ANOMALOUS TEMPERATURE COEFFICIENTS ASSOCIATED WITH AQUEOUS HALOGEN SOLUTIONS. AN EXPLANATION ASSUMING VARIABLE HYDRATION OF THE HALOGENS

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I. INTRODUCTION

Experimental evidence, new and old, will be presented to show that aqueous halogen solutions generally exhibit temperature coefficients of an unusual kind, for the heat terms associated with many of these temperature coefficients decrease more or less rapidly near 0°C. to approach nearly constant values as the temperature is increased. It will be shown that these anomalies find a quantitative explanation, satisfactory though beset by minor inconsistencies, in the assumption that the region of anomalous temperature coefficients is the region in which the degree of hydration of the halogens is changing. An inductive method of presentation that ignores historical sequence will be adopted, because it is simple, and because it emphasizes the rôle of a kinetic investigation in the rediscovery of the anomalies just mentioned.

II. HYDROLYSES OF THE HALOGENS

A. Iodine

Hydrogen peroxide added to an acid solution (23, 24, 27) is at first reduced according to the stoichiometric equation

$$H_2O_2 + 2H^+ + 2I^- = I_2 + 2H_2O \tag{1}$$

Conversely, hydrogen peroxide added to an aqueous iodine solution may be oxidized

$$H_2O_2 + I_2 = 2H^+ + 2I^- + O_2 \tag{2}$$

Once these facts have been established by experiment, it follows that neither reaction can be absolutely isolated so long as its products are not

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[1] This paper is a contribution jointly from the Chemical Laboratory of the University of California, where the calculations were completed in 1933, and from the Research Laboratory of the General Electric Company, where the material was recently cast into its present form.

completely removed. If the products of reaction 1 (reaction 2) are permitted to accumulate, then the *relative* rate of reaction 2 (reaction 1) will increase; and, if enough peroxide is present, this increase will continue until a *steady state* has been reached where the two rates are equal, and where the only measurable reaction is the sum of reactions 1 and 2, namely

$$2H_2O_2 = 2H_2O + O_2 \tag{3}$$

the decomposition of hydrogen peroxide. By combining data from rate and concentration measurements made at the steady state, it is possible to deduce the specific rates of the compensating reactions 1 and 2. At 25°C., the specific rates thus deduced are in excellent agreement with those obtained for reactions 1 and 2 when each reaction was alone of experimental importance; for reaction 1 it has been shown that this agreement extends over the temperature range from 0 to 50°C. These facts place the deduction from steady state data of the specific rate k'_2 (reaction 2) for temperatures other than 25°C. upon an exceptionally secure foundation.

Within a wide range of experimental conditions the rate of reaction 2 obeys the differential equation[2]

$$-\frac{d(H_2O_2)}{dt} = k'_2(H_2O_2)\frac{(I_2)}{(H^+)^2(I^-)} \tag{4}$$

which serves to define k'_2. As the investigation of the effect of temperature variation on k'_2 proceeded, it soon became evident that this rate constant fails completely of obeying the Arrhenius equation at temperatures below 50°C., for in this temperature interval the heat of activation decreases rapidly from 57,000 cal. (this heat term, computed from the 0°C. and 3.5°C. values of k'_2, corresponds to a 10°C. temperature coefficient of about 40) near 0°C. to 25,000 cal. at the higher temperature. From 50 to 70°C., this heat remains sensibly constant; i.e., the Arrhenius equation is the limiting law which k'_2 approaches as the temperature is increased. This anomalous character of the temperature coefficient of k'_2 was discovered in 1931; it led to an investigation of the literature, and to additional experimental work, in order to reveal whether this behavior is unique or whether

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[2] The usual conventions will be employed. Specific rates will be represented by small letters (k, κ); equilibrium constants by capitals (K, R, D). X may mean either Cl, Br, or I—thus, HXO is the formula of a hypohalous acid. ( ) usually denotes "concentration of" in moles per liter. → is restricted to steps that may be rate-determining; = to stoichiometric equations and to rapid reactions following a rate-determining step. Unit time is the minute. Heats of activation (as contrasted with energies of activation) are the energy terms corresponding to the empirically determined temperature coefficients of the specific rates, and are represented by Q's; heats of reaction (thermodynamic quantities) are represented by ΔH's, as is usual.

it is a general phenomenon to be expected for each of the three common halogens.

An examination of this anomalous temperature coefficient (see figure 1) permits certain conclusions to be drawn. While the heat of activation (Q) of a chemical reaction is to be regarded in general as a variable quantity, whose change with temperature may give some insight into the mechanism by which activation occurs, the change in figure 1 is obviously not of this type; $\partial Q/\partial t$ is far too large (it averages over 500 cal. per degree) and it departs too far from constancy (for it decreases virtually to zero near 50°C.). The same reasoning renders it highly improbable that an explanation for this behavior is to be found in the thermodynamic equation $\partial \Delta H/\partial T = \Delta c_p$. And finally, the anomaly does not result because reaction 2 is complex in the sense that it involves two or more (parallel and independent) rate-determining steps with different heats of activation; were this the case, the curvature would necessarily have to be convex (not concave) toward the $1/T$ axis.

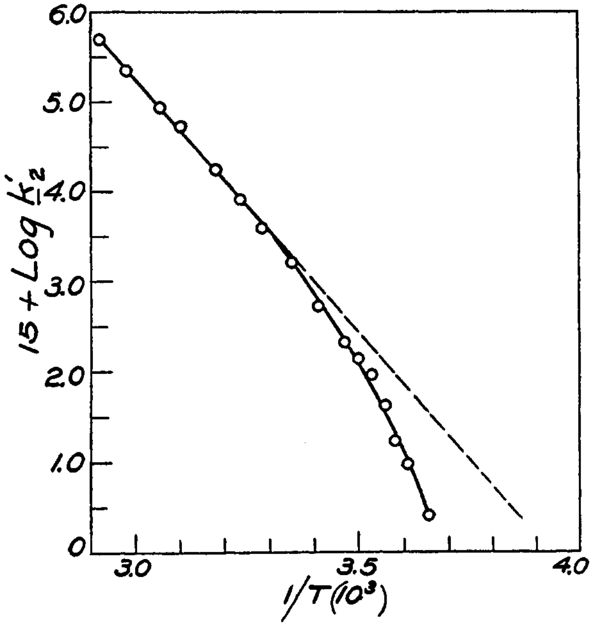

FIG. 1. Anomalous temperature coefficient shown by kinetic data. Effect of temperature change on the specific rate of reaction 2.

