333. *Reaction Velocities at Low Temperatures. Part I. A Convenient Low-temperature Thermostat. Part II. The Bromination of Acetone between* $-40°$ *and* $+10°$.

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It is shown that measurements of reaction velocities at low temperatures would be of value in investigating possible deviations from the Arrhenius equation, in particular those due to the " tunnel effect."

Part I.—A simple low-temperature thermostat is described, and details are given for its operation between 10° and — 40°.

Part II.—Data are given for the velocity of the acid-catalysed bromination of acetone in 90·9% and 95% aqueous acetone at temperatures between + 10° and — 40°, the catalysts used being hydrogen chloride and bromide. With hydrogen chloride there is catalysis by both hydrogen ions and undissociated acid, but with hydrogen bromide the hydrogen ion is the only effective catalyst and the reaction velocity is almost directly proportional to the acid concentration. The Arrhenius equation is obeyed within the limits of experimental error, and the activation energy is the same as for hydrogen-ion catalysis in aqueous solution.

Measurements of reaction velocity have rarely extended to temperatures below 0°, largely owing to the difficulty of maintaining and controlling such temperatures over sufficiently long periods. Such measurements would be of considerable value, since in addition to extending the range of reactions which can be studied kinetically, they might throw light on the question as to how far the Arrhenius equation can be regarded as an exact representation of the variation of reaction velocity with temperature. A statistical treatment of the problem (cf., *e.g.*, Tolman, " Statistical Mechanics," Chap. 21, New York, 1927) shows that the temperature coefficients of unimolecular and bimolecular reactions respectively are given by

$$\left.\begin{cases} \mathrm{d}\log k_1/\mathrm{d}T = (\bar{\bar{\varepsilon}} - \bar{\varepsilon})/\boldsymbol{k}T^2 \\ \mathrm{d}\log k_2/\mathrm{d}T = 1/2T + (\bar{\bar{\varepsilon}} - \bar{\varepsilon})/\boldsymbol{k}T^2 \end{cases}\right\} \quad . \quad . \quad . \quad . \quad (1)$$

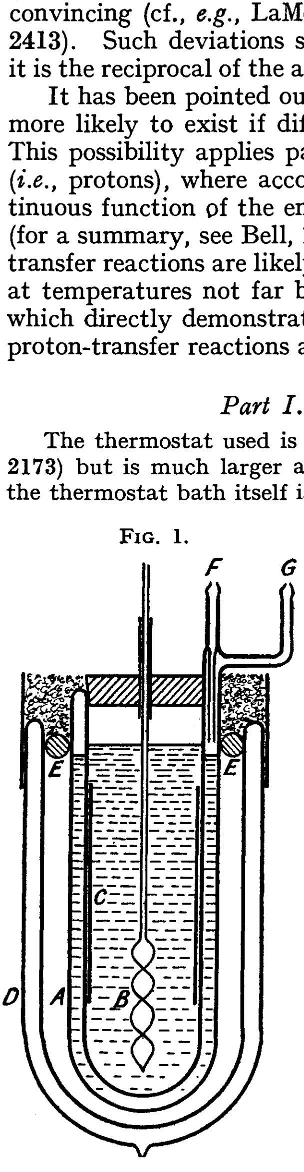
where ε is the average energy of the molecules which react, and $\bar{\varepsilon}$ that of all the molecules. The usual integrated form of (1) corresponds to the assumption that the activation energy $\bar{\bar{\varepsilon}} - \bar{\varepsilon}$ does not vary with the temperature. Both $\bar{\bar{\varepsilon}}$ and $\bar{\varepsilon}$ represent averages over a number of energy states, and it is clear in principle that this assumption is only a first approximation, just like the assumption of a constant heat of reaction in integrating the van 't Hoff isochore. On the other hand, experiment shows that in practice it is a very good approximation, since the reported deviations from the simple Arrhenius equation (apart from those due to a composite chemical mechanism) are neither numerous nor convincing (cf., *e.g.*, LaMer, *J. Amer. Chem. Soc.*, 1935, **57**, 2662, 2669, 2674; 1936, **58**, 2413). Such deviations should become much more apparent at low temperatures, since it is the reciprocal of the absolute temperature which enters into all the relevant equations.

