differences in the adsorption data for the two gases. All of our data on rates of reaction were obtained by measuring change of pressure with time. Because changes in pressure effect changes in the activation energies of adsorption processes,[12] no attempt has been made to calculate activation energies from the velocity curves. It is highly desirable to procure velocity data at constant pressure using a method for pressure control during the adsorption in the low pressure region (0 to 2 mm.).

Autocatalytic Adsorption at −78°.—One other example of autocatalytic adsorption has been observed previously by Benton and White[13] for hydrogen on iron at 0°. In these cases of autocatalytic adsorption the gas is apparently more readily adsorbed on those portions of the surface which are adjacent to atoms or molecules already adsorbed. There is little doubt that the adsorption of either hydrogen isotope on copper at −78°, which we have found to be autocatalytic, is of the activated type.[14] This possibility of an autocatalytic activated adsorption process presents a complicating factor which must be considered in connection with any adsorption theory of catalysis.

Summary

1. Very definite and complex differences have been found between the adsorptions of light and heavy hydrogen on active copper at low pressures (0 to 2 mm.).

2. At −78° the rate of adsorption is less for deuterium than for hydrogen, but equal amounts of the two isotopes are adsorbed at equilibrium.

3. In the temperature interval 0 to 125° the ratio H_2/D_2 adsorbed undergoes an inversion, hydrogen being more strongly adsorbed at the lower temperatures and less strongly at the higher temperatures.

4. The differential heats of adsorption have been measured by a direct calorimetric method, and are identical for the two isotopes within the limits of experimental error.

5. The early rate of adsorption of hydrogen at −78° is autocatalytic. The same is true for deuterium.

AMHERST, MASS. RECEIVED JUNE 28, 1935

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[12] Taylor and Strother, THIS JOURNAL, **56**, 586 (1934).

[13] Benton and White, *ibid.*, **54**, 1820 (1932).

[14] At −78° the adsorption proceeded at a measurably slow rate and the residual pressure, even after the third increment of gas, was less than 10^{-3} cm. Both these observations together with evidence not detailed here, indicate activated adsorption. See also Benton and White, *ibid.*, **53**, 3304 (1931).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Coefficient of Expansion of Silver Iodide and of the Halides of Thallium

BY GRINNELL JONES AND FREDERIC C. JELEN

Introduction

Silver iodide has been reported to have a negative cubical coefficient of expansion. Since this property is almost unique it seemed desirable to test the reliability of the reports by a new experimental method and to measure the expansion of several analogous salts in the hope that another similar case might be found. In this paper data on silver iodide and the halide salts of thallium are reported.

The coefficient of expansion of silver iodide was determined many years ago by Fizeau,[1] and by Rodwell[2] with very discordant results, although both agree as to the negative sign.[3] Fizeau, using an optical interference method, obtained agreeing results on a cylinder which had been previously fused and therefore consisted of closely packed crystals and on precipitated silver iodide which was compressed into a cylinder. He found the cubical coefficient to be -4.1×10^{-6} at a mean temperature of 40°. A single large crystal gave -2.7×10^{-6}. Rodwell who measured the cubical coefficient by a dilatometer method obtained a much larger value, namely -55.7×10^{-6} between 21 and 67°. Klemm, Tilk and v. Müllenheim,[4] using a dilatometer method have found the cubic coefficient of expansion from 20 to 120° of thallous chloride to be 1.68×10^{-4}, and of thallous bromide to be 1.72×10^{-4}.

Outline of the Principle of the New Method.—Our method was suggested by the Richards[5]

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[1] H. Fizeau, *Pogg. Ann.*, **132**, 292 (1867).

[2] G. F. Rodwell, *Chem. News*, **31**, 5 (1875).

[3] Grinnell Jones, THIS JOURNAL, **31**, 191 (1909).

[4] W. Klemm, W. Tilk and S. v. Müllenheim, *Z. anorg. allgem. Chem.*, **176**, 1 (1928).