In order to proceed further, it is advisable now to assign reaction 2 a definite mechanism in accord with its rate law (equation 4). The most reasonable (though not the only) mechanism that can be thus assigned is (24, 27)

$$\text{Rapid equilibrium: } I_2 + H_2O \xrightleftharpoons{K_{I_2}} H^+ + I^- + HIO \qquad (5)$$

$$\text{Rapid equilibrium: } HIO \xrightleftharpoons{K_6} H^+ + IO^- \qquad (6)$$

$$\text{Rate-determining step: } IO^- + H_2O_2 \xrightarrow{\kappa_2'} I^- + H_2O + O_2 \qquad (7)$$

If this mechanism is to give a satisfactory kinetic interpretation to equation 4, the complex specific rate k_2' must equal the product $K_{I_2}K_6\kappa_2'$. At 25°C., $k_2' = 2(10^{-12})$, $K_{I_2} = 3(10^{-13})$ (6), and $K_6 = 2(10^{-11})$ (10); whence $\kappa_2' = 3(10^{11})$. Let us now consider with which of the three reactions composing the above mechanism the decrease of 32,000 cal. in the heat term associated with k_2' can most plausibly be identified. Rate-determining steps with specific rates so large as κ_2' will scarcely have a large heat of activation; reaction 7 cannot therefore be responsible for this large decrease. The heat of dissociation of hypoiodous acid probably will not exceed, say, 10,000 cal., so that this equilibrium may likewise be eliminated from consideration. Only the hydrolysis equilibrium of iodine (reaction 5) remains. If this analysis of the anomalous temperature variation is correct, the explanation of the anomaly is therefore to be sought in the hydrolysis equilibrium of iodine, the equilibrium constant for which should reveal the curvature recorded in figure 1. Unfortunately, values of this equilibrium constant are not available for a number of temperatures sufficient to make possible a convincing comparison between the results of kinetic measurements (as given in figure 1) and those from equilibrium (in this case, conductivity) measurements made directly on the iodine hydrolysis. Indeed, it is not certain that direct equilibrium measurements accurate enough for this problem can be made near 0°C. because of the small extent to which iodine is hydrolyzed at these temperatures; if K_{I_2} does show the curvature given in figure 1, such measurements are probably impossible. In the absence of appropriate equilibrium data for the iodine hydrolysis, similar data for the other halogen hydrolyses are acceptable substitutes.

B. Chlorine

At the close of the last century Jakowkin (18) concluded his classic investigation of the chlorine hydrolysis,

$$Cl_2 + H_2O \xrightleftharpoons{K_{Cl_2}} H^+ + Cl^- + HClO \qquad (8)$$

in which he discovered (by measuring the distribution of chlorine between air and carbon tetrachloride, respectively, and aqueous solutions) that the heat term associated with K_{Cl_2} (cf. figure 2, where his data are plotted) does exhibit an anomalous temperature variation of the kind under discussion. In the case of reaction 8 the decrease (from 8000 cal. near 0°C. to 2900 cal. near 50°C.) is relatively even more marked than the corresponding change for reaction 2. There is, however, a marked difference between the two cases; for, as an examination of figure 2 will show, values of K_{Cl_2} do not fall (as did those of k_2') on a straight line for all temperatures above 50°C.; in fact, there is some doubt as to whether the line in figure 2 represents a limiting law,—as to whether the heat term associated with K_{Cl_2} is ever constant. Although further consideration of this case is conveniently postponed, it seems well to mention here that Jakowkin himself clearly appreciated this anomalous behavior, for he concluded that the heat of hydrolysis of chlorine decreases markedly with increasing temperature so that it becomes equal to zero between 85 and 95°C. For the present we shall point out only that the temperature variations of the specific rate k_2' (figure 1) and of the equilibrium constant K_{Cl_2} (figure 2) are so similar below 50°C. that they must almost certainly be due to the same cause. This fact leaves little doubt that the mechanism given above for reaction 2 is essentially correct, and supports the reasoning which establishes the iodine hydrolysis equilibrium as the most probable source of the failure of reaction 2 in conforming to the Arrhenius equation. We should expect, therefore, that rate-determining steps involving hydrolysis products like HXO or XO^- in equilibrium with the halogen X_2 will in general not be governed by this equation, and that the bromine hydrolysis equilibrium also will show departures from the thermodynamic relation

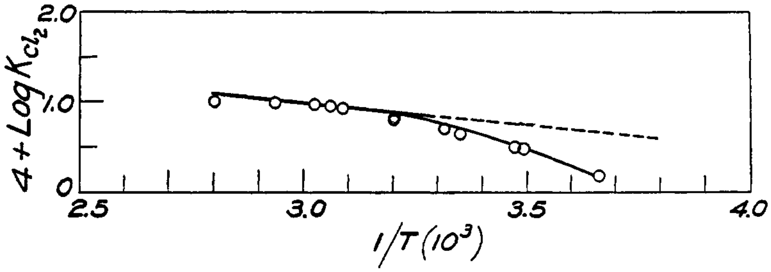

FIG. 2. Anomalous temperature coefficient shown by equilibrium data. Effect of temperature change on the equilibrium constant for the chlorine hydrolysis.

$$\frac{d(\ln K)}{d(1/T)} = \frac{-\Delta H}{R}$$

C. Bromine

In the case of bromine, kinetic data (for the reaction between bromine and hydrogen peroxide) and equilibrium data (for the bromine hydrolysis) both show anomalous temperature variations of the kind being discussed. Unfortunately, the deviations from linearity in the plots corresponding to figures 1 and 2 are much smaller for this halogen, with the result that the comparison between these two types of experimental data becomes thereby somewhat less convincing.

Bray and Livingston (7, 8, 29, 30) in a series of kinetic investigations have demonstrated conclusively that the catalytic decomposition of hydrogen peroxide by the bromine–bromide couple involves only the two compensating reactions

$$2H^+ + 2Br^- + H_2O_2 = Br_2 + 2H_2O \tag{9}$$

$$Br_2 + H_2O_2 = 2H^+ + 2Br^- + O_2 \tag{10}$$

(whose sum is reaction 3) over a wide range of experimental conditions. Both at the steady state and at a distance from it reaction 10 obeys the rate law

$$-\, d(H_2O_2)/dt = k_2(H_2O_2)\,\frac{(Br_2)}{(H^+)(Br^-)} \tag{11}$$

which, except for the inverse hydrogen ion term, is formally identical with equation 4. The authors give

$$\text{Rapid equilibrium: } Br_2 + H_2O \xrightleftharpoons{K_{Br_2}} HBrO + H^+ + Br^- \tag{12}$$

$$\text{Rate-determining step: } HBrO + H_2O_2 \xrightarrow{\kappa_2} H^+ + Br^- + O_2 \tag{13}$$

as the most probable mechanism for reaction 10; Makower and Liebhafsky (31) adduced additional (semiquantitative) evidence for this choice when they proved that hypobromous acid in the virtual absence of bromine reacted with hydrogen peroxide at a rate not less than one-tenth that to be expected if κ_2 is, as Bray and Livingston have found, somewhat greater than 10^6. The above mechanism for reaction 10 is thus established beyond a reasonable doubt; if the bromine hydrolysis equilibrium, reaction 12, exhibits an anomalous temperature variation, we shall therefore expect to find it reflected in k_2.

In order to discover whether or not this expectation is realized, rate and concentration measurements for the steady state were made (25) over the largest temperature range (0 to 70°C.) within which accurate results could be obtained. As in the case of iodine, values of the specific rate at different temperatures were deduced from these two sets of data; these values of k_2 are plotted in figure 3. Although the departure from linearity is not large even at 0°C., it is unmistakable; and, in conjunction with the experimental evidence already given for iodine and chlorine, it makes apparent that

K_{Br_2}, the equilibrium constant for the bromine hydrolysis, ought to show a similar divergence.

The electrical conductivities of aqueous bromine solutions at five temperatures have recently been measured (28) in order to establish whether the corresponding K_{Br_2} values do show a departure of this kind. These values, together with those similarly obtained by other investigators, are summarized in table 1.