It has been pointed out by LaMer (*J. Chem. Physics*, 1933, **1**, 289) that deviations are more likely to exist if different activated states have different probabilities of reaction. This possibility applies particularly to reactions involving the movement of light nuclei (*i.e.*, protons), where according to quantum theory the probability of reaction is a continuous function of the energy. A number of calculations of this effect have been made (for a summary, see Bell, *Trans. Faraday Soc.*, 1938, **34**, 229), and it appears that proton-transfer reactions are likely to exhibit considerable deviations from the Arrhenius equation at temperatures not far below 0°. No experimental evidence has so far been produced which directly demonstrates the existence of this "tunnel effect," and measurements on proton-transfer reactions at low temperatures are therefore of special interest.

Part I. A Convenient Low-temperature Thermostat.

The thermostat used is based on that described by Simon (*Ber.*, 1927, **60**, 568; 1928, **61**, 2173) but is much larger and can be operated continuously for long periods. A diagram of the thermostat bath itself is shown in Fig. 1. The bath liquid (1500 c.c. of trichloroethylene) is contained in the double-walled Monax vessel *A*, 30 cm. deep, and 11 cm. in external diameter. Temperature uniformity is ensured by the glass stirrer *B* and the stout copper cylinder *C*. The bath is cooled by the evaporation of a liquefied gas in the annular space of *A* (width 1 cm.), and the temperature is controlled by regulating the pressure under which this evaporation takes place. Thermal insulation is effected by the large Pyrex Dewar vessel *D* (with an unsilvered vertical strip for inspection) and by the layer of asbestos-wool resting on the rubber support *E*. The top of the bath is closed by a cork bung in which reaction vessels, etc., can be held.

FIG. 1.



The refrigerant was admitted through *F* from an inverted gas cylinder, and the gas was pumped off through *G* by means of a water-suction pump. The pressure regulator used was of the type described by Simon (*loc. cit.*). It incorporated a buffer vessel of 20 l. capacity, and the evacuated mercury vessel was mounted on a vertical steel column with a fine screw adjustment. In this way the pressure in the system could be adjusted and kept consant to within 1 mm. of mercury. When ammonia was used as refrigerant it was found that the water pump rapidly became blocked owing to deposition of calcium carbonate from the hard tap water. It was therefore necessary to cut off the flow of gas temporarily every few hours and to clear the pump by sucking through acid. During the night the same operation was performed by an automatic device incorporating an alarm clock.

When the apparatus is started, the system is evacuated as well as possible by the water pump, and the bath cooled to some degrees below the required temperature by adding solid carbon dioxide or by blowing liquid air into a metal tube immersed in the bath. The refrigerant is then admitted carefully from the cylinder until the pressure in the system approaches atmospheric. The temperature and pressure are allowed to fall again before a second addition is made, and this process is repeated until the refrigerant is within a few cm. of the top of the annular space. The mercury reservoir is then set to the required level, and after $\frac{1}{4}$—$\frac{1}{2}$ hour a steady temperature is reached. Over short periods (1—2 hours) the temperature is constant to about ± 0·02° and can be rapidly and accurately adjusted; *e.g.*, at

— 20° with sulphur dioxide as the refrigerant, if the mercury reservoir is lowered by 2 mm., the temperature falls about 0·1° and is steady again after 10 mins. Over longer periods there is a gradual steady rise of temperature—about 0·3° in 12 hours—probably caused by the change in level of the refrigerant. However, by occasional hand regulation, constancy can be maintained to ± 0·05° during the day, and it is easy to set the reservoir so that the average temperature during the night has the required value.

With the present apparatus about one-half of the liquid in the annular space is used in 12 hours, and the apparatus was therefore refilled with refrigerant night and morning, the same procedure being used as for the initial filling, except that the preliminary cooling was usually carried out by lowering the mercury reservoir. During this period (about ½ hour) the thermostat temperature deviates considerably both above and below the required value, but with practice the preliminary cooling can be so adjusted that the average temperature is very close to the desired value. In this way the thermostat can be worked continuously for an indefinite period.

