TABLE I

DECOMPOSITION OF ISOBUTYLENE

The last ten rows of figures contain the number of moles of the respective substance recovered per mole of isobutylene decomposed. In Experiment 6 the furnace broke near the end of the run and some material was lost.

Expt.	1	2	3	4	5	6	7	8	9	10
Moles C_4H_8 through furnace	1.21	0.354	0.69	2.89	3.38	2.88	2.98	2.76	1.76	1.30
Per cent. decomposed	2.6	49.5	43.9	7.8	5.6	7.1	5.7	3.6	9.8	5.5
Temp. furnace, °C.	885	945	897	790	790	717	773	714	753	630
Press. in furnace, mm.	8	10	12	8	9	20	100	250	250	743
Contact time, sec.	0.07	0.56	0.29	0.026	0.301	0.053	0.46	0.43	0.42	2.1
H_2	0.17	0.61	0.23	0.08	0.14	0.11	0.17	0.25	0.28	0.39
CH_4	0.81	1.58	0.94	0.73	0.83	0.61	0.95	1.10	0.93	1.16
C_2H_6	0.02	0.00	0.01	0.05	0.03	0.01	0.02		0.03	0.06
C_2H_4	0.07	0.29	0.11	0.05	0.03	0.02	0.04	0.025[a]	0.125	0.27
C_2H_2	0.01	0.19	0.05	0.03	0.02	0.02	0.01		0.01	0.02
C_3H_6	0.20	0.25	0.20	0.29	0.29	0.11	0.35	0.42	0.41	0.66
$CH_2{=}C{=}CH_2$	..	0.07	0.05	0.37	0.49	0.25	0.21	0.23	0.21	0.14
$CH_3C{\equiv}CH$	..	0.36	0.20	0.325	0.25	0.23	0.38	0.26	0.24	0.10
ΣC_3H_4	0.80	0.43	0.25	0.695	0.74		0.59	0.49	0.45	0.24
ΣC_3's	1.00	0.68	0.45	0.985	1.03		0.94	0.91	0.86	0.90

[a] This is the sum of C_2H_6, C_2H_4 and C_2H_2.

pentenes because they would be present in only small quantity and since they boil at a higher temperature than isobutylene, they would be reported as this substance.

We are inclined to think that the methylacetylene is formed from allene by means of a radical chain. A free methyl radical, for example, reacting either with methylacetylene or allene would, in each case, give the same radical $\overset{|}{C}H_2{-}\overset{|}{C}{=}\overset{|}{C}H$. When this radical removes a hydrogen atom from an organic molecule, methylacetylene is formed, if a hydrogen atom attaches itself to the left-hand side of the molecule and allene is formed if a hydrogen atom is attached to the right-hand side of the molecule. We plan to investigate this point in a later paper.

Summary

1. The thermal decomposition of isobutylene probably proceeds through a short chain, producing methane and allene.

2. Under proper conditions of temperature, pressure and contact time, the decomposition of isobutylene occurs without appreciable production of carbonaceous and tarry material.

3. Both allene and methylacetylene are major products of the reaction. It has not yet been determined whether the methylacetylene is produced by isomerization of allene or by molecular dehydrogenation of the isobutylene.

4. Under best conditions there were about 60 moles per cent. yields of allene–methylacetylene based on the decomposed isobutylene.

WASHINGTON, D. C. RECEIVED JULY 25, 1947

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Apparent Molal Expansibilities of Potassium, Barium and Lanthanum Chlorides as a Function of Concentration and Temperature[1]

BY GRINNELL JONES,[2] E. FOLGER TAYLOR[3] AND RICHARD C. VOGEL[4]

The apparent molal thermal expansibility of a solute may be defined by the equations

$$\phi\bar{E}_2 = V_s\alpha_s - V_w\alpha_w = \left(\frac{\partial\phi V_2}{\partial T}\right)_P \qquad (1)$$

where V_s is the volume of solution containing one mole of solute, V_w is the volume of water used, α_s and α_w are the thermal coefficients of expansion of the solution and water, respectively, and ϕV_2 is the apparent molal volume of the solute.

Gucker[5] has obtained the limiting law for the partial molal expansibility, $\bar{E}_2$ of the solute as a function of the concentration from the Debye–Hückel theory, when $\bar{E}_2$ is defined by the equation

$$\bar{E}_2 = (\partial\bar{V}_2/\partial T)_P \qquad (2)$$

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[1] This paper represents part of the thesis material submitted by E. Folger Taylor and by R. C. Vogel in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Harvard University, Cambridge, Massachusetts.

[2] Deceased, June 23, 1947.

[3] Present address: Du Pont Company, Waynesboro, Virginia. E. Folger Taylor is responsible for the development of the mercury dilatometer described in this paper and for the studies carried out on water and on solutions of potassium chloride from 20 to 80°.

[4] Present address· Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois. R. C. Vogel was the grateful holder of an Allied Chemical and Dye Corporation Fellowship. He conducted experiments on water and solutions of barium chloride and lanthanum chloride from 20° to 60°.

[5] F. T. Gucker, Jr., THIS JOURNAL, **56**, 1017 (1934).

where $\bar{V}_2$ is the partial molal volume of the solute. If each molecule furnishes ν_i ions of charge z_i' then

$$\bar{E}_2 - \bar{E}_2^0 = \frac{A}{2}\,\frac{(\Sigma \nu_i z_i^2)^{3/2}}{D^{3/2}T^{1/2}} f(D,P,V,T)c^{1/2} \qquad (3)$$

and

$$f(D,P,V,T) = -1/2\left[\frac{3}{D}\frac{\partial D}{\partial T} + \frac{1}{T} + \alpha\right]\left(\frac{3}{D}\frac{\partial D}{\partial P} - \beta\right) + \frac{\partial}{\partial T}\left[\frac{3}{D}\frac{\partial D}{\partial P} - \beta\right]$$

$$A = \left[\frac{\pi N^3 \epsilon^6}{1000k}\right]^{1/2} = 2.457 \times 10^{14} \text{ in c. g. s. units}$$

The coefficient of compressibility of the solvent is β, and the dielectric constant is D; T is the absolute temperature, N is Avogadro's number, ϵ the charge on the electron, k is Boltzmann's constant, and c is the volume concentration. On the basis of this equation and by an estimation of the value of $\partial^2 D/\partial T \partial P$, Gucker arrives at the limiting law

$$\phi E_2 = \phi E_2^0 + 8 \times 10^{-3} c^{1/2} \qquad (4)$$

for the apparent molal expansibility of uni-univalent electrolytes at 20°.

Without considering the numerical value of the coefficient, Gucker's equations predict three things: (a) at low concentration ϕE_2 should be a linear function of $c^{1/2}$; (b) the limiting slopes, $\partial \phi E_2/\partial c^{1/2}$, should be the same for all electrolytes of the same valence type; and (c) the limiting slopes should be greater for electrolytes of higher valence types. If the numerical value of the slope is considered, a fourth prediction will be that the slope should be positive.

Gucker[5] calculated the apparent molal expansibilities from the data on the density of aqueous solutions found in the literature for sodium chloride, potassium chloride, lithium chloride, hydrochloric acid, lithium hydroxide and sodium sulfate by an approximate method. Gibson and Kincaid[6] have obtained the apparent molal expansibilities of barium chloride, potassium nitrate, potassium bromide, lithium bromide and sodium iodide at 25° and at 35°. The lowest concentration which these investigators studied was 0.25 mole per liter for the barium chloride solutions and about 0.5 mole per liter for the rest of the solutions. The apparent molal expansibility of barium chloride showed an unusually large departure from linearity when plotted against $c^{1/2}$. Gibson and Loeffler[7] recently determined the apparent molal expansibilities of sodium chloride and of sodium bromide from 25° to 85°. The lowest concentration studied was around 0.5 mole per liter.

All of these investigators found that an increase of temperature decreased the apparent molal expansibility for a given concentration and increased the slope of ϕE_2 plotted against $c^{1/2}$. From the data of these investigators it is apparent that of the four predictions made by Gucker's limiting law, only one is correct in the concentration ranges studied, *i. e.*, ϕE_2 is usually a linear function of $c^{1/2}$ for uni-univalent electrolytes. But contrary to the predictions from Gucker's equations, the data show that at 25° the slopes are widely different for various uni-univalent electrolytes, and in the case of the uni-bivalent electrolyte, sodium sulfate, the slope is considerably less than that of any uni-univalent electroyte yet studied.

Perhaps part of the lack of agreement between theoretical predictions and experimental results is because the solutions studied have been no more dilute than about 0.25 mole per liter. In the calculation of apparent molal expansibilities from experimental data, the experimental error in measuring the coefficient of expansion is multiplied by about $1000/c$. Therefore, if a study of dilute solutions is to be undertaken, apparatus capable of giving results more accurate than those yet obtained must be used.