The experimental results of table 1 are remarkably concordant and warrant the conclusion (28) that "the temperature variation of K_{Br_2} becomes anomalous in the neighborhood of 0°; but the departure of $d(\log K_{Br_2})/d(1/T)$ from constancy is much less than that observed by Jakowkin in the case of chlorine." This conclusion derives further support from the fact that the temperature coefficients are probably more accurately established than are the absolute values of K_{Br_2}; for these temperature coefficients were obtained for each bromine solution within a short time and without refilling the conductivity cell, so that they are virtually independent (as the absolute values are not) of the presence of conducting substances not produced in reaction 12; the detailed experimental results (reference 12, table 2) clearly show this to be true.

TABLE 1

Summary of $K_{Br_2}(10^9)$ values for different temperatures

INVESTIGATORS	0°C.	10°C.	25°C.	30°C.	35°C.
Bray and Connolly (6)			5.6*		
Jones and Hartmann (20)	0.68*				
Jones and Baeckström (19)			5.8		
Liebhafsky (28) (measured)	0.69	1.76	5.8	8.4	11.3
Liebhafsky (computed)	0.76	1.80	(5.8)†	8.3	(11.3)†

* Experimental results recalculated by Liebhafsky to yield this value.

† Value assumed in deriving the equation $\log K_{Br_2} = 1.37804 - 2866.1/T$.

If reaction 10 has been assigned its correct mechanism (equations 12 and 13), if $d(\log \kappa_2)/d(1/T)$ is sensibly constant, and if the conductivity measurements have been correctly interpreted, then the results in table 1 should show a departure from linearity identical with (not only similar to) that of the rate constants plotted in figure 3. Now, this departure is measured at 0°C. for the K_{Br_2} results by $\log 0.76/0.69 = 0.04$; the corresponding quantity for figure 3 is 0.21, the logarithm of the quotient for that temperature of k_2(calcd.)/k_2(measd.), k_2(calcd.) being the extrapolated value given by the limiting straight line. The difference between 0.04 and 0.21 is too large to be attributed to experimental error, but it can in all likelihood be materially reduced without violating the kinetic data, by choosing a limiting line of slightly different slope. (As matters stand, no attempt has been made to bring the equilibrium and kinetic measurements into agreement; this could easily be done on the assumption that in figure 3, as in figure 2, the experimental points never quite conform to a limiting line). We conclude provisionally, therefore, that a slight inconsistency exists between the results of figure 3 and those of table 1, which might, if real, compel a reëxamination of the conductivity data to determine whether these have been correctly interpreted or whether some additional equilibrium (like $Br_2 \rightleftharpoons Br^+ + Br^-$) also needs to be taken into account (36). In spite of this inconsistency, however, our main thesis—namely, that aqueous halogen solutions exhibit anomalous temperature coefficients—seems proved by both equilibrium and kinetic measurements for the case of the bromine hydrolysis.[3]

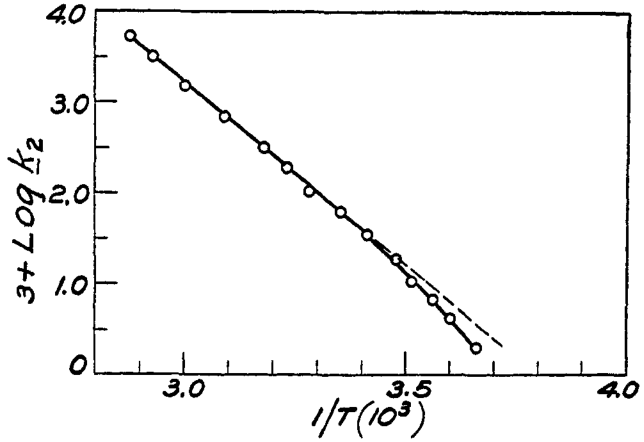

FIG. 3. Anomalous temperature coefficient shown by kinetic data. Effect of temperature change on the specific rate of reaction 10.

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[3] In addition to the two sets of experimental data discussed above, there are available in the case of bromine the following results of kinetic measurements directly on reaction 10: χ_2 = 0.043 (35°C.), 0.018 (25°C.), and 0.00062 (0°C). The first two values are based on measurements by Bray and Livingston (8), who recalculated Balint's results to obtain the third. $\chi_2 = k_2\gamma^2$ (HBr); the activity coefficient term is introduced to compensate the effect of changing ionic strength on the bromine hydrolysis (reaction 12). Since the γ values were assumed to be independent of temperature, the χ_2 values will yield the same heat of activation as the k_2's from which they were derived. From the results for 35°C. and 25°C., we find d(log χ_2)/d($1/T$) = 3473, whence Q = 15,900 cal. If Q remains constant to 0°C., then χ_2 (calcd.) = 0.00065 at that temperature, a value greater by 5 per cent than 0.00062 = χ_2 (measd.). This difference of 5 per cent corresponds closely to the departure (which has been discussed above) of d(log K_{Br_2})/d($1/T$) from constancy near 0°C.

Unfortunately this excellent agreement cannot be accepted without reservation.

The experimental evidence relating to the hydrolysis equilibria of the halogens is now complete and leads to the conclusion that the heat terms associated with these equilibria all show the same type of anomalous temperature variations. The next logical step is to determine, if possible, whether this anomaly can be "localized,"—i.e., whether it arises from the behavior of the substances (the halogens, X_2, and water) on the left side of these equilibria as they are written, or from the behavior of those (HXO, H^+ and X^-) on the right.

III. DISTRIBUTION OF THE HALOGENS BETWEEN AIR AND WATER

If it can be shown that a set of aqueous halogen equilibria involving a set of products differing from HXO, H^+, and X^- exhibits anomalous temperature coefficients similar to those for the halogen hydrolyses, then the "localization" will probably have been accomplished; for that would be strong indication that the anomaly arises from the interaction of X_2 and H_2O, the only two substances common to both sets of equilibria. We shall now summarize the experimental evidence relating to reactions of the type

$$X_2(aq) \xrightleftharpoons{D_{X_2}} X_2(g) \qquad (14)$$

where

$$D_{X_2} = P_{X_2} \text{ (in atm.)}/(X_2) \text{ (in moles per liter)} \qquad (15)$$

Data permitting the calculation of D_{X_2} for each of the three common halogens as a function of temperature is already in the literature. For iodine, the solubility data given in the International Critical Tables (17) were combined with the results of Baxter and Grose (2) for the vapor pressure of solid iodine (calculating these vapor pressures from more recent equations would have produced no change significant for our purposes). For

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Bray and Livingston give ±10 per cent as the average spread of the χ_2 values they have calculated from Balint's data; it is thus not necessary to consider the divergence of their own results to show that the above 5 per cent difference cannot be very securely established, and we must conclude that the χ_2 data do not prove reaction 10 to have a variable heat of activation. This conclusion is not incompatible with the statement by Bray and Livingston that the temperature coefficient of reaction 10 (presumably for a 10°C.-temperature interval) decreases with increasing temperature, since $\Delta(1/T)$ for any fixed temperature interval decreases with increasing T, and this causes a reaction with constant heat of activation to have a variable (but not an *anomalous*) temperature coefficient.