The following table shows the refrigerants used at various temperatures, the rate at which they were consumed, and the approximate pressures used. It will be seen that the cost of running the thermostat is not excessive.

Temp.	+10°	−11°	−20°	−30°	−40°
Refrigerant	Et_2O	SO_2	SO_2	SO_2	NH_3
Pressure (mm. mercury)	290	720	480	290	540
Consumption (g. per 24 hrs.)	175	500	690	870	380

The temperature of the thermostat was measured by a two-junction copper–constantan thermo-couple, the other junctions being at 0°. This was connected to a direct-reading galvanometer which could be read to 10^{-5} volt, corresponding to about 0·1°. The thermocouple was calibrated at the f. p.'s of chlorobenzene (— 45·35°) and carbon tetrachloride (— 22·9°), and at various temperatures between 0° and 25° on a standard thermometer. A pentane thermometer was used for observing small changes of temperature, but could not be used for actual temperature measurement owing to the large and uncertain stem correction.

Part II. The Bromination of Acetone between — 40° *and* + 10°.

The reaction of acetone with the halogens is well known as a case of prototropy, its velocity being independent of the halogen concentration, but dependent on the various acid or basic catalysts present. Most of the kinetic work has been carried out in dilute aqueous solution, but for low-temperature measurements it was necessary to use aqueous acetone which contained a high percentage of acetone, and therefore had a low freezing point. The mixtures used contained 90·9% and 95·0% of acetone by weight and remained liquid and homogeneous at least down to — 50°.

It was wished to study catalysis by the hydrogen ion, and preliminary experiments were first made with perchloric acid as catalyst, since this acid is completely dissociated even in anhydrous acetone (cf. Hartley *et al.*, *Ann. Reports*, 1930, **27**, 344). However, this acid appears to react with acetone to give a product which liberates iodine from potassium iodide, and hydrogen bromide was therefore used as catalyst in most of the experiments. There is no direct information about its dissociation in acetone, but hydrogen chloride is a very weak acid in pure acetone, and at least a moderately strong one in acetone containing 12½% of water (Brownson and Cray, J., 1925, **127**, 2923). Hydrogen bromide should be considerably stronger than this, and we may expect that it will be almost completely dissociated in 90% acetone. It will be seen later that this expectation is confirmed by the kinetic results. In view of the very great effect of adding small quantities of water to acids in pure acetone (Hartley and Hughes, *Phil. Mag.*, 1933, **15**, 610), it is clear that the hydrogen ion formed in aqueous acetone is H_3O^+.

Preliminary experiments carried out with iodine as the reacting halogen showed that under the conditions employed the system came to equilibrium with a small residual concentration of iodine. With bromine, on the other hand, the reaction went to completion in 90·9% acetone, and nearly so in 95% acetone; this halogen was therefore employed throughout.

Materials.—Acetone. A commercial product (from the bisulphite compound) was dried over fused potassium carbonate and fractionally distilled, the portion boiling within 0·1° being used. The required amount of water was added by weight.

TABLE I.

Temp., −11·3°. Catalyst, HBr. Solvent, 90·9% acetone. Initial acid concn., 0·0221N. Final concn., 0·0231N.

Time (mins.)	3	34	57	77	97	130	152	190	220
Titre, c.c./g. obs.	1·70	1·49	1·35	1·21	1·06	0·85	0·70	0·43	0·23
Titre, c.c./g. calc.	1·71	1·50	1·34	1·21	1·07	0·85	0·69	0·44	0·23

Hydrogen chloride was prepared from pure sodium chloride and concentrated sulphuric acid. Hydrogen bromide was prepared from bromine, red phosphorus, and water, and was passed successively over moist red phosphorus and phosphoric oxide. The concentration of the stock solutions in 90·9% and 95% acetone was determined by weight titration. In 90·9% acetone the solutions were stable for at least a month, as regards both titre and kinetic results. The solutions of hydrogen bromide in 95% acetone gradually became yellow, and their titre decreased. They were obviously not stable, and were used within a few days of preparation.