[5] T. W. Richards and W. N. Stull, *Publ. Carnegie Inst. Wash.*, No. 7 and No. 76; T. W. Richards and Grinnell Jones, THIS JOURNAL, **31**, 158 (1909).

method for the determination of the compressibility of solids and liquids, which it resembles in principle. The glass dilatometer is first weighed and then filled with mercury and the exact temperature needed to bring the mercury meniscus to a reference mark in a capillary tube is determined. Then a weighed drop of mercury is added and a new lower temperature determined which will bring the greater quantity of mercury to the same reference mark. This step may be repeated as often as is desired until the range of temperature to be studied has been covered. The total weight of mercury present is then found by weighing the dilatometer and its contents. It is evident that these data permit a computation of the difference between the coefficient of expansion of mercury and of glass per gram of mercury and per degree centigrade averaged over each temperature interval used in the experiments. Then a large part of the mercury in the dilatometer is replaced by a known weight of some other solid or liquid substance and the measurements repeated. By taking the difference between these series of measurements the effect of the variation in volume of the glass dilatometer is eliminated and the result is the difference between the cubical coefficient of expansion of the solid or liquid under investigation and that of an equal volume of mercury. The cubical coefficient of expansion of mercury,[6] which is known more precisely than that of any other substance (with the possible exception of water) may then be added to this experimental result to give the coefficient of expansion of the solid or liquid.

The principle of the method is simple and direct, but mercury does not wet most solids so it is necessary to have present a small amount of some wetting liquid. The necessity of determining the amount of wetting liquid present complicates the procedure and diminishes the precision of the result. Toluene was chosen for the wetting liquid because it does not dissolve any of the salts to be investigated and its boiling point and volatility are suitable for the purpose. Its coefficient of expansion was of course determined separately in our dilatometer.

Another novel feature of our method is that the dilatometer serves also as a thermo-regulator and automatically adjusts its own temperature so that the dilatometer is completely filled to the reference mark. This feature contributes greatly to the convenience of the experimentation and the precision of the final result.

Experimental

The dilatometer, which is shown in Fig. 1(D), was made of Pyrex glass and had an internal diameter of 2 cm. and a volume up to the point, P, of about 60 cc. It had two pieces of platinum, P and Q, extending into side tubes as shown in the figure. A little mercury in the side tubes served to make electrical contact and to make the platinum seals gas-tight. The stiff platinum rod P has a sharp point which is located in the center of the capillary at the height where it commences to flare. It will be sufficiently obvious from the figure that when the dilatometer is filled with mercury in whole or part it will also serve as a regulator and automatically adjust the temperature of a thermostat in which it is immersed so that it will be completely filled up to the tip of the pointed platinum rod, P.

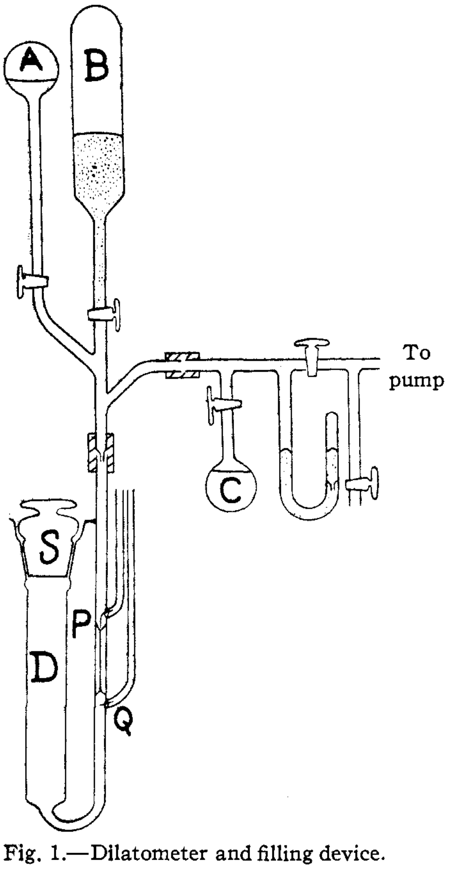

Fig. 1.—Dilatometer and filling device.