Rate measurements at a number of temperatures and for reaction mixtures initially identical in composition should, of course, show reaction 10 to have a variable heat of activation, in agreement with the two sets of data discussed in the text.

chlorine the data of Jakowkin (reference 18, p. 655) were employed. The data for bromine are given in different units by Hantzsch and Vagt (reference 12, p. 726, table 13) in their paper dealing with the solvation of the halogens. In every case the experimentally measured aqueous halogen concentration has been diminished by the equilibrium concentration of the hypohalous acid (a hydrolysis product) to give the true concentration of dissolved halogen. Jakowkin applied this correction himself; for bromine

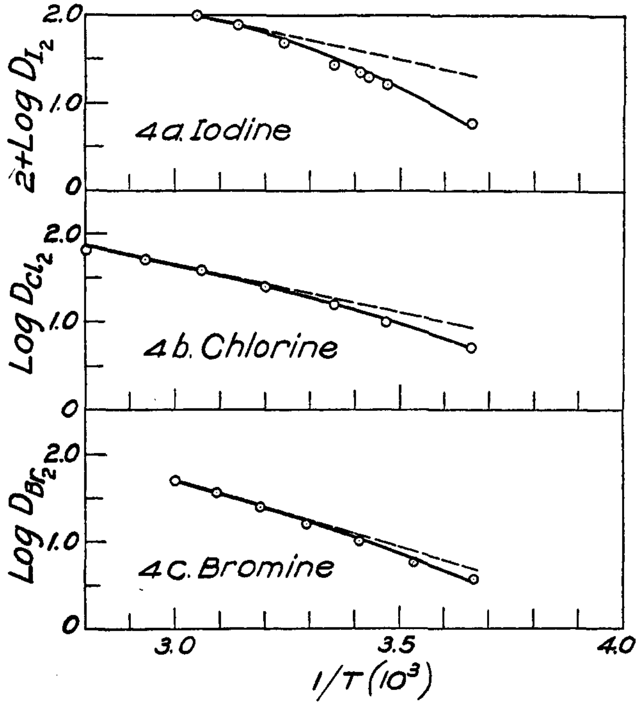

FIG. 4. Anomalous temperature coefficients shown by equilibrium data. Effects of temperature change on the distribution ratios of the halogens between air and water.

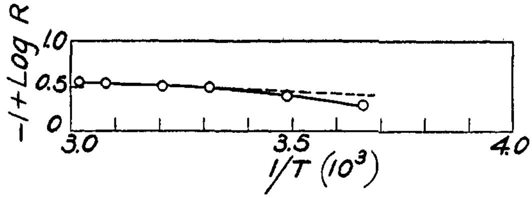

Fig. 5. Anomalous temperature coefficient shown by equilibrium data. Effect of temperature change on the distribution ratio of chlorine between carbon tetrachloride and water.

and iodine it has been made by estimating values of K_{X_2} (equations 5 and 12), and, since this correction is much less important for these two halogens, the details will not be given. D_{X_2} as a function of temperature is given for each halogen in figure 4.

An examination of figure 4 immediately reveals its close similarity to the preceding three figures dealing with the halogen hydrolyses; we conclude, therefore, that the anomalies we have been discussing do in fact originate principally in the interaction of the halogens and water. This conclusion is borne out, furthermore, by Jakowkin's values for $R_{Cl_2} = (Cl_2)_{CCl_4}/(Cl_2)_{H_2O}$, which are plotted in figure 5 (R_{Cl_2} is Jakowkin's h_1; cf. reference 18, p. 652, table 46, line 6). Many of the data that have been presented graphically will be given later (tables 2 and 3), when an attempt will be made to interpret them quantitatively, in the light of the explanation now to be proposed.

IV. AN EXPLANATION OF THE OBSERVED ANOMALIES

It has long been known that the halogens are hydrated, and that these hydrates decompose as the temperature is increased. In 1885 Roozeboom (32) had already completed a quantitative investigation of the dissociation pressures of the solid bromine and chlorine hydrates, to which he assigned the formulas $Cl_2 \cdot 8H_2O$ (1) and $Br_2 \cdot 10H_2O$ (9); for both hydrates these pressures increase with the temperature, reaching one atmosphere near 10°C. Although these solid hydrates were discovered over a century ago, their composition is still somewhat uncertain; and the formulas $Cl_2 \cdot 6H_2O$ and $Br_2 \cdot 8H_2O$, "established" after Roozeboom's work, have recently been confirmed, as has the existence of the bromine decahydrate (14). An examination of the literature suggested that two or more solid hydrates differing in stability and in composition may exist for each of these two halogens. A solid hydrate of iodine (34) appears to have been obtained only in the presence of a foreign gas (oxygen, nitrogen) at high pressures (150 to 350 atm.) and at moderate temperatures (3 to 8°C.); this hydrate is remarkable for its surprising color, which unexpectedly differs from that of the brown aqueous iodine solutions by being violet. The same factors, traceable ultimately to its atomic structure, that cause iodine to differ from the other halogens by being a dense solid sparingly soluble in water are probably also responsible for its failure to form a solid hydrate under ordinary conditions. The experimental evidence concerning the solid bromine and chlorine hydrates would lead us to expect that these halogens (if not iodine also) in aqueous solutions at low temperatures will form hydrates to which it may be impossible to assign a single definite formula, and that these hydrates will become increasingly unstable as the temperature is raised.

The state of the dissolved halogens is intimately related to the colors of their solutions; not unnaturally, solutions of iodine, whose brilliantly colored vapor undergoes the most marked color change (from violet to brown) when dissolved in certain solvents like water, have been most extensively investigated. These investigations almost without exception support the conclusion that the brown solutions contain solvated iodine (3, 4, 5), and the fact, already recorded in 1890, that this brown color tends to change to violet on heating (37) shows the solvates to be unstable at higher temperatures. We shall discuss the colors of iodine solutions in some detail later; for the present we observe only that the experimental evidence concerning them complements what is known concerning the solid hydrates of bromine and chlorine. Consequently, we may regard all three halogens in aqueous solutions as being hydrated, and the corresponding hydration equilibria as shifting toward the less hydrated forms as the temperature is raised.

The body of past experience is thus entirely in accord with an attempt to explain the anomalous temperature coefficients encountered in aqueous halogen solutions on the assumption that the halogens in these solutions exist in two forms, U and H, differing from each other only in the degree of hydration. The simplest conditions would obtain if U were unhydrated and H had the formula $X_2 \cdot H_2O$; but the argument to be presented does not depend upon the realization of these simplest conditions, so that H may contain any reasonable number of water molecules, so long as it is hydrated to a greater extent than U. The equilibrium between these two forms of X_2,

$$U + (h - u)H_2O \xrightleftharpoons{(H)/(U)} H \tag{16}$$

must shift toward U as the temperature is raised in order to conform with the color change (from brown to violet) of many iodine solutions and the dissociation of the solid bromine and chlorine hydrates, both of which are favored by a temperature increase. To test the assumption that the hydration of the halogens leads to anomalous temperature coefficients for their aqueous solutions, we shall at first confine ourselves to the hydrolysis equilibria as examples. The extension of our reasoning to other types of equilibria will involve no difficulty.

If the hydration equilibrium (equation 16) really exists, these hydrolysis equilibria may be written in three ways:

$$H_2O + U \xrightleftharpoons{K_U} H^+ + X^- + HXO + uH_2O \tag{17}$$

$$H_2O + H \xrightleftharpoons{K_H} H^+ + X^- + HXO + hH_2O, \text{where } h > u \tag{18}$$

$$H_2O + X_2 \xrightleftharpoons{K_{X_2}} H^+ + X^- + HXO + xH_2O \tag{19}$$

the third of which is the conventional (cf. equations 5, 8, and 12). So long as the hydration equilibrium is established either equation 17 or equation 18 may be used to represent the hydrolysis equilibrium; for K_U and K_H are obviously related because

$$(H)/(U) = \text{const. (at constant temperature)} \tag{16a}$$

Since

$$(X_2) = (H) + (U) \tag{20}$$

it follows that K_{X_2} cannot be a true equilibrium constant if (H) and (U) are comparable in magnitude. These considerations are borne out by a comparison of the expressions for the equilibrium constants of reactions 17, 18, and 19:

$$K_U = \frac{(H^+)(X^-)(HXO)}{(U)} \text{ and } K_H = \frac{(H^+)(X^-)(HXO)}{(H)} \tag{17a and 18a}$$

$$K_{X_2} = \frac{(H^+)(X^-)(HXO)}{(U) + (H)} \tag{19a}$$

We shall now examine the temperature variation to be expected for K_{X_2} if H and U are always in rapid equilibrium and sometimes of comparable concentration. We shall assume all heats of reaction to be constant and distinguish three regions within the temperature range to be considered.