A new type of dilatometer has been developed which is capable of measuring changes in volume of electrolyte solutions over a wide range of temperature to ±0.0003 cc., the total volume being about 275 cc. This apparatus has been used to study solutions of potassium chloride from 20 to 80° and solutions of barium chloride and of lanthanum chloride from 20 to 60° The lowest concentrations which gave reproducible results were 0.06 molar.

Experimental Technique

Dilatometers.—The mercury dilatometer, which measures a change in volume in terms of the weight of mercury expelled or drawn in when the temperature is varied, is a well-known instrument used by a number of investigators. The first dilatometer to employ the unique principle of being a thermal regulator for its thermostat as well as a dilatometer was used by Jones and Jelen[8] for determining the cubical coefficients of expansion of solids. Thus, this type of dilatometer controls the temperature of the bath so that the dilatometer's contents exactly occupy the entire volume. The Jones and Jelen dilatometer was redesigned for use with solutions.

Two dilatometers, as nearly alike as the glassblower could make them, were used in this research. They each (Fig. 1) have an over-all height of 30 cm. and are made of Pyrex glass. The main part of the dilatometer, A, is closed at the top by stopcock F. A smaller tube, B, is attached at the bottom of the main part of the dilatometer. In the upper part of B there is a capillary restriction, D, about 2 cm. long and 1 mm. in inside diameter. A tantalum wire, J, is sealed in tube, B, above the capillary, D, in such a manner that its sharp point extends into the upper end of the capillary. Below the capillary, D, is sealed a platinum wire, K. Both the tantalum wire, J, and the platinum wire, K, extend into wells which may be filled with mercury. By placing wires from a thyratron circuit in the mercury-filled wells, H and C, the dilatometer can be made to control part of the heat input to the thermostat by making or breaking the circuit through the tantalum wire and the mercury in the capillary, D. This principle is exactly the same as that of a conventional mercury thermo-regulator. The capacity of each dilatometer (275 cc.) is such that when they are filled with mercury and water in a typical experiment a temperature change of 0.001° at 25° will produce a change in height of the mercury in capillary D of 0.1 mm. and at 75° of 0.2 mm.

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(6) R. E. Gibson and J. F. Kincaid, THIS JOURNAL, **59**, 25 (1937).

(7) R. E. Gibson and O. H. Loeffler, *ibid.*, **63**, 443 (1941).

(8) Grinnell Jones and F. T. Jelen, *ibid.*, **57**, 2532 (1935).

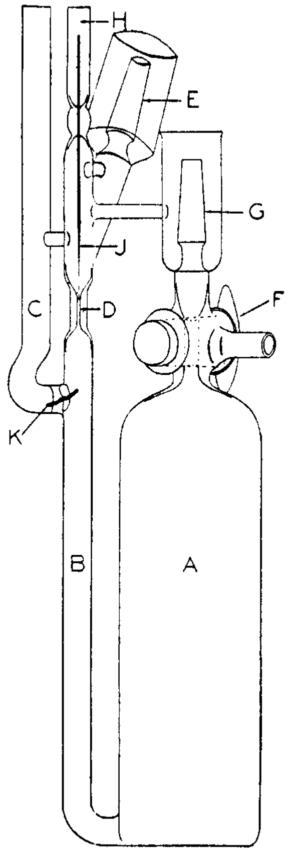

Fig. 1.—Mercury dilatometer.

The tube, E, is provided for the withdrawal or addition of mercury. After one equilibrium temperature has been determined, some mercury is removed from the dilatometer, and the instrument will then equilibrate at a higher temperature. The mercury removed is weighed. It is also possible to go from a higher to a lower equilibrium temperature by adding a weighed quantity of mercury through the tube, E.

The dilatometers are first calibrated, using mercury as a standard. During these runs the instruments are completely filled with mercury. At an equilibrium temperature the mercury is in the capillary, D, just at the tip of the tantalum wire, and thereby controlling the intermittent heaters in the usual manner, through a thyratron tube. When a water (or solution) experiment is being carried out, the mercury fills the tube, B, and forms a layer about 1 cm. deep on the bottom of the dilatometer, A, with water (or solution) on top of this layer of mercury filling the rest of the volume of the dilatometer.

A tantalum wire is much better for the upper contact than platinum because tantalum is not wet by mercury. There is no tendency for a small drop of mercury to cling to the sharp point of the tantalum wire causing erratic regulation of the thermostat. For this reason tantalum is to be highly recommended for use in thermoregulators. The resistance of tantalum to hot nitric and sulfuric acids, which are used in cleaning the dilatometers, was tested, and the metal was found to be quite inert.

Filling the Dilatometers.—There are two different filling techniques. One is used in calibration experiments when the dilatometer is to be entirely filled with mercury. The other is used when the dilatometer is to be partly filled with water or solution. Since the standard on which all the changes in volume of the solutions are based is mercury, the first experiments dealt with this substance.

The stopcock, F, is greased with Dow-Corning silicone stopcock grease. During the first part of this research Fisher's Cellogrease was used, but the new silicone grease was found to be superior at higher temperatures. The empty dilatometer is weighed. Mercury is filtered through a sintered glass disk, and it then is allowed to run down through a long capillary tube which has been inserted through the bore of the stopcock, F. This capillary tube reaches very nearly to the bottom of the dilatometer. When the dilatometer is completely full, the capillary is withdrawn and a rubber tube is attached to the joint, E (Fig. 1). The position of the mercury in the tube, B, of the dilatometer is adjusted to a point slightly above the capillary, D, by increasing or decreasing the pressure through the rubber tube. After this adjustment the stopcock, F, is turned through an angle of 90°, thus closing off A completely, but connecting the bore of the stopcock and the tube above to the side outlet tube on stopcock, F. The excess mercury in the bore of the stopcock and in the tube above it is then removed. There should now be enough mercury in the dilatometer to establish the first thermal equilibrium at about 20°. The dilatometer is weighed on a large balance to the nearest milligram.

If a water run is to be conducted, the stopcock, F, is greased, mercury is placed in the wells, C and H, and the dilatometer is weighed. After weighing, 50 cc. of mercury is placed in the bottom of the dilatometer in the same manner as if the dilatometer were to be completely filled with mercury. The instrument is reweighed.

A special 500-cc. round-bottom flask is used to fill the dilatometer with water. To the bottom of this flask (Fig. 2) is sealed a stopcock, *n*, and below the stopcock is sealed a ground joint, h. The movable plug of the stopcock has a three-way bore. Thus, by facing the bore in a "T" position with respect to the ground joint, h, it is possible to evacuate the bore. On the neck of the flask is a large ground-glass joint, m. The inside diameter of this joint is about 2 cm. The neck of the flask is 20 cm. long, and the 500 cc. graduation mark is about 4 cm. above the body of the flask. The large diameter and length of the neck allows the water (or solution) in the flask to be boiled without liquid being splashed or carried by entrainment from the flask. A special stopper for the flask consists of a large ground glass joint fitting the one on top of the flask; a stopcock, e, is sealed on top of this joint, and above the stopcock is another ground glass joint, d.

This special flask is used in removing the dissolved gases from the water. The flask is connected at the joint, d, to a trap which is cooled externally by a "Dry Ice"-alcohol mixture which is in turn connected to a vacuum pump. Thus, when the stopcocks a, b, and e are opened, and c and e are closed, and tube p is plugged (Fig. 2) the water boils under reduced pressure, and that vaporized is caught in the trap. When the dissolved gases are expelled, the stopcock, e, is closed.

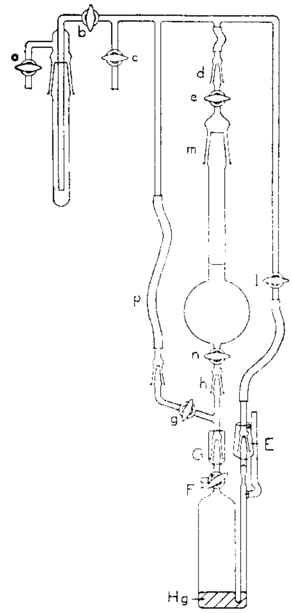

Fig. 2.—Mercury dilatometer and auxiliary apparatus assembled for filling with water or solution.

An extension tube is placed on the dilatometer at the joint, G (Fig. 1), and to the extension tube is attached the filling flask. The joint, E, of the dilatometer and the arm on the extension tube are attached to the vacuum line. The joints, G and E, of the dilatometer are not greased but are mercury sealed. The other joints are greased. The stopcocks, a and b, are closed, and g, l and F are opened. The vacuum supplied by a Langmuir mercury vapor diffusion pump backed by an oil pump is applied to the system by opening stopcock c. When the system is evacuated according to a McLeod gage, the stopcocks c, g and l are closed and n is slowly opened; the water flows into the dilatometer on top of the mercury.