In order that the location of the stopper, S, should be as definite and reproducible as possible it was made with somewhat greater taper than the standard grindings and was rotated to a standard position by the aid of suitable guide marks. Our experience showed that determinations of the total volume were reproducible within 0.02 cc., which is sufficiently precise. It is of much greater importance that the stopper should not move vertically with reference to the jacket during a series of measurements. It was found impossible to get the desired precision without

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(6) "Smithsonian Physical Tables," 1923, 7th ed., p. 121.

the use of a sealing compound which is solid at the highest temperature used in the measurements (about 60°).

When toluene is used as a wetting liquid, organic waxes or resins are excluded on account of their solubility. Having found that anhydrous metaphosphoric acid may be used, a suitable quantity of molten metaphosphoric acid was placed on the upper part of the grinding of the stopper where it immediately froze. The stopper was then inserted into the dilatometer (either empty or containing a weighed amount of salt) and the upper part of the instrument heated in a free flame until the acid melted, whereupon the stopper was pressed into place and then on cooling the metaphosphoric acid froze and held the stopper completely immobile during the experiment. To prevent solution of the metaphosphoric acid in the water of the thermostat melted "arochlor" (Swann Chemical Company) was poured into the annular channel above the ground glass joint. Arochlor is sufficiently stiff at 60° and insoluble in water and adheres to glass so it served its purpose well.

A good grade of thallous nitrate was twice recrystallized. Iodine was purified by distillation from a solution of an iodide, washed and converted into hydriodic acid by reaction with yellow phosphorus and water, and the resulting hydriodic acid distilled twice. Dilute solutions of thallous nitrate and of hydriodic acid (in excess) were mixed and the precipitated thallous iodide washed repeatedly. The salt was then fused in a Pyrex test-tube and allowed to solidify from the bottom upward. There were a few minute cracks in the material which toluene could penetrate but mercury could not. The other salts were prepared by a similar procedure. Thallous bromide and thallous iodide were prepared by the addition of ammonium bromide and hydrochloric acid solutions, respectively, to thallous nitrate solutions. Silver iodide was precipitated from a nitrate solution by the addition of a potassium iodide solution.

Since the coefficient of expansion of gases is very great in comparison with liquids and solids it is necessary to fill all of the space in the dilatometer not occupied by salt with mercury or with toluene and without any air bubbles. This was accomplished by the device shown in Fig. 1. After the salt had been placed in the dilatometer, the stopper frozen in place and the contents weighed, it was connected to the filling device by a stout rubber connection as shown. All air had been removed completely from the bulbs A, B, C in advance. The air in the dilatometer was replaced by toluene vapor by alternately exhausting and opening the cock of bulb C. This was repeated about a dozen times, thus removing the air completely. Then about a gram of liquid toluene was run into the dilatometer by opening the cock of bulb A, followed by opening the cock of bulb B to admit sufficient mercury to seal the lower bend in the dilatometer. The liquid toluene in the narrow arm of the dilatometer was then evaporated. More mercury was added, thus completely filling the dilatometer. During this process the layer of toluene on top of the mercury rises and wets every particle of salt. The filling was not considered a success unless there was a slight surplus of liquid toluene visible under the stopper and no air bubbles were present. The dilatometer was then separated from the filling device. The capillary in the dilatometer was cleaned by treatment in succession with nitric acid, water, and acetone, followed by evaporation of the acetone. The amount of mercury was adjusted until it would fill the instrument at approximately 60°, and the total weight of the instrument and contents was determined. The dilatometer was then placed in the thermostat where it functioned as a thermostat regulator and adjusted its own temperature until the mercury meniscus came exactly to the platinum tip, P. A thyratron tube was used instead of the usual electromagnetic relay.

The proper amount of mercury to require a lowering of about 10° in the temperature was then weighed out and added to the dilatometer, which again functioned as a regulator and established a new lower temperature of about 50°, which was read as before. In a similar manner readings were taken at about 40, 30 and 20°.

Then without disturbing the stopper the bulk of the mercury and toluene were removed into a weighed Pyrex dish. The toluene remaining inside the dilatometer was removed by evaporation at room temperature by repeatedly exhausting and admitting air. The dish was placed in a vacuum desiccator and the toluene removed in a similar manner. The loss in weight gives the weight of toluene.