Region I. The higher temperatures

The hydration equilibrium (equation 16) is displaced far to the left, so that $(U) \gg (H)$ while $(X_2) = (U)$, very nearly. Then, by equations 17a, 18a, and 19a

$$K_{X_2} = \frac{(H^+)(X^-)(HXO)}{(U)} = K_U \ll K_H \tag{21}$$

and

$$d(\log K_{X_2})/d(1/T) = d(\log K_U)/d(1/T) = -\Delta H_U/4.58 \tag{22}$$

At these temperatures, log K_{X_2} plotted against $1/T$ will therefore yield a straight line, the slope of which measures ΔH_U, the heat of reaction 17.

Region III. The lower temperatures

The hydration equilibrium (equation 16) is displaced far to the right, so that $(H) \gg (U)$ while $(X_2) = (H)$, very nearly. Then, again by equations 17a, 18a, and 19a

$$K_{X_2} = \frac{(H^+)(X^-)(HXO)}{(H)} = K_H \ll K_U \tag{23}$$

and

$$d(\log K_{X_2})/d(1/T) = d(\log K_H)/d(1/T) = -\Delta H_H/4.58 \qquad (24)$$

At these temperatures, log K_{X_2} plotted against $1/T$ will therefore yield a straight line, the slope of which measures ΔH_H, the heat of reaction 18.

Region II. The intermediate temperatures

The two halogen species U and H are present at comparable concentrations. Equations 17a, 18a, and 19a now yield

$$K_U > K_{X_2} = \frac{(H^+)(X^-)(HXO)}{(U) + (H)} < K_H \qquad (25)$$

Also,

$$\frac{(H^+)(X^-)(HXO)}{(U) + (H)} \frac{(U) + (H)}{(U)} = K_{X_2}[1 + (H)/(U)] = K_U \qquad (26)$$

(A corresponding equation may obviously be written for K_H). In this region of intermediate temperatures, (H) is increasing with $1/T$ at the expense of (U). As this region is traversed toward the direction of lower temperatures (higher values of $1/T$), $[(H) + (U)]/(U)$ increases rapidly from a value near unity, while $[(H) + (U)]/(H)$ decreases rapidly to approach that value. Therefore, by equations 17a, 18a, and 19a,

$$\begin{aligned} d(\log K_U)/d(1/T) &= -\Delta H_U/4.58 < d(\log K_{X_2})/d(1/T) \\ &< -\Delta H_H/4.58 = d(\log K_H)/d(1/T) \qquad (27) \end{aligned}$$

If all three regions are realized in the case of a hydrolysis equilibrium, the following temperature variation for K_{X_2} is therefore to be expected: At higher temperatures, log K_{X_2} will give a straight line when plotted against $1/T$. As $1/T$ increases, a downward divergence will gradually occur, so that the straight line becomes a curve concave toward the $1/T$ axis. As $1/T$ is increased still further, this curve merges into a straight line steeper than the limiting line for higher temperatures. This type of temperature dependence is illustrated in figure 6; comparison of this with the five previous figures shows that the hypothetical curve for regions I and II is qualitatively identical with those describing the actual measurements, but that the realization of region III is doubtful because it does not occur at temperatures sufficiently above 0°C., the freezing point of water. Before proceeding to a quantitative test of hydration hypothesis, we observe that the above equations can easily be made applicable to any set of aqueous halogen equilibria; the formulas of the products in the new equilibria must of course replace H^+, X^-, and HXO in the equations, and the changes in nomenclature which this substitution requires must be made. Since the concentration of water does not appear in the above equations, they can be readily modified also for the cases of other solvents.

A quantitative test of the hydration hypothesis can readily be made. From equation 26,

$$\log K \;-\; \log K_{X_2} = d = \log\,[1 + (H)/(U)] \tag{28}$$

(H)/(U), the hydration equilibrium constant, may thus be evaluated from d, the divergence (caused by the existence of H) of K_{X_2} at any temperature from the extrapolated value of K_U for that temperature. Now

$$d\,[\log\,(H)/(U)]/d(1/T) = -\frac{\Delta H_{hn}}{4.58} \tag{29}$$

If the hydration hypothesis is valid, log [(H)/(U)] plotted against $1/T$ should give straight lines, whose slopes correspond to reasonable values of

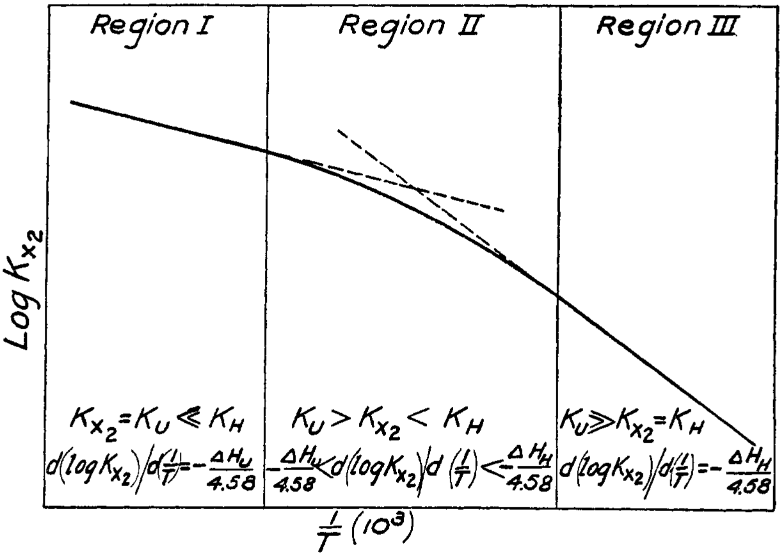

FIG. 6. Idealized effect of temperature change on an aqueous halogen equilibrium according to the hydration hypothesis.

the heat of hydration ΔH_{hn}. The procedure for testing this hypothesis will be sketched for the data of figure 1. The equation for the best straight line through the experimental points at the higher temperatures was determined; the values of k_2' in this temperature region will be proportional to $K_U = K_{X_2}$. From this equation values of k_2' (calcd.), still proportional to K_U, were obtained for the lower temperatures, at which the experimental points fall on a curve. Here (region 2, figure 6) k_2' (measd.) is still proportional to K_{X_2}; so that $d = \log k_2'$ (calcd.) $- \log k_2'$ (measd.). Values of (H)/(U) for the various temperatures were obtained from these values of d by means of equation 28, and log [(H)/(U)] was then plotted against $1/T$. The results (from both kinetic and equilibrium measurements) for the halogen hydrolyses are summarized in table 2 and plotted in figure 7. The results for the distribution equilibria are summarized in table 3 and plotted in figure 8.

