ibid.*, **129**, 285 (1927); E. Lange and E. Schwarz, *ibid.*, **133**, 129 (1928); E. Lange and G. Messner, *Z. Elektrochem.*, **33**, 431 (1927).

[4] Grinnell Jones and Malcolm Dole, unpublished results.