TABLE I

DATA OF TYPICAL EXPERIMENT ON CHANGE IN VOLUME OF PYREX DILATOMETER

T, °C.	Mercury added, g.	Round T, °C.	Mercury required for 10° depression, g.	Spec. vol. mercury cc./g.	ΔV_D, cc.	$(\Delta V_D/V_D) \times 10^6$
59.80_7	1.4102	60	1.443_0	0.0743592	0.0246_2	$392._3$
50.03_4	1.4670	50	1.446_9	.0742250	$.0184_2$	$293._5$
39.89_5	1.4359	40	1.451_6	.0740910	$.0123_0$	$195._9$
30.00_3	1.4575	30	1.453_9	.0739571	$.0062_1$	$99._0$
19.97_8		20		.0738233	0	0

Weight of mercury filling dilatometer at 59.807° = 844.32 g.

Results on Pyrex Glass.—The data of one typical experiment with mercury alone in the dilatometer are given in sufficient detail in Table I to permit a judgment in regard to the factors which control the precision of the results and to make clear how the data are interpreted. The results of other similar experiments are given only in a summarized form in Table II.

In this experiment it was found that when the dilatometer contained 844.32 g. of mercury (corrected to vacuum) it was completely full up to the point P at 59.80_7°. Then 1.4102 g. of mercury was added which required a drop in temperature to 50.03_4°, to permit the extra mercury to enter the instrument. Then in succession the several amounts of mercury shown in column 2 were added and the equilibrium temperature after each addition of mercury is shown on the line below in the first column. The weights of mercury which would have been required for successive drops of exactly 10°, assuming that the initial temperature had been exactly 60°, are shown in column 4. The weight of mercury required to fill the dilatometer at each ten-degree interval is easily computed from these data. By using the known values for specific volume of mercury given in column 5, the volume at each temperature may be computed. The increase in volume of the dilatometer from 20°, ΔV_D, is shown in column 6. The total expansion per cubic centimeter of dilatometer at 20° is given in column 7. This is of course a measure of the expansion of Pyrex glass.

TABLE II

SUMMARY OF CHANGES IN VOLUME OF PYREX DILATOMETER FROM 20° TO t° PER CC. OF VOLUME AT 20°. $\Delta V/V_{20} \times 10^6$

	Temp., °C.				
	20	30	40	50	60
	0	99.0	195.9	293.5	392.3
	0	100.5	198.7	296.2	393.8
	0	98.5	197.7	294.4	393.9
	0	99.4	196.2	291.5	389.9
	0	98.3	198.9	297.7	396.3
Average	0	99	197	295	393

The equation $V_t = V_{20}[1 + 9.85 \times 10^{-6}(t - 20)]$ agrees with these results within the experimental error. These experiments therefore give $9.8_5 \times 10^{-6}$ as the cubical coefficient of expansion of Pyrex glass over the range from 20 to 60°. The linear coefficient of expansion of Pyrex glass is given in the "International Critical Tables" on the authority of the Corning Glass Company as 3.2×10^{-6} over the range 19 to 350°. This corresponds to a cubical coefficient of 9.6×10^{-6}.

TABLE III

SUMMARY OF EXPERIMENTS ON EXPANSION OF TOLUENE

The volume of toluene at the temp., t, divided by its volume at 20°: $V_{T,t}/V_{T,20}$.

	Temp., °C.				
	20	30	40	50	60
	1.00000	1.01089	1.02208	1.03362	1.04552
	1.00000	1.01086	1.02206	1.03358	1.04547
	1.00000	1.01086	1.02204	1.03356	1.04545
	1.00000	1.01087	1.02205	1.03358	1.04545
Av.	1.00000	1.01087	1.02206	1.03359	1.04547
Comp.	1.00000	1.01086	1.02206	1.03359	1.04546

Results on Toluene.—Four complete experiments were carried out in which the dilatometer contained toluene for about three-fourths of its volume. The results are summarized in Table III.

The figures given in Table III are the volumes which 1 cc. of toluene measured at 20° would occupy at the temperatures specified at the top of the columns. These results may be expressed within the limit of error of the experiments by the equation $V_t = V_{20}[1 + 0.001069(t - 20) + 0.00000169(t - 20)^2]$ as shown in the last line of Table III. The true coefficient of expansion dV/Vdt, at any temperature is readily found by differentiation of the above equation. The values are as follows: 20°, 0.001069; 30°, 0.001091; 40°, 0.001112; 50°, 0.001133; 60°, 0.001151.