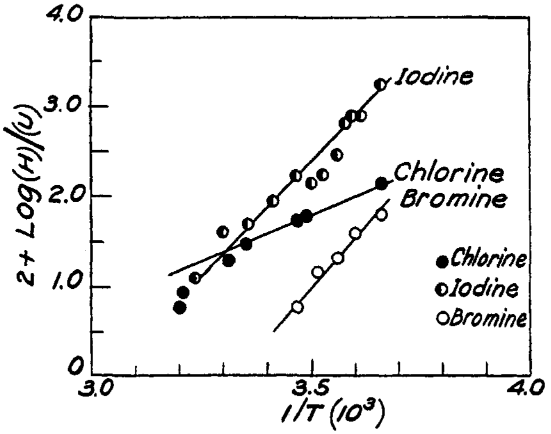

FIG. 7. Effects of temperature change on the hydration equilibria as computed from hydrolysis data for the halogens (cf. table 2).

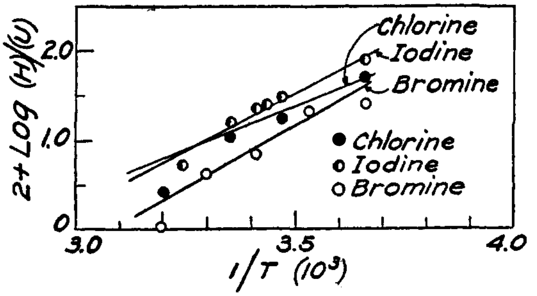

FIG. 8. Effects of temperature change on the hydration equilibria as computed from distribution data for the halogens (cf. table 3).

V. DISCUSSION OF RESULTS

In deciding whether or not the extensive experimental evidence summarized in tables 2 and 3 proves the hydration hypothesis we have outlined, several things deserve consideration. First, the experimental errors associated with the measurements in region II are all reflected in figures 7 and 8, since no "smoothing out" of these results has been done. Second, the errors in d appear considerably enlarged in log [(H)/(U)] at the higher

TABLE 2

Equilibrium constants for the halogen hydrations from their hydrolyses

a. For iodine from reaction 2 (cf. figures 1 and 7)

T in °C	35.7	30.0	25.0	19.8	15.4	12.5	10.4	7.7	6.2	4.8	3.5	0.0
$10^{15} \times k'_2$ (measd.)	8260	3280	1590	547	209	146	91.8	42.1	17.4	12.7	9.58	2.56
d	0.051	0.122	0.136	0.277	0.413	0.377	0.438	0.594	0.875	0.926	0.942	1.265
(H)/(U)	0.12	0.32	0.37	0.89	1.59	1.39	1.74	2.93	6.50	7.44	7.75	17.43

$d = \log k'_2$ (calcd.) $-$ $\log k'_2$ (measd.) $15 + \log k'_2$ (calcd.) $= 21.5185 - 5419.8/T$ $\Delta H_{\text{hn}} = -22{,}800$ cal.

b. For chlorine from reaction 8 (cf. figures 2 and 7)

T in °C	39.1	38.6	28.6	25.0	15.0	13.4	0.0
$10^4 \times K_{\text{Cl}_2}$ (measd.)	6.86	6.63	5.16	4.48	3.16	3.02	1.556
d	0.024	0.036	0.078	0.114	0.193	0.200	0.379
(H)/(U)	0.057	0.086	0.196	0.300	0.556	0.583	1.397

$d = \log K_{\text{Cl}_2}$ (calcd.) $-$ $\log K_{\text{Cl}_2}$ (measd.) $4 + \log K_{\text{Cl}_2}$ (calcd.) $= 2.87850 - 630.0/T$ $\Delta H_{\text{hn}} = -9{,}900$ cal.

c. For bromine from reaction 10 (cf. figures 3 and 7)

T in °C	14.9	11.1	7.5	4.5	0.0
$10^3 \times k_2$ (measd.)	18.25	10.92	6.84	4.14	1.996
d	0.024	0.058	0.077	0.138	0.213
(H)/(U)	0.057	0.143	0.194	0.375	0.633

$d = \log k_2$ (calcd.) $-$ $\log k_2$ (measd.) $\log k_2$ (calcd.) $= 12.43840 - 4076/T$ $\Delta H_{\text{hn}} = -25{,}000$ cal.

d. For bromine from reaction 12 (cf. table 1)

T in °C	35.0	25.0	10.0	0.0
$10^9 \times K_{\text{Br}_2}$ (measd.)	11.3	5.8	1.76	0.69
d	($d = 0$ assumed)		0.010	0.042
(H)/(U)			0.023	0.120

$d = \log K_{\text{Br}_2}$ (calcd.) $-$ $\log K_{\text{Br}_2}$ (measd.) $\log K_{\text{Br}_2}$ (calcd.) $= 1.37804 - 2866.1/T$ $\Delta H_{\text{hn}} = -25{,}400$ cal.

TABLE 3

Equilibrium constants for the halogen hydrations from distribution ratios

a. For iodine from reaction 14 (cf. figures 4a and 8)

T in °C	55.0	45.0	35.0	25.0	20.0	18.0	15.0	0.0
$10^2 \times D_{I_2}$ (measd.)	112	77.9	50.4	30.1	23.1	20.5	17.3	6.15
d	(d = 0 assumed)		0.021	0.066	0.087	0.100	0.115	0.250
(H)/(U)			0.052	0.164	0.221	0.259	0.302	0.778

$d = \log D_{I_2}$ (calcd.) $- \log D_{I_2}$ (measd.) $2 + \log D_{I_2}$ (calcd.) $= 7.0660 - 1646/T$ $\Delta H_{\text{hn}} = -11{,}800$ cal.

b. For chlorine from reaction 14 (cf. figures 4b and 8)

T in °C	67.6	53.6	39.1	25.0	15.0	0.0		
D_{Cl_2} (measd.)	51.8	37.7	25.53	16.18	11.41	5.45		
d	(d = 0 assumed)		0.013	0.046	0.070	0.182		
(H)/(U)			0.031	0.111	0.175	0.519		

$d = \log D_{Cl_2}$ (calcd.) $- \log D_{Cl_2}$ (measd.) $\log D_{Cl_2}$ (calcd.) $= 4.9293 - 1095.4/T$ $\Delta H_{\text{hn}} = -9{,}700$ cal.

c. For bromine from reaction 14 (cf. figures 4c and 8)

T in °C	60.0	50.0	40.0	30.0	20.0	10.0	0.0	
D_{Br_2} (measd.)	51.55	36.63	25.16	16.50	10.63	6.020	3.600	
d	(d = 0 assumed)		0.005	0.019	0.030	0.085	0.101	
(H)/(U)			0.011	0.045	0.072	0.215	0.261	

$d = \log D_{Br_2}$ (calcd.) $- \log D_{Br_2}$ (measd.) $\log D_{Br_2}$ (calcd.) $= 6.5158 - 1600.0/T$ $\Delta H_{\text{hn}} = -13{,}100$ cal.

d. For chlorine from R_{Cl_2} (cf. figure 5)

T in °C	57.5	51.2	38.6	28.6	13.4	0.0		
R_{Cl_2} (measd.)	35.23	34.10	32.35	30.50	25.40	20.21		
d	(d = 0, very nearly)			0.004	0.049	0.114		
(H)/(U)				(0.01)	0.12	0.30		

$d = \log R_{Cl_2}$ (calcd.) $- \log R_{Cl_2}$ (measd.) $\log R_{Cl_2}$ (calcd.) $= 2.1450 - 198.0/T.$ $\Delta H_{\text{hn}} = -10{,}700$ cal. (two lowest temperatures only) temperatures; a small error in k_2' (measd.) at 35.7°C. (table 2a) appears multiplied nearly tenfold in the hydration equilibrium constant. Third, if the limiting law in region I is in any case not exactly the straight line law we have assumed, then this will introduce an error in the calculated values used in determining *d*; and such an error for a given point in region II will be larger the lower the temperature. Finally, because of the diversity of the experimental results, discussion of the errors peculiar to each set is scarcely feasible and will not be attempted.