As the water collects on the mercury, the mercury rises up into the tube, B (Fig. 1), of the dilatometer. The position of the mercury in B is adjusted to about 6 mm. above the top of the capillary by opening stopcock e slightly, thus applying pressure to the water in the filling flask. When the dilatometer is full and the position of the mercury above the capillary, D, is adjusted correctly, stopcock F is closed in such a manner that the bore is connected to the outlet tube. Full atmospheric pressure is then applied to the system by opening stopcocks c and l.

The mercury in the mercury seal cups of joints E and G and the water in the bore of the stopcock, F, are removed through the tube on the side of the stopcock barrel, and the apparatus is disassembled. The dilatometer is weighed.

If, instead of water, the dilatometer is to be filled with a solution, the filling procedure is the same except that the proper weighed amount of salt is dissolved in water in the flask. The solution is boiled under reduced pressure until the flask contains exactly 500 cc., and the solution is free of air. However, in the case of lanthanum chloride, because of the indefinite amount of water of crystallization in the salt, it is not possible to make solutions of known concentration by directly weighing the salt. The concentration can be determined by using the equation developed by Jones and Ray[9] giving the density in grams per milliliter at 25° as a function of concentration

$$d = 0.997074 + 0.229398c - 0.011911c^{3/2} \quad (5)$$

Since the density data are known from the experimental data of the authors, the above equation may be solved for c.

Operation of the Dilatometer.—After the dilatometer has been filled with mercury (or mercury and water or solution) it is clamped in a special brass frame. The dilatometer is then mounted in the thermostat and wires from the thyratron circuit are placed in the mercury wells, C and H (Fig. 1), so that the dilatometer acts as the thermoregulator.

In order that the substance whose coefficient of expansion is to be determined is at a standard pressure of one atmosphere, pressure adjustments are applied. The ground glass joint, E (Fig. 1), is attached to a manometer by means of a rubber tube. If the dilatometer contains only mercury, the air pressure on the mercury in the capillary D is adjusted to 760 mm. The pressure adjustment when mercury alone is in the dilatometer is really only a formality unless the barometric pressure is very high or very low. A pressure change of 34 mm. will change the temperature of the bath by only 0.001°. When there is solution or water in the dilatometer, a pressure change in barometric pressure of 2 mm. will cause the temperature of the bath to change by 0.001° and, therefore, the pressure adjustment must be applied much more carefully. There is a pressure on the water or solution in addition to atmospheric pressure due to the head of mercury in the tube B (Fig. 1). There is also an additional pressure caused by the capillary depression of the mercury. Thus the pressure on the dilatometer's contents must be decreased by the sum of the two amounts in addition to the proper compensation for the difference between the prevailing atmospheric pressure and 760 mm.

After the dilatometer has been placed in the thermostat, the thyratron circuit connected and the pressure adjusted, various thermostat controls (steady heater, intermittent heaters, cooling coils) are adjusted until the dilatometer comes to equilibrium at about 20°. Equilibrium is attained when the intermittent heaters in the thermostat go off and on quite rapidly and the temperature is constant within 0.001°. The temperature is then determined.

The equilibrium temperatures of the thermostat were determined with a 25 ohm four-lead platinum resistance thermometer, made by Leeds and Northrup, provided with a Bureau of Standards certificate giving the constants. The resistance of the thermometer was measured by means of a Mueller bridge (Leeds and Northrup). The bridge was calibrated by using a 10-ohm standard resistance calibrated by the Bureau of Standards. In addition to calibrating the Mueller bridge, the resistance of the thermometer at the ice-point must be determined. The ice-bath used was prepared in the manner recommended by Roper.[10] A table was compiled from these data giving the resistance of the thermometer at various temperatures. A change of 0.001° brings about a change in resistance of about 0.0001 ohm. This change can be reliability determined by the Mueller bridge.

After the first equilibrium temperature is determined, the dilatometer is placed in an auxiliary water-bath whose temperature is 31°. This will cause the mercury to expand up above the capillary, D. Weighed pipets of special design (Fig. 3) are used to withdraw mercury. The tip of a pipet reaches down through the joint E (Fig. 1) of the dilatometer to the mercury which has been expelled from the main volume of the dilatometer through the capillary, D. When a pipet has been inserted into the dilatometer, a ground glass joint attached to a rubber tube is fixed to the pipet at B (Fig. 3), and most of the mercury above the capillary of the dilatometer is sucked out of the dilatometer, through the tube A into the pipet. The slight bend in the main part of the pipet, D, is to slow down the descent of the mercury as it falls to the bottom of the pipet thereby minimizing the scattering of mercury droplets. The constriction C in the tube A of the pipet is to prevent the escape of any mercury drops remaining in A from the pipet.

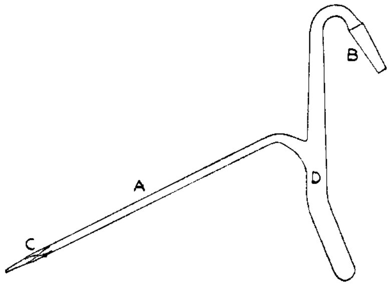

Fig. 3.—Pipet used for withdrawal and addition of mercury.

After the mercury has been withdrawn from the dilatometer, which is in the auxiliary bath, the dilatometer is returned to the thermostat and the thermostat comes to a new equilibrium temperature at about 30°. In the manner just outlined, readings are obtained at approximately 10° intervals from 20° to 60°. In the case of the earlier work on potassium chloride solutions, the observations were carried to 80°. After the dilatometer has been adjusted to regulate the bath at 60° (if this is the highest temperature), the pipets containing mercury are all weighed at once against a tare. In this manner the weights of mercury withdrawn from the dilatometer to produce each new temperature equilibrium are determined.

The procedure followed in going from higher temperatures to lower temperatures is but slightly different from the one used in adjusting the dilatometers on the "up run." After the highest equilibrium temperature has been determined, the dilatometer is placed in the auxiliary bath which is 5° warmer than the equilibrium temperature. The tip of the pipet containing the mercury withdrawn from the dilatometer in the last adjustment is placed below the surface of the mercury which has expanded above the top of the capillary, D, of the dilatometer. The pipet during this step is held in such a manner that the mercury in the bottom of the compartment D (Fig. 3) is undisturbed. The pipet is now rotated about the tube A as an axis until the main part, D, of the pipet is practically horizontal. The mercury in the pipet will run down the tube A into the dilatometer. The tip of the tube A is kept below the surface of the mercury to prevent splashing of drops of mercury. The dilatometer has now been adjusted to equilibrate at 50° (70° if the highest equilibrium temperature was 80° instead of 60°). In this way the "down run" is carried out in ten degree intervals down to 20°. As the pipets are emptied, they are again weighed. There are always a few milligrams of mercury remaining in each pipet. Therefore the tem-

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[9] Grinnell Jones and Wendell A. Ray, This Journal, **63**, 288 (1941).

[10] E. E. Roper, *ibid.*, **60**, 866 (1938).

peratures on the down run are not the same as on the up run.

Careful experiments were carried out to determine if there was any possibility that hysteresis of the glass might have introduced an error. The dilatometer was kept at a specific equilibrium temperature in the thermostat for an extended time, then immersed in either colder or hotter water, and kept in this auxiliary bath for several hours. Then the dilatometer was returned to the thermostat, and the same equilibrium temperature was very quickly obtained, thus demonstrating that hysteresis of the glass does not introduce an error.

Purification of Materials.—Mercury is purified by placing a small amount in a large beaker. Concentrated sulfuric acid is poured into it, and the mixture is stirred. The sulfuric acid is allowed to remain on top of the mercury for about half an hour, and it is then poured off. This treatment ensures that all of the Dow-Corning silicone stopcock grease will be removed from the mercury. The mercury is then thoroughly washed with water. The mercury is next allowed to fall in fine drops down a tower filled with 8% nitric acid solution.[11] After treatment in the tower, the mercury is distilled in a stream of air under reduced pressure according to the method of Hulett.[12] The distillate is then pinholed and redistilled. The redistilled mercury is pinholed into a clean storage bottle. Before using in the dilatometer, it is passed through a sintered glass disk to remove any particles of dust or traces of grease it may have picked up while standing in the laboratory.

The water used was conductivity water prepared in a Barnstead still. This water is free from dissolved materials except for air. The dissolved gases were removed by boiling under reduced pressure.

The potassium chloride was purified by recrystallization and fusion according to the method of Jones and Bradshaw.[13]

The barium chloride was purified by recrystallizing twice from an ethyl alcohol-water solution. The alcohol was purified by double distillation. The barium chloride was then further purified by a recrystallization from pure water. The barium chloride dihydrate obtained was dried at room temperature under a bell jar arranged in such a manner that circulation of dust-free air was permitted. After the barium chloride had dried in this manner for about a month, it was removed and ground up in a clean mortar and further dried for another month in the same manner. An analysis showed that the salt contained 14.799% water. The theoretical value is 14.752%. The experimentally obtained value was used in calculating the solution concentrations.