Results on Salts.—The data for one typical experiment on a salt are given in sufficient detail in Table IV to permit a judgment of the factors which control the precision of the results, and the results of the other experiments are given only in summarized form in Table V. In our first experiment with thallous bromide, the dilatometer contained 229.51 g. of thallous bromide, 1.09 g. of toluene and, when completely filled at 20°, it contained 391.68 g. of mercury. The volume of the dilatometer at 20° was 60.994 cc., of which 1.09/0.866 = 1.259 cc. was occupied by toluene; and 391.68 × 0.0738233 = 28.915 cc. was occupied by mercury. The volume of the thallous bromide was therefore 60.994 − 1.259 − 28.915 = 30.820 cc. The significance of the first four columns will be sufficiently obvious by analogy with Table I. The change in volume of the dilatometer is computed from our special experiments with mercury alone in the instrument. Column 6 gives the change in volume of the mercury present. The seventh column gives the change in volume of the toluene which is computed from the weight of toluene and its coefficient of

TABLE IV

DATA ON TYPICAL EXPERIMENT WITH THALLOUS BROMIDE

T, °C	Mercury added, g.	Round T, °C	Mercury added for 10° dep., g.	ΔV_D	ΔV_{Hg}	ΔV_T	ΔV_S	$V_{S,t}/V_{S,20}$
59.79_2	1.4256	60	1.464_9	+0.02404	−0.22284	+0.05724	+0.18964	1.00615_3
50.06_0	1.4886	50	1.455_8	.01805	− .16589	.04227	.14167	1.00459_7
39.83_5	1.4280	40	1.452_1	.01214	− .10993	.02777	.09430	1.00306_0
30.00_1	1.4475	30	1.446_8	.00608	− .05459	.01369	.04698	1.00152_4
19.99_6		20						1.00000_0

Weight of thallous bromide used, 229.51 g. Weight of toluene, 1.09 g. Weight of mercury at 20°, 391.68 g.

TABLE V

SUMMARY OF EXPERIMENTAL DATA ON THE EXPANSION OF SOME SALTS

Salt		Comparative volumes at °C. 20	30	40	50	60
AgI		1.000000	1.00000_0	0.99999_8	0.99998_5	0.99997_2
AgI		1.000000	0.99999_4	$.99997_9$	$.99996_6$	$.99993_7$
AgI		1.000000	$.99999_2$	$.99997_9$	$.99995_4$	$.99993_2$
AgI		1.000000	$.99998_8$	$.99996_7$	$.99993_9$	$.99990_3$
AgI	Av.	1.000000	0.99999_3	0.99998_1	0.99996_1	0.99993_6
TlI		1.000000	1.00135_0	1.00271_0	1.00407_0	1.00544_7
TlI		1.000000	1.00135_0	1.00268_0	1.00403_6	1.00540_4
TlI		1.000000	1.00135_4	1.00269_9	1.00405_1	1.00541_8
TlI		1.000000	1.00135_2	1.00270_2	1.00405_6	1.00542_4
TlI	Av.	1.000000	1.00135_2	1.00269_9	1.00405_3	1.00542_3
TlBr		1.000000	1.00152_4	1.00306_0	1.00459_7	1.00615_3
TlBr		1.000000	1.00152_5	1.00304_9	1.00460_2	1.00615_1
TlBr	Av.	1.000000	1.00152_5	1.00305_5	1.00460_0	1.00615_2
TlCl		1.000000	1.00157_9	1.00316_8	1.00477_0	1.00638_2
TlCl		1.000000	1.00158_7	1.00318_0	1.00478_7	1.00640_9
TlCl	Av.	1.000000	1.00158_3	1.00317_4	1.00477_9	1.00639_6

expansion already determined. It is obvious that the change in volume of the salt $\Delta V_S = \Delta V_D - \Delta V_T - \Delta V_{Hg} = +0.04698$. Column 9 gives the volume of the salt at temperature, *t*, relative to the volume at 20°; $(V_S + \Delta V_S)/V_S = V_{S,t}/V_{S,20} = (30.820 + 0.04698)/30.820 = 1.00152_4$.