When these considerations are given proper weight, it appears that the six sets of results plotted in figures 7 and 8 are sufficiently concordant to establish the hydration hypothesis as essentially correct. To this end, it should suffice to show that log [(H)/(U)] for each set of results is a linear function of $1/T$; examination of the figures leaves little doubt that this is true. (The data for reaction 2, table 2a, present the most convincing case, for here (H)/(U) varies nearly 150-fold.) To summarize: the evidence for the hydration hypothesis is all that could reasonably have been expected, although it is not completely free of inconsistencies.

Of these inconsistencies, the failure of reactions 10 and 12 to yield the same value of *d* where one reaction—the bromine hydrolysis—is involved, has already been discussed; those that remain are perhaps more serious. If our simple hydration hypothesis is to explain all the observed temperature coefficient anomalies, then we ought to obtain the same heat of hydration for a halogen no matter from what type of data this heat is deduced. Comparison of tables 2 and 3 shows that for chlorine the heats of hydration correspond to three sets of data to agree almost closely enough to require apology; but that for bromine and iodine large discrepancies exist. The source of these discrepancies may lie in the circumstance that the kinetic data (tables 2a and 2c; note, however, the agreement between tables 2c and 2d) and the equilibrium data (tables 3a and 3c) are not concordant; but what seems more likely, is that the anomalies cannot be completely "localized,"—i.e., that H^+, X^-, and HXO (which are hydrated) are not in all cases simply interchangeable, as concerns our argument, with gaseous X_2 (which is not). We may dismiss these unexplained inconsistencies with the statement that they do not seem sufficiently serious to threaten our main thesis, namely, that equilibria involving halogens in aqueous solution show anomalous temperature coefficients for which the simple hydration of the halogens is responsible.

The chlorine data, however, deserve further discussion. Figures 1 and 3 show that k_2' and k_2 (which are proportional, respectively, to K_{X_2} for iodine and for bromine) can be satisfactorily represented (to within 1 or 2 per cent) by a limiting straight line at all temperatures above the intermediate region II. We have already mentioned that K_{Cl_2} does not behave thus, and that Jakowkin expected it to become independent of T in the neighborhood of 100°C. Examination of figures 2 and 4b shows that K_{Cl_2} and D_{Cl_2} for the highest temperatures fall appreciably below the straight lines given in the figures. That this divergence almost certainly exceeds the experimental error follows from an examination of Jakowkin's work, and from a closer analysis of both sets of results. In the case of K_{Cl_2}, for example, the three points establishing the straight line conform to it very closely (the divergences in order of increasing temperatures are 0.3, 1.1, and 0.2 per cent); the next point falls 4 per cent below the line; while the last, at the highest temperature, is 19 per cent below. The corresponding departure for D_{Cl_2} is 9 per cent, an amount that may well be too small, since only two measurements are available to establish the straight line in figure 2a. We have now to extend our hydration hypothesis to explain this behavior.

In sketching this extension we shall assume that the limiting condition $K_U = K_{X_2}$ (region I) is in fact fulfilled for chlorine at temperatures between 40 and 60°C.; if the close agreement of K_{Cl_2} for these temperatures with the straight line of figure 2 had not been obtained, we could have explained figure 2 on the assumption that this limiting condition is not reached even at the highest temperature. As matters stand, it seems more logical to assume that the temperature interval just above 60°C. represents a second transition region (analogous to region II) for chlorine, in which the hydrates, U and (say) U′, are both present in appreciable amounts. Obviously, we have insufficient data to test this assumption or to establish whether $\Delta H_{U'}$ will be zero or even negative (ΔH_U, of course, is positive). If $\Delta H_{U'}$ is negative, heat will actually be liberated when U′ hydrolyzes. This emphasizes how little significance may attach to the heat of hydrolysis of a halogen so long as the particular hydrate involved is left unspecified; this statement applied with equal force to all reactions of halogens in aqueous solutions and may be applicable to many others.

The question naturally arises as to what types of curves a hydration hypothesis like ours is capable of explaining. If $\Delta H_{U'}$ for chlorine is negative, the complete log K_{Cl_2} curve will be concave toward the $1/T$ axis with its upper section nearly parallel thereto. (The logarithms of many dissociation constants give curves resembling this type (13)). It may be that any log K versus $1/T$ curves that are experimentally realizable and concave toward the $1/T$ axis can be explained by assuming various hydrates of the *reactants* to exist in rapid equilibrium with each other. Whether such curves are concave or convex toward the $1/T$ axis depends, of course, on the way in which the equilibrium constants are written. Our curves are concave because we have followed convention in placing the concentrations of the reactants in the denominator of the equilibrium constant expression;

were these concentrations written in the numerator of the equilibrium constant, all our curves would be convex. Also, the hydration of *resultants* (e.g., HXO in the reaction $X_2 + H_2O = H^+ + X^- + HXO$) could yield log K versus $1/T$ curves convex toward the $1/T$ axis if the corresponding equilibrium constants are written in the conventional way. The situation becomes most complex when both reactants and resultants in a reaction at equilibrium exhibit a variable degree of hydration.

It is of interest, especially in connection with other equilibria that show anomalous temperature coefficients, to consider the application of the thermodynamic equation $\partial\Delta H/\partial T=\Delta c_p$ to the type of data we have been discussing; for this purpose we shall return to the idealized figure 6. In the limiting regions I and III, Δc_p will be zero (or very small) since ΔH_{X_2} does not vary appreciably; in the intermediate region II, however, $\partial\Delta H_{X_2}/\partial T = \Delta c_p$ will reach a maximum (which may be very large) in the center, and decrease rapidly on either side as the limiting temperature regions are approached. Such behavior for a thermodynamic function indicates that a reformulation of the equilibrium involved may be necessary, which, of course, is exactly what we have done by means of our hydration hypothesis; our reformulation yielded constant heats of hydration (e.g., figure 7), and it did eliminate values of Δc_p that were unreasonably large (e.g., figure 1). Unfortunately, the experimental data themselves are scarcely accurate enough to warrant tabulation of the corresponding $\partial\Delta H_{X_2}/\partial T = \Delta c_p$ values; if our hydration hypothesis is correct (as it appears to be) then such "heat capacity" values are altogether without real significance.