The lanthanum chloride was originally prepared by Professor Charles James[14] of the University of New Hampshire. It was purified by recrystallization from alcoholic hydrochloric acid using gaseous hydrogen chloride. It was then kept over solid sodium hydroxide to remove the excess solvent and hydrochloric acid.

Experimental Data

Mercury.—The dilatometers are first calibrated using mercury as a standard because (a) it is necessary to know the grams of mercury which must be withdrawn per gram of mercury in the dilatometer to raise the equilibrium temperature of the dilatometer one degree centigrade, and (b) it is necessary to know the coefficient of expansion of the Pyrex glass of which the dilatometers are made. Since the density of mercury has been determined at various temperatures in containers whose coefficient of expansion is very well known[15] the coefficient of expansion of the Pyrex can be calculated.

A sample data sheet obtained for one "up run" of dilatometer No. 1 is given in Table I. Column 1 gives the temperatures at which the equilibria were established. Column 2 gives the temperature difference, Δt, between each two successive equilibria. Column 3 gives the average temperature, t_{av}, of two successive equilibria. Column 4 gives the number of grams of mercury, ΔW, which are withdrawn to establish a new equilibrium. Column 5 is the total weight of mercury, W, in the dilatometer at the corresponding equilibrium temperature given in Column 1. Column 6 is the mercury factor, f_{Hg}, and is $\Delta W/W\Delta t$. The weight of mercury in Column 5 used to calculate f_{Hg} is that at the higher temperature. The use of the weight of mercury at the higher temperature may appear arbitrary but can be justified by an algebraic treatment of the method of calculating the ultimate results of the water and solution runs.

TABLE I

SAMPLE DATA SHEET FROM A MERCURY RUN

(1)	(2) Δt	(3) $t_{av.}$	(4) ΔW	(5) W	(6) f_{Hg}
20.048				3766.502_9	
	12.113	26.105	7.8098		0.0001715_3
32.161				3758.693_1	
	7.552	35.937	4.8567		$.0001713_2$
39.713				3753.836_4	
	8.878	44.152	5.6952		$.0001711_5$
48.591				3748.141_2	
	10.574	53.878	6.7619		$.0001709_2$
59.165				3741.379_3	

The mercury factor, f_{Hg}, expresses the grams of mercury withdrawn per degree centigrade per gram of mercury in the dilatometer at the higher temperature.

A linear equation relating f_{Hg} to t_{av} has been obtained for each of the two dilatometers using the method of least squares to evaluate the parameters. For dilatometer no. 1, the early equation (Taylor) used in connection with the potassium chloride solutions is

$$f_{Hg} = 0.0001719_4 - 0.000000017_4 t_{av} \quad (6)$$

For dilatometers 1 and 2, respectively, the equations (Vogel) used in calculating the barium chloride and lanthanium chloride data are

$$f_{Hg} = 0.0001721_3 - 0.0000000218_5 t_{av} \quad (7)$$

and

$$f_{Hg} = 0.0001719_4 - 0.0000000161_5 t_{av} \quad (8)$$

From an analysis of the data based on the differences between the observed values of f_{Hg} and those calculated by means of Equation (6), it is found that the probable error of a single observation is ±0.000000145. The probable error of a single observation for dilatometer no. 1 using Equation (7) is ±0.000000039, and for dilatometer no. 2 using Equation (8) it is ±0.000000114.

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(11) J. H. Hildebrand, THIS JOURNAL, **31**, 933 (1909); C. J. Moore, *ibid.*, **32**, 971 (1910).

(12) G. A. Hulett, *Phys. Rev.*, **33**, 307 (1911).

(13) Grinnell Jones and B. C. Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

(14) This material had been used by Grinnell Jones and C. F. Bickford, *ibid.*, **56**, 602 (1934).

(15) J. A. Beattie, B. E. Blaisdell, J. Kaye, H. T. Gerry and C. H. Johnson, *Proc. Am. Acad. Arts Sci.*, **74**, 371 (1941).

TABLE II

SAMPLE DATA SHEET FOR A WATER RUN[a]

(1) t°C.	(2) Δt	(3) t_{av}	(4) f_{Hg} at t_{av}	(5) W	(6) G. Hg expelled due to expansion of Hg	(7) ΔW	(8) G. Hg expelled due to expansion of H_2O	(9) f_w
19.513				676.5239				
	10.429	24.728	0.0001715_9		1.1944	9.0759	7.8815	0.003318_6
29.942				667.4480				
	10.288	35.086	$.0001713_7$		1.1558	11.8675	10.7117	$.004572_2$
40.230				655.5804				
	10.300	45.380	$.0001711_4$		1.1303	14.4021	13.2718	$.005658_3$
50.530				641.1783				
	9.908	55.484	$.0001709_2$		1.0588	15.9870	14.9282	$.006616_3$
60.438				625.1913				

[a] Wt. of water in dilatometer = 227.723_6 g.

The slight superiority of dilatometer no. 1 is believed to be due to the unavoidable difference in the shape of the capillary D at the point where the tip of the tantalum wire enters the capillary. Equations (7) and (8) cover a range of temperature from 25° to 55°, while Equation (6) covers a range from 25° to 75°. Since dilatometer no. 2 does not appear to function quite as well as dilatometer no. 1, the former was used for the more concentrated solutions where the experimental error is not as important. The values of f_{Hg} given in Table I were some of those used in arriving at Equation (7).

It is necessary to obtain the cubical coefficient of expansion, a, of the Pyrex glass of the dilatometer. An implicit definition of a is given by

$$V_t = V_{20}[1 + a(t - 20)] \qquad (9)$$

where V_t is the volume of the dilatometer at the temperature t°C., and V_{20} is the volume of the dilatometer at 20°. Since

$$V_t = W_t/d_t \qquad (10)$$

where W_t is the weight of mercury in the dilatometer and d_t is the density in grams per cc. of mercury at t°C., we get

$$\frac{W_t d_{20}}{d_t W_{20}} - 1 \Big/ (t - 20) = a \qquad (11)$$

If a calculation of a is to be made, d_{20}/d_t needs to be known for various temperatures. Accurate densities of mercury have been determined recently by Beattie, Blaisdell, Kaye, Gerry and Johnson.[15] After determining the apparent density of mercury in vitreous silica bulbs these investigators cut cross-sections from the bulbs and determined the coefficient of expansion of the silica by an interferometer method. They then corrected their data for the expansion of the silica.

In addition to d_{20}/d_t, W_{20} needs to be known. This was calculated by determining f_{Hg} for 20° from the equations relating f_{Hg} to t_{av}. Using this value of f_{Hg}, all the weights of mercury observed close to 20° were corrected to exactly 20°. The ratios, W_t/W_{20}, for each up and down run for both dilatometers were determined and hence a number of values of the coefficient of expansion of Pyrex glass, a, were obtained. These were averaged. Using the mercury calibration data obtained by R. C. Vogel in 1945 for dilatometers 1 and 2, a was found to be 0.00000966 for both instruments. Using the mercury calibration data of E. F. Taylor obtained in 1940 for dilatometer no. 1, a was found to be 0.00000968.

Saunders and Tool[16] found that the annealing temperature is the dominant factor in determining the coefficient of thermal expansion of Pyrex. Dilatometer no. 1 was annealed at 594° which should mean that a is 0.00000985 per degree centigrade, according to Saunders and Tool. Dilatometer no. 2 was annealed at 646° and thus should have a coefficient of expansion of 0.00001023 per degree centigrade. Our measurements do not support the idea that the coefficient of expansion of the Pyrex is controlled by the annealing temperature, at least within the range (594–646°) which we used. Moreover, trial calculations have shown that the same coefficient of expansion of Pyrex must be used for both dilatometers in order to get identical results for water.

Water.—Since the coefficient of expansion of water is needed to calculate the apparent molal expansibility of an electrolyte, it is necessary to make water runs with both dilatometers. It is also desirable to be able to compare the specific volumes of water at various temperatures calculated from our data with the best values obtained by other investigators.

A sample data sheet obtained for an up run for one of the dilatometers is given[17] in Table II. Columns 1, 2 and 3 have the same significance for the water data as for the mercury data. Column 4 gives the mercury factor, f_{Hg}, calculated at t_{av} using Equation (7). Column 5 gives the total weight of mercury in the dilatometer at t°C., the equilibrium temperature. Column 7 gives the weight of mercury withdrawn from the dilatometer to establish each new equilibrium temperature. Column 6 gives the grams of mercury expelled from the dilatometer in going from one equilibrium temperature to another due to the expansion of the mercury only. Column 8 shows

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(16) J. B. Saunders and A. Q. Tool, *Bur. Standards J. Res.*, **11**, 799 (1933).