The experimental error in the determination of the weight of mercury required to be added for each ten-degree interval may be as much as 0.1% since the error in measuring this interval may be as much as 0.01°. Errors in temperature, however, are not cumulative. In this experiment an error of 0.1% in the weight of mercury for a change of 10°, will cause an error of 0.00011 cc. in the ΔV_{Hg} and hence in ΔV_S. On the other hand, an error of as much as 0.8 g. in the total weight of mercury present would be required to cause an equally great error (0.00011 cc.) in ΔV_{Hg} but since the weight of mercury can be determined within about a centigram the error from this cause is negligible. Further, an error of 0.01 g. in weight of toluene used would make an error of 0.00013 cc. in ΔV_T and therefore in ΔV_S. It is evident that great care must be taken in the determination of the weight of toluene and the unavoidable error in finding the weight of toluene used is probably the greatest single source of error in the final result. Table V summarizes the results for the four salts studied.

These results may be expressed in the form

$$V_t = V_{20}\,[1 + a(t - 20) + b(t - 20)^2]$$

$$\text{for AgI;}\quad V_t = V_{20}\,[1 - 0.0000016\,(t - 20)]$$

$$\text{for TlI;}\quad V_t = V_{20}\,[1 + 0.00013419\,(t - 20) + 0.0000000321\,(t - 20)^2]$$

$$\text{for TlBr;}\quad V_t = V_{20}\,[1 + 0.00015182\,(t - 20) + 0.0000000493\,(t - 20)^2]$$

$$\text{for TlCl;}\quad V_t = V_{20}\,[1 + 0.00015754\,(t - 20) + 0.0000000586\,(t - 20)^2]$$

These equations agree with our experimental data over the range from 20 to 60° with an average deviation of less than three parts in a million for thallous iodide, and within one part in a million for the other three salts. The true coefficient of expansion at any temperature, *t*, would be

$$\frac{\mathrm{d}V}{V\mathrm{d}t} = \frac{a + 2b\,(t - 20)}{1 + a\,(t - 20) + b\,(t - 20)^2}$$

The coefficients of expansion of these salts are as follows:

TABLE VI

COEFFICIENTS OF EXPANSION

	Temp., °C. 20	30	40	50	60
TlCl	$1.57_6 \times 10^{-4}$	$1.58_5 \times 10^{-4}$	$1.59_4 \times 10^{-4}$	$1.60_3 \times 10^{-4}$	$1.61_3 \times 10^{-4}$
TlBr	$1.51_8 \times 10^{-4}$	$1.52_6 \times 10^{-4}$	$1.53_4 \times 10^{-4}$	$1.54_0 \times 10^{-4}$	$1.54_8 \times 10^{-4}$
TlI	$1.34_2 \times 10^{-4}$	$1.34_6 \times 10^{-4}$	$1.35_1 \times 10^{-4}$	$1.35_6 \times 10^{-4}$	$1.36_0 \times 10^{-4}$
AgI	$-0.01_6 \times 10^{-4}$	$-0.01_6 \times 10^{-4}$	$-0.01_6 \times 10^{-4}$	$-0.01_6 \times 10^{-4}$	$-0.01_6 \times 10^{-4}$

A discussion of the correlation of the coefficient of expansion with the compressibility and other properties will be postponed until data on more salts are available.

Summary

1. A new form of differential weight dilatometer for the determination of the cubical coefficient of expansion of solids and liquids is described. The instrument functions simultaneously as a thermostat regulator and controls its own temperature so that it is exactly filled.

2. Measurements have been made on six substances between 20 and 60°, giving the following mean cubical coefficients of expansion: Pyrex glass, $9.8_5 \times 10^{-6}$; toluene, 1.111×10^{-3}; silver iodide, $-1._6 \times 10^{-6}$; thallous chloride, 1.59×10^{-4}; thallous bromide, 1.53×10^{-4}; thallous iodide, 1.35×10^{-4}.

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