Measurement of Reaction Velocity.—The reactions were carried out in vessels of the type previously described (Bell and Levinge, *Proc. Roy. Soc.*, 1935, *A*, **151**, **211**), which were immersed in the thermostat to above the internal seal, and for measurements below 0° were fitted with calcium chloride tubes to prevent the condensation of moisture on the ground cap.

TABLE II.

HCl in 90·9% acetone.

−20·6°	c	0·0108	0·0215	0·0427	0·0636	0·0744	0·0880	0·117	0·145
	10^6v	2·28	5·34	12·2	21·4	26·0	36·0	50·7	68·2
	$10^4v/c$	2·11	2·48	2·86	3·36	3·49	4·09	4·34	4·69

HBr in 90·9% acetone.

+10·1°	c	0·0111	0·0144	0·0254	0·0360	0·0391
	10^4v (obs.)	0·880	1·20	2·11	3·01	3·31
	10^4v (calc.)	0·903	1·18	2·11	3·04	3·31

$$v = 8{\cdot}00 \times 10^{-3}c(1 + 1{\cdot}5c).$$

0·0°	c	0·0137	0·0148	0·0209	0·0330	0·0511	0·0671	0·0830
	10^5v (obs.)	3·00	3·35	4·62	7·56	11·8	15·9	20·1
	10^5v (calc.)	3·02	3·27	4·66	7·48	11·9	15·9	20·2

$$v = 2{\cdot}16 \times 10^{-3}c(1 + 1{\cdot}5c).$$

−11·3°	c	0·0205	0·0226	0·0372	0·0767
	10^6v (obs.)	9·82	10·7	17·1	37·8
	10^6v (calc.)	9·51	10·5	17·7	38·5

$$v = 4{\cdot}50 \times 10^{-4}c(1 + 1{\cdot}5c).$$

−20·6°	c	0·0191	0·0222	0·0554	0·0598	0·0861	0·1125
	10^6v (obs.)	2·02	2·41	6·59	6·89	10·1	13·8
	10^6v (calc.)	2·08	2·43	6·36	6·91	10·3	13·9

$$v = 1{\cdot}06 \times 10^{-4}c(1 + 1{\cdot}5c).$$

−29·8°	c	0·0101	0·0254	0·0428	0·0627	0·0862
	10^7v (obs.)	2·94	7·05	11·6	18·0	24·3
	10^7v (calc.)	2·66	6·86	11·8	17·8	25·3

$$v = 2{\cdot}60 \times 10^{-5}c(1 + 1{\cdot}5c).$$

−40·0°	c	0·0157	0·0291	0·0570	0·0753	*0·0753	0·1029
	10^8v (obs.)	6·45	12·9	24·7	31·5	33·2	48·5
	10^8v (calc.)	6·45	12·2	24·7	33·5	33·5	48·5

$$v = 4{\cdot}00 \times 10^{-6}c(1 + 1{\cdot}5c).$$

HBr in 95·0% acetone.