(17) The complete data may be obtained from the Harvard University thesis, "Dilatometry of Mercury, Water, and Solutions of Electrolytes," by E. F. Taylor, pp. 101–108, and "Dilatometry of Mercury, Water, and Solutions of Electrolytes," by Richard C. Vogel, pp. 125–128, 130. Photostats can be obtained for a nominal fee by writing to Librarian, Department of Chemistry, Harvard University, Cambridge, Mass.

TABLE III

SPECIFIC VOLUMES OF WATER MEASURED BY VARIOUS INVESTIGATORS IN CUBIC CENTIMETERS PER GRAM

t°C.	Taylor dilatometer no. 1	Vogel dilatometer no. 1	Vogel dilatometer no. 2	Tilton and Taylor	"I. C. T."
20	(1.001796_6)	(1.001796_6)	(1.001796_6)	1.001796_6	1.001797_9
30	1.004368	1.004368	1.004369	1.004367_6	1.004369_3
40	1.007837	1.007840	1.007842	1.007840_5	1.007842_4
50	1.012098	1.012101	1.012103		1.01210
60	1.017074	1.017078	1.017079		1.01708
70	1.022718				1.02273
80	1.029000				1.02902

the grams of mercury expelled from the dilatometer due to the expansion of water alone and is obtained by subtracting Column 6 from Column 7. Column 9, the water factor f_W, is calculated by dividing Column 8 by Column 2 and by the weight of water in the dilatometer. It represents the grams of mercury expelled from the dilatometer per degree centigrade per gram of water.

By using Newton's method of non-linear interpolation, the water factors, f_W, have been determined at average temperatures, t_{av}, of 25, 35, 45, 55 and for part of the data, 65 and 75°.[2,3] When f_W is multiplied by the specific volume of mercury at the lower temperature of the interval over which f_W is calculated, the apparent change of the specific volume of water in Pyrex glass results. If to this apparent change in specific volume is added the change in specific volume due to the expansion of the Pyrex glass of the dilatometer, the true change in the specific volume over each ten-degree interval is obtained. Thus, to the specific volume at 20° of water, which is taken as a starting point, is added the true change in specific volume due to raising the temperature to 30°. This gives the specific volume at 30°. The specific volumes at other temperatures are calculated in the same manner. The specific volume of water at 20° is assumed to be 1.001796_6 cc. per gram. This is the value given by Tilton and Taylor[18] based on the excellent data of Chappuis.[19] The specific volumes of mercury in cc. per gram given by Beattie, Blaisdell, Kaye, Gerry and Johnson[15] are used. The results are given in Table III.

The integral coefficient of expansion of water at the average temperature of the temperature change in question can be obtained by dividing the change in specific volume by the specific volume of water at the average temperature and by the temperature change. Thus, if $\tilde{V}$ is the specific volume, the coefficient of expansion would be $\tilde{V}_{30} - \tilde{V}_{20} \div 10\ \tilde{V}_{25}$. Since the change in specific volume at best is known to about 0.01%, it is only necessary to know the specific volume at the average temperature, *i. e.*, $\tilde{V}_{25}$, to one part in ten thousand. A linear interpolation of specific volumes between round temperatures ten degrees apart may introduce an error of about one part in ten thousand. Thus, specific volumes calculated in this manner are sufficiently accurate for computing the coefficients of expansion of water and also of salt solutions. These are given in Table IV.

TABLE IV

INTEGRAL COEFFICIENTS OF EXPANSION OF WATER AND SOLUTIONS OF POTASSIUM, BARIUM AND LANTHANUM CHLORIDES IN RECIPROCAL DEGREES CENTIGRADE × 10^4

Molality	25°	35°	45°	55°	65°	75°
			Water			
0.0000[a]	2.5628	3.4515				
.0000[b]	2.5633	3.4491	4.2194	4.9047	5.5333	6.1235
.0000[c]	2.5632	3.4507	4.2198	4.9049		
.0000[d]	2.5647	3.4514	4.2189	4.9055		
			Potassium Chloride			
0.06022	2.6018	3.4705	4.2258	4.9018		
.06022	2.6038	3.4704	4.2268	4.8988		
.10053	2.6277	3.4842	4.2296	4.8985	5.5122	6.0850
.10053	2.6273	3.4851	4.2285	4.8984	5.5108	6.0837
.10064	2.6265	3.4881	4.2297	4.8974	5.5115	6.0843
1.0294	3.0798	3.7496	4.3281	4.8583	5.3513	5.8220
1.0308	3.1049	3.7513	4.3292	4.8592	5.3499	5.8240
1.0308	3.1063	3.7499	4.3309	4.8600	5.3516	5.8210
3.2731	3.6642	4.0365	4.3885	4.7238	5.0436	5.3579
			Barium Chloride			
0.01005	2.5718	3.4579	4.2196	4.9029		
.01005	2.5744	3.4562	4.2207	4.9020		
.06028	2.6409	3.4898	4.2299	4.8917		
.06028	2.6421	3.4887	4.2302	4.8926		
.10054	2.6921	3.5187	4.2389	4.8859		
.10054	2.6922	3.5194	4.2400	4.8856		
.25239	2.8776	3.6229	4.2782	4.8729		
.25239	2.8804	3.6192	4.2794	4.8719		
.50852	3.1581	3.7779	4.3434	4.8609		
.50852	3.1575	3.7788	4.3446	4.8587		
1.03382	3.6008	4.0410	4.4533	4.8436		
1.03382	3.5995	4.0425	4.4553	4.8409		
			Lanthanum Chloride			
0.06464	2.6108	3.4498	4.1826	4.8355		
.06464	2.6119	3.4521	4.1804	4.8360		
.09045	2.6337	3.4520	4.1688	4.8116		
.09045	2.6332	3.4525	4.1695	4.8116		
.16154	2.6850	3.4610	4.1384	4.7494		
.16154	2.6865	3.4597	4.1385	4.7502		
.36453	2.8242	3.4836	4.0638	4.6011		
.36453	2.8240	3.4835	4.0648	4.5991		
.70812	3.0060	3.5023	3.9601	4.3892		
.70812	3.0071	3.5045	3.9618	4.3854		
1.04320	3.1215	3.5023	3.8681	4.2172		
1.04320	3.1226	3.5040	3.8679	4.2161		

[a] Calculated from the data of Tilton and Taylor.[18] [b] Calculated from the results of E. Folger Taylor using dilatometer 1. [c] Calculated from the results of R. C. Vogel using dilatometer 1. [d] Calculated from the results of R. C. Vogel using dilatometer 2.

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(18) L. W. Tilton and J. K. Taylor, *J. Research Nat. Bur. Standards*, **18**, 205 (1937).

(19) P. Chappuis, Travaux et Mémoires du Bureau International des Poids et Mésures, **13**, d3 (1907).

Solutions of Potassium, Barium and Lanthanum Chlorides.—The data for solutions are treated in general in the same manner as those of water. In calculating the specific volume of the solution, the amounts of mercury and of solution in the dilatometer at exactly 40° (50° for potassium chloride solutions) are calculated by adding to the weight of mercury a correction term which compensates for the fact that weights of the contents of the instrument are known at temperatures slightly different from 40°. This correction term consists of the weight of mercury associated with the expansion of solution over the temperature interval between equilibrium temperature and exactly 40°, and a similar term for the expansion of mercury. The solution term is calculated by multiplying the weight of solution by the average value of the factors, f_S, at 35° and 45° (f_S is the same for solutions as f_W is for water) and by the difference between the equilibrium temperature and exactly 40°. The mercury term is calculated by multiplying the weight of mercury by the mercury factor, f_{Hg}, for 40° and by the same difference in temperature. Since the volume of the dilatometer and the specific volume of mercury are known at 40°, the volume of the solution is calculated easily.

After the specific volumes at 40° are calculated for each solution, the specific volumes at other temperatures are then computed by adding or subtracting the sum of the apparent change in volume of solution in Pyrex glass and the change in volume of the Pyrex glass from the value at 40°. The coefficients of expansion of solutions are calculated in exactly the same manner as they were for water. These are given in Table IV and plotted in Figs. 4, 5 and 6 against temperature.

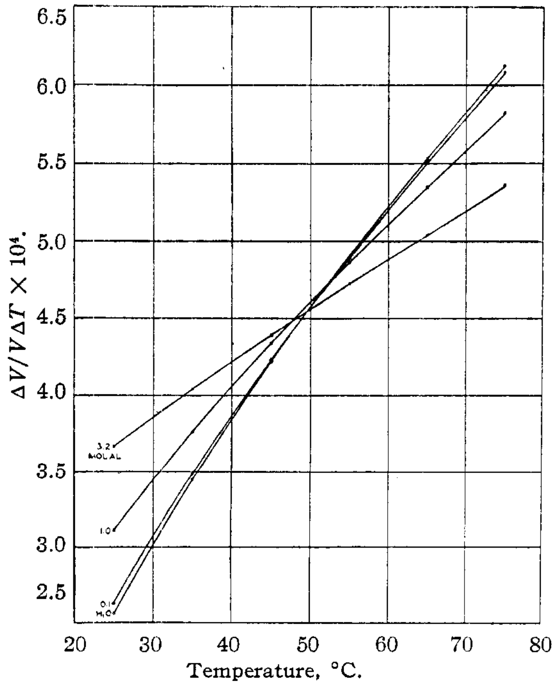

Fig. 4.—Coefficients of expansion of potassium chloride solutions plotted against temperature.