Another question of importance in connection with our hydration hypothesis will now be considered. This hypothesis has been advanced to explain temperature coefficient anomalies in an intermediate temperature region, the lower limit of which probably lies not far from 0°C.; we shall now discuss the position of this lower limit. Were the detailed experimental data sufficiently accurate, values of $\partial Q/\partial T$, or of $\partial^2 Q/\partial T^2$, might be used to establish at what temperature region II (figure 6) ends, and region III begins. Since the data do not appear to be sufficiently accurate, we must rely on the following cruder test. Examination of figure 6 and of the equations underlying it will show that the sum $\Delta H_U + \Delta H_{hn}$ must equal ΔH_H. For each set of data, the first two quantities are given in tables 2 and 3, and the heat term corresponding to the two lowest temperatures may be calculated from the experimental results for these temperatures. Now if this heat term is approximately equal to $\Delta H_U + \Delta H_{hn}$, then it is approximately equal also to ΔH_H, and we may consequently assume that these experimental points lie very close to region III. Such comparisons have been made for all the data in tables 2 and 3, and, with the exception to be given, they have shown that region III is not realized above 0°C. (i.e.,

$\Delta H_U + \Delta H_{hn}$ is appreciably larger than the heat term corresponding to the two lowest temperatures. Reaction 2 is the exception. Q for this reaction increases from 24,800 cal. above 50°C. to 56,700 cal. between 3.5 and 0°C.; ΔH_{hn} (table 2) is 22,800 cal. Now, Q should differ from $\Delta H_U + \Delta H_{hn}$ and from ΔH_H by approximately the same amount (namely, by the sum of the heat of dissociation of hypoiodous acid and the heat of activation of reaction 7), so that $24{,}800 + 22{,}800 = 47{,}600$ should equal 56,700. This discrepancy of 9,000 cal., while large, is not alarming. The kinetic data for reaction 2 therefore indicate that region III occurs at a higher temperature for iodine than for bromine or chlorine.

VI. CONSEQUENCES AND APPLICATIONS OF THE HYDRATION HYPOTHESIS

Halogen equilibria in non-aqueous solutions

There seems to be no reason, *a priori*, why anomalous temperature coefficients for the halogens should be confined to aqueous solutions,—why such variations should not be characteristic of every solvent that contains an atom or a group of atoms with which the halogen can unite to form a solvate that becomes increasingly unstable as the temperature is increased. (Such solvates seem most easily formed with atoms—like oxygen, nitrogen, and sulfur—so combined in the solvent that they are capable of forming "onium" compounds.) It appears probable, therefore, that our hydration hypothesis can be expanded to a solvation hypothesis, and that the discovery for a solvent of a temperature coefficient like those under discussion is proof positive that a definite solvated compound exists.

Colors of halogen solutions

The bulk of the experimental material concerning the colors of halogen solutions deals with those of iodine, and we shall confine our discussion to this substance.

In connection with iodine solutions, two experimental facts (already mentioned above) are outstanding: Certain solvents give brown, others give violet solutions; it is sometimes possible to demonstrate a reversible color change from brown to violet by increasing the temperature. Beckmann's hypothesis that the brown color is evidence of solvation has received abundant support (15, 16, 33, 35); the quantitative study of the temperature effects (without which our understanding of these solutions can never be complete) is sometimes complicated by the occurrence of irreversible reactions between iodine and the solvent, and is difficult to carry out in detail (21). Getman (11) has recently published the results of an exceptionally careful quantitative investigation of light absorption by various iodine solutions, presumably at room temperature; measurements like his should be extended over temperature ranges within which any such solutions show temperature coefficient anomalies, in order to discover whether the absorption curves reflect these peculiarities. Such a correlation of anomalous temperature coefficients due to solvation with the absorption spectra of halogen solutions would obviously contribute much to an understanding of these solutions.

Kinetics of halogen reactions

The hypohalous acids and their anions are extraordinarily reactive and unstable substances, so that it is often impossible to isolate them for kinetic studies. Consequently, the principal evidence that these substances, and not the halogens themselves, are frequently the actual reactants when the latter act as oxidizing agents in aqueous solution has been the proof that the rate laws for such reactions are formally analogous to equation 4 or 11; i.e., the rates of these reactions are usually inversely proportional to some function of (H^+) and (X^-), and this proportionality usually is taken to indicate that the hydrolysis equilibrium

$$X_2 + H_2O \overset{K_{X_2}}{\rightleftharpoons} H^+ + X^- + HXO \tag{30}$$

is maintained and that HXO (or XO^-, but not X_2) is actually involved in the rate-determining step. Rate-law evidence of this type, however, is not conclusive proof of mechanism (12); such proof is at hand only when it has been shown that HXO (or XO^-) in the (virtual) absence of X_2 does react with the reducing agent in question with the specific rate to be predicted from the reaction of this reducing agent with X_2. (In the case of reaction 10, for example, this specific rate, κ_2, equals k_2/K_{Br_2}). Such conclusive proof of mechanism is usually difficult or impossible to obtain, so that another test of mechanism, to be applied in the cases of rate laws involving inverse (H^+) and (X^-) terms is highly desirable.

The experimental evidence, new and old, which has been presented above seems strong enough to warrant the conclusion that any log K_{X_2} versus $1/T$ plot must show a curvature concave toward the $1/T$ axis. (Although this curvature finds a plausible explanation in our hydration hypothesis, its existence is empirically established and consequently independent of the validity of this hypothesis.) This curvature may now be utilized as a simple test of mechanism: If HXO or XO^- is the only halogen-containing substance involved in a rate-determining step, then the specific rate of the corresponding stoichiometric reaction must at all temperatures be proportional to K_{X_2} (cf. equations 2, 4, 5, 6, and 7; or equations 10, 11, 12, and 13) and must thus reflect this curvature in a log k versus $1/T$ plot. Since this argument has already been employed for reactions 2 and 10, it need not be elaborated; the fact that the specific rates of these reactions meet this test increases our confidence in the mechanism we have outlined for them.

The value of this proposed test of mechanism cannot be assessed until it has been applied (as it will be) to other aqueous halogen reactions—in particular, to reactions whose mechanism has been "verified" in the sense that Makower and Liebhafsky (31) verified the mechanism of the bromine-oxalate reaction. If the test is valid, we must accept also the following corollary: If the rate of an aqueous halogen reaction is governed by the Arrhenius equation, HXO or XO^- cannot be the only halogen-containing substance involved in a rate-determining step, even though the rate law involves inverse (H^+) and (X^-) terms.

Determination of equilibrium constants

The statement has been made above that it will probably be impossible to obtain accurate direct measurements of K_{I_2}, the hydrolysis constant of iodine, near 0°C. If the data in figures 1 and 4a can be reconciled so that the curvature for a log K_{I_2} versus $1/T$ plot can be predicted either from the kinetic data (figure 1) or from the distribution data (figure 4a), then a knowledge of this curvature may be used in the calculation of K_{I_2} values for temperatures at which accurate direct measurements are impossible; for this calculation the results of such measurements must of course be available for some of the higher temperatures, at which they can be made. Further consideration of this problem will be postponed until the conductivity data obtained some time ago for aqueous iodine solutions (26) are prepared for publication; the problem is outlined here to emphasize the importance, not always appreciated, of correlating kinetic with equilibrium data, whenever this is possible.

VII. CONCLUSION

Experimental evidence from kinetic and from equilibrium measurements has been adduced to show that aqueous halogen solutions generally exhibit anomalous temperature coefficients. This evidence, obtained from many sources, seems conclusive; and it will consequently be necessary to take the existence of these anomalies into account whenever the effect of changing temperature on such a halogen solution is being considered.

The quantitative explanation which has been proposed for these anomalies is necessarily on less secure ground than are the experimental facts themselves. This explanation assumes that the temperature region in which the anomalies occur is the region in which the degree of hydration of the halogens is changing,—in which, therefore, two halogen species exist at comparable concentrations and in rapid equilibrium with each other. When the consequences of this hydration hypothesis have been experimentally tested, and when its further applications have been explored, then its true value can be more readily assessed.

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