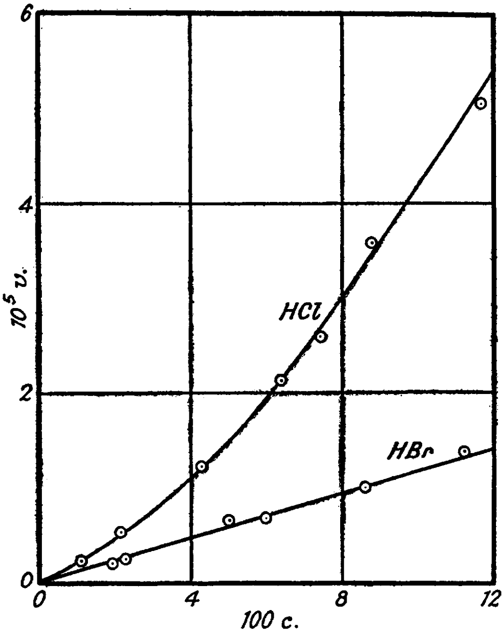
0·0°	c	0·0118	0·0192	0·0327	0·0452	0·0624	0·0820	
	10^4v	0·465	0·753	1·31	2·03	2·72	3·74	
	$10^3v/c$	3·96	3·92	4·00	4·49	4·37	4·48	Mean = 4·20
−11·3°	c	0·0113	0·0251	0·0341	0·0458	0·0724		
	10^5v	0·87	1·88	3·01	3·45	6·36		
	$10^4v/c$	7·70	7·48	8·82	7·53	8·79		Mean = 8·06
−20·6°	c	0·0135	0·0217	0·0375	0·0455	0·0752	0·0818	
	10^6v	2·15	3·37	6·44	8·30	13·3	12·8	
	$10^4v/c$	1·59	1·55	1·72	1·87	1·77	1·56	Mean = 1·68

When the cap was removed for adding or extracting solution, a current of dry air was passed into the space surrounding the ground portion, and the cap was dried before being replaced. Four vessels could be placed in the thermostat at once. At + 10°, — 11°, and — 20° the experiments were completed between successive refillings of refrigerant, and at — 30° and — 40° calculation showed that the temperature disturbances caused by refilling had a negligible effect on the course of the reaction. The experiments at 0° were done in ice.

In carrying out an experiment, about 10 c.c. of acid of the required concentration was left in a reaction vessel in the thermostat for ½ hour. A small quantity of bromine was then added from a capillary, the initial bromine concentration varying from 0·001 to 0·003N. About 1 c.c. of reaction mixture was pipetted out from time to time into a weighed flask containing 15 c.c. of a buffer solution, N/5 with regard to both acetic acid and sodium acetate, plus 0·5 c.c. of N/10-potassium iodide solution. In this solution the rate of iodination of acetone is so slow that no measurable reaction takes place before titration. The iodine liberated was titrated with N/300-thiosulphate solution from a 2-c.c. micro-burette, the over-all accuracy of the titrations being about 0·02 c.c.

Table I gives the data for a typical experiment in 90·9% acetone, the calculated titres being on the assumption that the bromine is used at a constant rate. The acid concentration changes slightly during the reaction owing to the hydrogen bromide produced: however, this change was always less than 10%, and the plot of titre against time was always effectively straight. The reaction velocity was taken from the slope of this line, and the catalyst concentration was taken as the mean of the initial and final values.

FIG. 2.



In 95% acetone the reaction with bromine did not go quite to completion, and the plots of titre against time were curved. The velocities given were taken from the initial slopes of these plots, but are much less accurate than those in 90·9% acetone. Since a change in the proportion of acetone from 90·9% to 95% results in an increase in velocity of about 70%, the velocity is not unduly sensitive to the water concentration in this range.

Results.—In Table II, *c* is the mean catalyst concentration in g.-mols./1000 g. of solution, and *v* is the reaction velocity expressed as g.-mols. of bromine reacting per 1000 g. of solution per minute. The equations used for obtaining the calculated values of *v* are given at the foot of each section of the table. In one experiment at — 40° (marked *) the glass surface was increased about 6-fold by packing the reaction vessel with capillary tubes. The resultant increase in velocity (5%) is within the probable experimental error, and there can thus be no appreciable heterogeneous reaction.

DISCUSSION.

Fig. 2 shows a plot of reaction velocity against catalyst concentration for both hydrogen bromide and hydrogen chloride in 90·9% acetone at — 20·6°. It will be seen that the two curves approach one another in dilute solutions, but that in the former case the velocity is nearly proportional to the catalyst concentration, whereas in the latter case it increases much more rapidly. We attribute this large difference between the two acids to the fact that hydrogen bromide is effectively completely dissociated at the concentrations in question, while the hydrogen chloride solutions contain an appreciable amount of undissociated acid, which is a more powerful catalyst than an equivalent concentration of hydrogen ions. In passing from hydrogen chloride to hydrogen bromide, the increase in the catalytic power of the undissociated molecules will be more than compensated by the decrease in their concentration, so that their relative effect becomes smaller. Such a difference between these two acids is to be anticipated on theoretical grounds, and has been observed in other reactions (cf. Bell and Burnett, *Trans. Faraday Soc.*, 1939, **35**, 474).