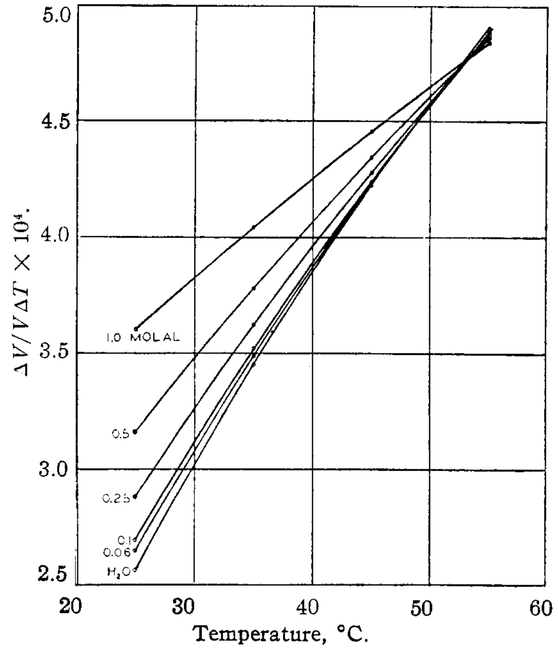

Fig. 5.—Coefficients of expansion of barium chloride solutions plotted against temperature.

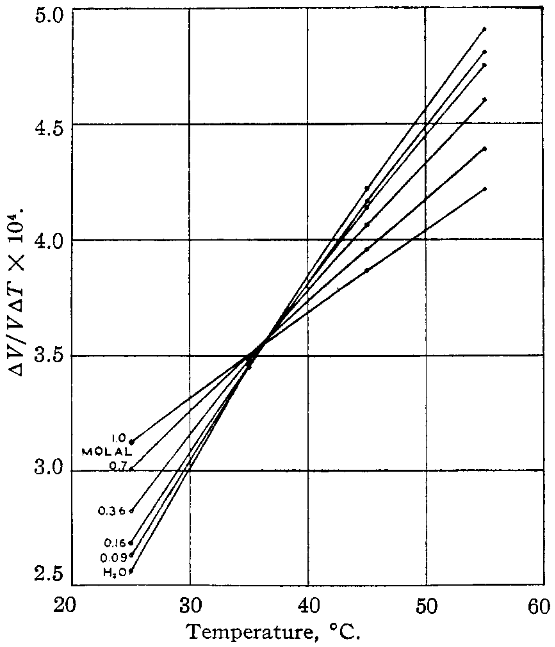

Fig. 6.—Coefficients of expansion of lanthanum chloride solutions plotted against temperature.

As previously mentioned, the concentrations of the lanthanum chloride solutions were determined from the solution densities obtained from the dilatometer data. It was decided that a linear interpolation of the specific volumes at 20° and

TABLE V

THE APPARENT MOLAL EXPANSIBILITIES OF POTASSIUM, BARIUM AND LANTHANUM CHLORIDES AT VARIOUS TEMPERATURES IN CC. PER MOLE PER °C.

25°		35°		45°		55°		65°		75°	
c	ϕE_2	c	ϕE_2	c	ϕE_2	c	ϕE_2	c	ϕE_2	c	ϕE_2
						KCl					
0.05994	0.0720	0.05976	0.0433	0.05953	0.0226	0.05926	0.0091				
.05994	.0753	.05976	.0431	.05953	.0243	.05926	.0041				
.09996	.0715	.09965	.0449	.09927	.0222	.09882	.0076	0.09831	−0.0003	0.09774	−0.0228
.09996	.0711	.09965	.0458	.09927	.0211	.09882	.0075	.09831	− .0077	.09774	− .0241
.10007	.0701	.09976	.0486	.09938	.0221	.09893	.0064	.09841	− .0072	.09784	− .0236
.99675	.0592	.99335	.0404	.98934	.0235	.98481	.0100	.97979	− .0021	.97434	− .0127
.99817	.0617	.99476	.0405	.99074	.0236	.98620	.0100	.98118	− .0022	.97571	− .0125
.99817	.0618	.99476	.0404	.99074	.0238	.98620	.0101	.98118	− .0020	.97571	− .0128
2.9562	.0454	2.9449	.0311	2.9325	.0195	2.9191	.0098	2.0049	+0.0012	2.8899	−0.0065
						$BaCl_2$					
0.01002	0.094	0.00999	0.082	0.00995	0.008	0.00990	−0.005				
.01002	.120	.00999	.065	.00995	.019	.00990	− .014				
.06001	.1364	.05982	.0749	.05959	.0287	.05932	− .0086				
.06001	.1383	.05982	.0731	.05959	.0292	.05932	− .0071				
.09998	.1356	.09967	.0776	.09928	.0310	.09883	− .0056				
.09998	.1357	.09967	.0783	.09928	.0321	.09883	− .0059				
.24993	.1328	.24912	.0788	.24814	.0356	.24700	+ .0012				
.24993	.1339	.24912	.0774	.24814	.0361	.24700	+ .0008				
.49987	.1259	.49814	.0756	.49612	.0376	.49338	+ .0059				
.49987	.1258	.49814	.0758	.49612	.0379	.49384	+ .0054				
.99989	.1113	.99608	.0698	.99185	.0369	.98725	+ .0093				
.99989	.1112	.99608	.0700	.99185	.0371	.98725	+ .0091				
						$LaCl_3$					
0.06437	0.0788	0.06418	0.0052	0.06393	−0.0503	0.06364	−0.0998				
.06437	.0805	.06418	.0088	.06393	− .0538	.06364	− .0995				
.0900	.0833	.0898	.0081	.0894	− .0486	.0890	− .0954				
.0900	.0828	.0898	.0087	.0894	− .0478	.0890	− .0954				
.1605	.0812	.1600	.0137	.1594	− .0422	.1587	− .0880				
.1605	.0821	.1600	.0129	.1594	− .0422	.1587	− .0875				
.3604	.0779	.3593	.0171	.3579	− .0334	.3564	− .0739				
.3604	.0779	.3593	.0171	.3579	− .0332	.3564	− .0745				
.6934	.0703	.6911	.0164	.6885	− .0265	.6857	− .0625				
.6934	.0705	.6911	.0168	.6885	− .0263	.6857	− .0631				
1.0107	.0623	1.0074	.0148	1.0037	− .0230	.9996	− .0551				
1.0107	.0624	1.0074	.0150	1.0037	− .0230	.9996	− .0552				

30° would not be accurate enough to obtain the specific volume at 25° in this case. The factor f_S is obtained for 27.5° for each solution. This is multiplied by 5°, the temperature interval, and by the specific volume of mercury at 25°. The coefficient of expansion of Pyrex was also multiplied by 5 and by the less accurate specific volume of the solution at 25° obtained by linear interpolation. The sum of these two corrections was subtracted from the specific volumes at 30° to give the specific volume at 25°. The concentration can then be obtained as previously described. This method was checked by calculating the specific volumes of barium chloride solutions from an equation giving the densities as a function of concentration derived by Jones and Ray.[20] These specific volumes checked with those obtained from the dilatometer data within a few parts per one hundred thousand, which shows that the method is sufficiently accurate.

Apparent molal expansibility of the salts may be calculated by means of Equation (1), and these are presented in Table V and plotted against $c^{1/2}$ at various temperatures in Figs. 7, 8 and 9. The value of the integral coefficient of expansion of water used at a given temperature to calculate ϕE_2 was determined by the dilatometer in which the particular solution was studied and the observer (Vogel or Taylor). The values of ϕE_2 for barium chloride are quite erratic when the concentration is as low as 0.01 molar. The reason for this is that at low concentrations the apparent molal expansibility represents the difference between two quantities which are almost identical. In order to obtain significant results for 0.01 molar solutions, the coefficients of expansion will have to be known ten times better than they are now known. The value of the apparent molal expansibility of the 0.06 molal lanthanum chloride solution at 25° appears to be in error. It is difficult to offer an explanation for this.

As has been previously mentioned, the coefficients of expansion obtained by our method of calculation are integral coefficients and not differential coefficients. Strictly speaking, the latter should be used in calculating the apparent molal expansibility. The molal expansibility as we have calculated it is

$$\phi E_2' = \frac{V_s}{\tilde{V}_s}\frac{\Delta \tilde{V}_s}{\Delta t} - \frac{\tilde{V}_w}{\tilde{V}_w}\frac{\Delta \tilde{V}_w}{\Delta t}$$

where $\tilde{V}_s$ and $\tilde{V}_w$ are the specific volumes of solu-

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[20] Grinnell Jones and Wendell A. Ray, THIS JOURNAL, 63, 288 (1941).

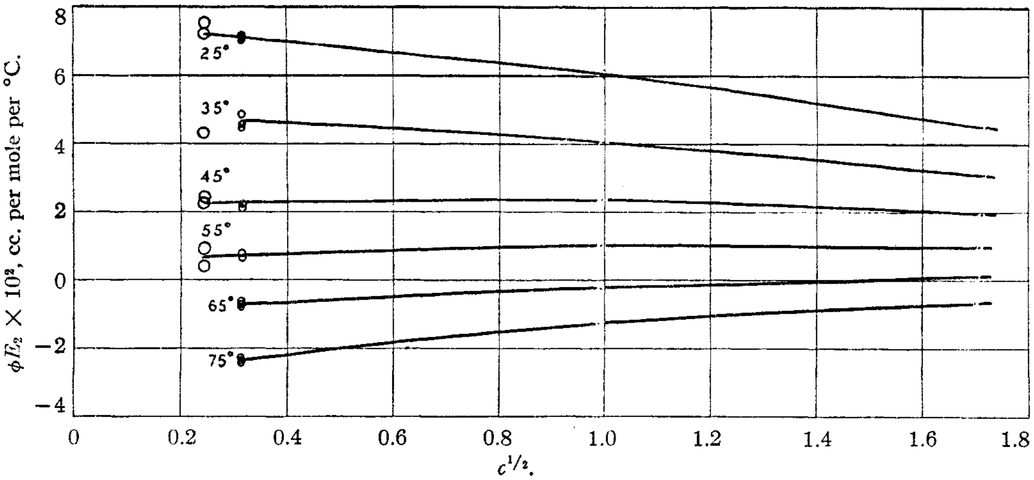

Fig. 7.—Apparent molal expansibility of potassium chloride plotted against $c^{1/2}$.

tion and water, V_s is the volume of solution containing a mole of solute and V_w is the volume of water used to make the solution. Let

$$\frac{\partial \bar{V}_s}{\partial t} = \frac{\Delta \bar{V}_s}{\Delta t} + x$$

$$\frac{\partial \bar{V}_w}{\partial t} = \frac{\Delta \bar{V}_w}{\Delta t} + y$$

Then if ϕE_2 is the true apparent molal expansibility, as defined by Equation (1)

$$\phi E_2 - \phi E_2' = W_w\,(x - y) + M_2 x$$

where W_w is the weight of water used to make the solution containing one mole of solute and M_2 is the molecular weight of the solute.

When $\bar{V}_{w,t} - \bar{V}_{w,25°}$ is plotted against temperature (Fig. 10) on the same graph with plots of $\bar{V}_{s,t} - \bar{V}_{s,25°}$ a rather remarkable fact becomes clear for many of the dilute solutions. These points fall approximately on the same curve. This means that

$$\frac{\partial \bar{V}_s}{\partial t} = \frac{\partial \bar{V}_w}{\partial t} \text{ and } \frac{\Delta \bar{V}_s}{\Delta t} = \frac{\Delta \bar{V}_w}{\Delta t}$$

which leads to the fact that for dilute solutions x equals y.

From the equation derived by Tilton and Taylor[18] giving the density of water as a function of temperature, the differential coefficients of expansion can be obtained.

$$\frac{1}{\bar{V}_w}\left(\frac{\partial \bar{V}_w}{\partial t}\right)_{25°} = 0.0002570_4 \text{ and } \frac{1}{\bar{V}_w}\left(\frac{\partial \bar{V}_w}{\partial t}\right)_{35°} = 0.0003456_5$$

Since the dilatometer data give $\frac{1}{\bar{V}_w}\,\frac{\Delta \bar{V}_w}{\Delta t}$, y can be determined. At 25° and 35° y is 5×10^{-7}.

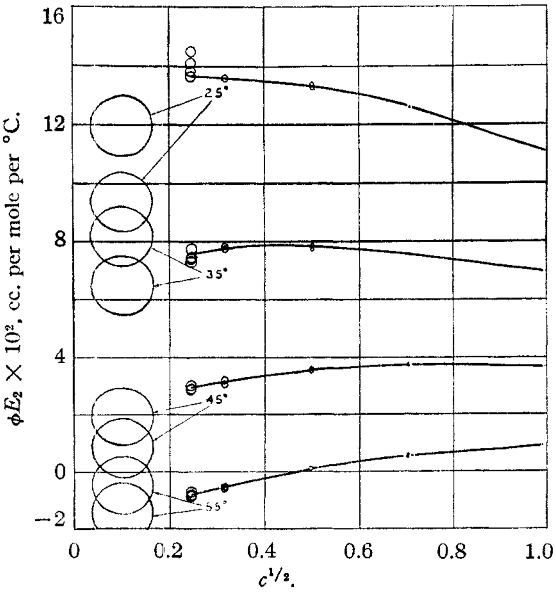

Fig. 8.—Apparent molal expansibility of barium chloride plotted against $c^{1/2}$.

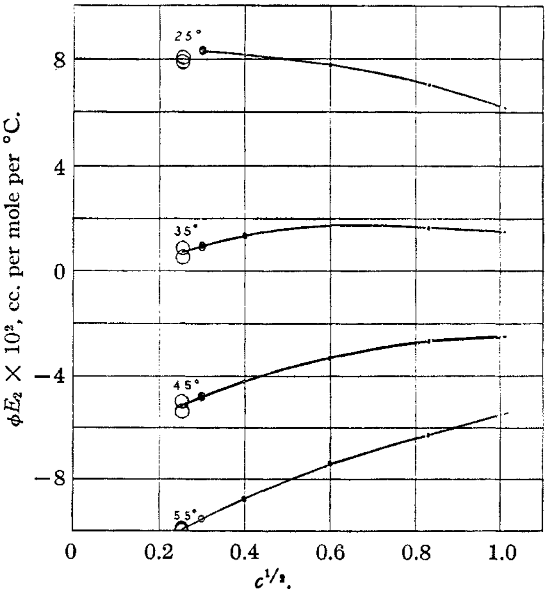

Fig. 9.—Apparent molal expansibility of lanthanum chloride plotted against $c^{1/2}$.

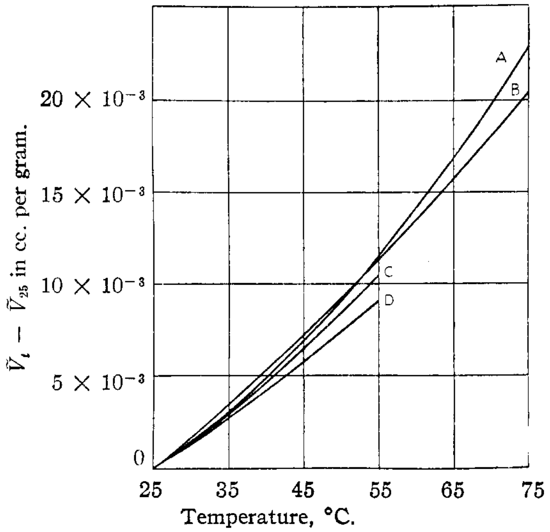

Fig. 10.—$\bar{V}_t - \bar{V}_{25°C.}$ plotted against temperature for water and solutions: curve A, water, 0.06 *M* KCl, 0.1 *M* KCl, 1 *M* KCl, 0.06 *M* $BaCl_2$, 0.1 *M* $BaCl_2$, 0.5 *M* $BaCl_2$, 1 *M* $BaCl_2$, 0.06 *M* $LaCl_3$ and 0.9 *M* $LaCl_3$; curve B, 3 *M* KCl; curve C, 0.36 *M* $LaCl_3$, curve D, 1 *M* $LaCl_3$.

This is also the value of x. Since as temperature increases the curvature of the plot of $\bar{V}_t - \bar{V}_{25°}$ decreases, the value 5×10^{-7} represents a maximum value of both x and y. Now $\phi E_2 - \phi E_2'$ can be calculated, and it is found that for lanthanum chloride, the salt of largest M_2, the error involved in using the integral coefficient instead of the differential coefficient of expansion would be only 0.0001 cc. per mole per degree. This treatment applies to 0.06, 0.1 and 1 *M* KCl solutions, to 0.06, 0.1 *M* $BaCl_2$ and very nearly to the 0.5 and 1 *M* $BaCl_2$ solutions. It also applies to 0.06 and 0.09 *M* $LaCl_3$ solutions.