All the remaining experiments were therefore carried out with hydrogen bromide as catalyst. With this acid there is a slight increase of catalytic power with concentration which may be due either to catalysis by a very small concentration of undissociated molecules, or to a salt effect. The latter explanation is more probable, since the results in 95% acetone (though less accurate) do not indicate any accentuation of this effect. In 90·9% acetone the results can be expressed within the limits of experimental accuracy by assuming that at all temperatures v/c increases linearly by 15% between $c = 0$ and $c = 0{\cdot}1$N: this is shown by the agreement between the observed and the calculated values of v in Table II.

The values of v/c at infinite dilution obtained in this way obey the Arrhenius equation very accurately, as is shown in the following table, where the observed values of v_0/c are compared with those calculated from the equation $v_0/c = 10^{13{\cdot}28}\, e^{-19,900/RT}$.

HBr in 90·9% acetone.

Temp.	+10·1°	0·0°	−11·3°	−20·6°	−29·8°	−40·0°
v_0/c (obs.) ...	$8{\cdot}0 \times 10^{-3}$	$2{\cdot}16 \times 10^{-3}$	$4{\cdot}50 \times 10^{-4}$	$1{\cdot}06 \times 10^{-4}$	$2{\cdot}60 \times 10^{-5}$	$4{\cdot}00 \times 10^{-6}$
v_0/c (calc.) ...	$8{\cdot}0 \times 10^{-3}$	$2{\cdot}19 \times 10^{-3}$	$4{\cdot}47 \times 10^{-4}$	$1{\cdot}10 \times 10^{-4}$	$2{\cdot}45 \times 10^{-5}$	$4{\cdot}03 \times 10^{-6}$

There is thus no indication that the " tunnel effect " plays any appreciable rôle in this reaction. The prototropic change concerned involves the movement of a proton between an oxygen atom and a carbon atom. If these two atoms approach to within 3·0—3·5 A. (the normal distance for non-bonded atoms), then the proton moves through a distance of 1—1·5 A. Calculations for potential barriers of this width (Bell, *Proc. Roy. Soc.*, 1935, *A*, **148**, 241) indicate that with an activation energy of 20,000 cals. deviations from classical behaviour should certainly be large at temperatures below − 20°, and probably at higher temperatures. This conclusion appears to be contradicted by the present experimental results. However, it must be remembered that the acid-catalysed prototropy of acetone takes place in two steps, *viz.*,

$$CH_3{\cdot}CO{\cdot}CH_3 + H_3O^+ \rightleftharpoons CH_3{\cdot}C(OH^+){\cdot}CH_3 + H_2O \longrightarrow CH_2{:}C(OH){\cdot}CH_3 + H_3O^+$$

and that the first of these steps represents an equilibrium, the rate being determined by the second step (cf. Pedersen, *Trans. Faraday Soc.*, 1938, **34**, 243; Bonhoeffer and Reitz, *Z. physikal. Chem.*, 1937, *A*, **179**, 135). A considerable proportion of the measured activation energy will be associated with this equilibrium, and any non-classical transfer can, of course, only affect the second step: hence the deviations from classical behaviour may be undetectable.

It is noteworthy that the activation energy found in the present work, 19,900 cals. in 90·9% acetone, is very close to the value of 20,700 cals. found by Smith (J., **1934**, **1744**) for hydrogen-ion catalysis in the iodination of acetone in aqueous solution. The data for 95% acetone are much less accurate, but lead to substantially the same value (22,000 ± 3000). Since the catalyst has a single positive charge, the proton transfers concerned do not involve a change in the total number of charges, and thus would not be greatly affected by a change in medium.

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