A further analysis is needed in the case of the rest of the solutions. An extreme case is the 1 molar lanthanum chloride solution (Curve D, Fig. 10). This curve falls considerably below the curve for water, approaching a straight line. Thus x will tend to become zero. If we assume that x is zero, the error will be approximately $W_w y$ or 0.0005 cc. per mole per degree. The assumption that x is zero is an extreme one since it is quite obvious that the curve for 1 molar lanthanum chloride is still slightly curved. Although 0.0005 cc. per mole per degree is an appreciable error since it is applicable for concentrated solutions and could not possibly influence the shape of the curves of ϕE_2 plotted against $c^{1/2}$ it is clear that a more complicated treatment is not justified.

Discussion of Results.—A study of Figs. 4, 5, and 6, in which the coefficient of expansion of solutions of potassium chloride, barium chloride and lanthanum chloride are plotted against the temperature, show that in all cases, within the range of temperature studied, 20° to 60° (or 80°) and throughout the range of concentrations studied it is true that

$$\frac{\partial V}{V\partial t} > 0, \quad \frac{\partial}{\partial t}\left(\frac{\partial V}{V\partial t}\right) > 0, \quad \frac{\partial^2}{\partial t^2}\left(\frac{\partial V}{V\partial t}\right) < 0$$

At 25° all three salts studied have the effect of increasing the coefficient of expansion of water; $(\partial/\partial c)(\partial V/V\partial t) > 0$. For each salt there is a particular temperature at which the coefficient of expansion becomes independent of the concentration; $(\partial/\partial c)(\partial V/V\partial t) = 0$. In the case of potassium chloride solutions and of barium chloride solutions this temperature is about 52°, whereas for lanthanum chloride solutions it is about 37°. At higher temperatures $(\partial/\partial c)(\partial V/V\partial t) < 0$ in all cases. A qualitative explanation may be that at lower temperatures the introduction of the ions causes a change in the structure of the water (a depolymerization) so as to permit a closer packing, similar to the effect caused by raising the temperature. Then when the temperature of the solutions is raised there is less opportunity for this shift in structure and therefore less compensation for the normal thermal expansion.

Gucker's limiting equations (7 and 14) predict that, at low concentrations, the apparent molal expansibility ϕE_2, should (1) be a linear function of $c^{1/2}$; (2) the slopes $\partial\phi E_2/\partial c^{1/2}$ should be positive; (3) the slopes should increase greatly for salts of higher valence types. An examination of Fig. 7, 8 and 9 and Table V shows that (1) the curves are not linear for any of the salts, although approximately so for potassium chloride. (2) At 25° the slopes are negative throughout the range of concentrations studied, although a study of the curves indicates the possibility that if sufficient precision could be obtained at lower concentrations the slopes might become positive. Raising the temperature tends to increase the slopes and at 55° or above the slopes are all positive. (3) The great influence of the valence type, which is predicted by the theory does not seem to be supported by the curves.

It is therefore concluded that it is not possible to confirm these predictions from Gucker's equation at the concentrations which can be successfully studied experimentally. A substantial further increase in precision would be necessary to obtain significant data in solutions so dilute that they could be used with confidence to test the validity of a limiting law.

Summary

1. A new type of precision dilatometer which also serves as the thermoregulator of its own thermostat is described.
2. The new instrument has been used to determine the thermal expansion of water over the interval from 20° to 80°. Values for the specific volume of water at ten-degree intervals have been computed from these data.
3. Coefficients of expansion of aqueous solutions of potassium chloride ranging in concentration from 0.06 to 2.9 molal have been mea-

sured at ten-degree intervals from 25° to 75°.

4. Coefficients of expansion of aqueous solutions of barium chloride and of lanthanum chloride ranging in concentration from 0.06 to 1 molal have been determined at ten-degree intervals from 25° to 55°.

5. The apparent molal expansibilities of potassium chloride, barium chloride and lanthanum chloride in aqueous solutions have been calculated and their significance in relation to Gucker's theoretical equations is discussed.

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Conductivities of Quaternary Ammonium Chlorides Containing Two Long-chain Alkyl Groups

BY A. W. RALSTON, D. N. EGGENBERGER AND P. L. DU BROW

The concentration of colloidal electrolyte at the critical point for micelle formation has repeatedly been shown to decrease with increase in the chain length of the colloidal electrolyte. That this is true for the cationic colloidal electrolytes has been shown by a comparison of the equivalent conductivities of the alkylammonium chlorides of varying chain length[1] and of several of the alkyltrimethylammonium bromides.[2] It has recently been observed[3] that the position of the critical point is not materially influenced by the substitution of short-chain hydroxyalkyl groups for methyl groups in the higher alkyltrimethylammonium chlorides. The opinion has previously been expressed by Hartley[4] that the critical concentration is more dependent upon the chain length than upon the nature of the ionized groups. On the other hand, compounds which form two long-chain ions, such as octyltrimethylammonium octanesulfonate[5] and 1,1-dimethyl-3-hydroxybutylammonium caprylate,[6] form micelles at much lower concentrations than compounds which yield only one of the single long-chain, component ions. When we consider the long-chain alkyltrimethylammonium chlorides it appears that, although the replacement of methyl groups by other short-chain groups may not decidedly influence the electrical behavior, if a methyl group is replaced by a radical the chain length of which is comparable with that of the original long chain, such a substitution should be attended by a decided change in the conductivity values. We have, therefore, determined the equivalent conductivities of aqueous solutions of dioctyl-, didecyl-, didodecyl-, ditetradecyl-, dihexadecyl- and octyldodecyl-dimethylammonium chlorides and have compared the results with those obtained for several of the higher alkyltrimethylammonium chlorides. The comparisons have shown that significant differences exist between the conductivity behaviors of the higher dialkyldimethylammonium chlorides and those of the alkyltrimethylammonium chlorides. This comparison suggests that with the former the total number of carbon atoms in the long chains is determinative as regards their conductivity characteristics.

Experimental

Preparation of Dioctyl-, Didecyl-, Didodecyl-, Ditetradecyl- and Dihexadecyldimethylammonium Chlorides.—All the quaternary ammonium chlorides were similarly prepared. The preparation of didodecyldimethylammonium chloride will be described in detail as an example of the procedure employed.

Predistilled dodecylamine was carefully fractionated through a Stedman-packed column. In a two-necked flask fitted with a mercury-sealed stirrer and an air condenser, 212 g. of this distillate (f. p. 28.26°) and 8.5 g. of 50% Raney nickel suspended in dodecylamine were heated with stirring at 200° for two and one-half hours. The resulting product was taken up in ethyl acetate, the Raney nickel removed by filtration, and the didodecylamine crystallized from the solvent.

To 77 g. of the recrystallized didodecylamine dissolved in 200 cc. of ethanol, 49 cc. of 85% formic acid was slowly added, the temperature being maintained at about 40°. After this addition, 46 cc. of a 36% aqueous formaldehyde solution was added and the temperature raised to 60°. After the evolution of carbon dioxide had subsided, the temperature was maintained at the reflux point for one-half hour. The solution was then neutralized with aqueous sodium hydroxide, and the top layer was drawn off, dried over anhydrous potassium carbonate, filtered, and distilled (b. p. 183° at 0.35 mm.). The didodecylmethylamine so obtained (f. p. 10.4°) was dissolved in ethyl acetate, methyl chloride was added, and the mixture was heated in a bomb at 80° for one hour. The didodecyldimethylammonium chloride was recrystallized twice from ethyl acetate to give a white, crystalline, hygroscopic product. Dioctyldimethyl- and didecyldimethylammonium chlorides are extremely hygroscopic. This property was not observed with ditetradecyldimethyl- and dihexadecyldimethylammonium chlorides. The freezing points of the intermediate methyldialkylamines are as follows: methyldioctyl-, −30.1°; methyldidecyl-, −7.4°; methylditetradecyl-, 26.0°; and methyldihexadecylamine, 36.5–37.5°.

Preparation of Octyldodecyldimethylammonium Chloride.—To 102 g. of dodecyl chloride dissolved in 50 cc. of ethanol was added 38.7 g. of methylamine and the solution was heated in a bomb at 125° for eight hours. The contents of the bomb were neutralized with aqueous sodium hydroxide, the top layer dissolved in Skellysolve F, dried over anhydrous potassium carbonate, filtered, and the methyldodecylamine distilled. To 64 g. of distillate was added 56.3 g. of freshly distilled octyl bromide and the mixture was heated at 90° for five hours. One-half of the

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(1) Ralston and Hoerr, THIS JOURNAL, **64**, 772 (1942).

(2) Scott and Tartar, *ibid.*, **65**, 692 (1942).

(3) Ralston and Eggenberger, *ibid.*, **69**, 2095 (1947).

(4) Hartley, *Kolloid-Z.*, **88**, 22 (1939).

(5) Scott, Tartar and Lingafelter, THIS JOURNAL, **65**, 698 (1943).

(6) Gonick, *ibid.*, **68**, 177 (1946).