

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RADCLIFFE COLLEGE]

A REVISION OF THE ATOMIC WEIGHT OF LANTHANUM. I.
THE ANALYSIS OF LANTHANUM BROMIDE. II. THE
SPECIFIC GRAVITIES OF LANTHANUM CHLORIDE AND
BROMIDE. III. THE INCREASED EFFICIENCY OF CALCIUM
BROMIDE AS A DRYING AGENT AT LOW TEMPERATURES

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RECEIVED OCTOBER 23, 1931

PUBLISHED FEBRUARY 5, 1932

The atomic weight of lanthanum in current use, 138.90,¹ is based on two series of analyses of anhydrous lanthanum chloride by Baxter, Tani and Chapin,² and Hopkins and Driggs.³ Since the concordance of neither series of determinations was all that could be desired, we have continued the work of the former authors by further purification of the material used and by analyzing the anhydrous bromide. This work has yielded a value slightly higher than the one given above, 138.926, and more nearly in accord with Aston's finding that lanthanum is a simple element.⁴

Purification of Reagents.—Water and nitric acid were purified by distillation. Oxalic acid was three times crystallized, the first time after the addition of a small amount of nitric acid. Bromine was purified by the method already described.⁵

In the dehydration of lanthanum bromide in a current of hydrogen bromide described later the hydrogen bromide was collected in pure water and the solution was oxidized with a slight deficiency of permanganate for the recovery of the bromine. Since neither chloride nor organic matter were introduced in the process, the recovered material was of the same degree of purity as the original.

Hydrogen bromide was prepared with the apparatus shown in Fig. 1. Electrolytic hydrogen from the cells A, containing zinc amalgam-hydrochloric acid-platinized platinum, was passed over fused potassium hydroxide in the towers B and bubbled through bromine in the flask C at about 44° before passing over hot platinized asbestos in D. If a solution of the gas was desired it was passed through E into pure water. To obtain dry gas it was bubbled through ferrous bromide solution in G and H to remove traces of bromine and dried by means of fused calcium bromide in J. Before use the solution was fractionally distilled with a quartz condenser, with rejection of the head and tail portions. A colorless product resulted.

¹ Report of the Committee on Atomic Weights of the International Union of Chemistry, THIS JOURNAL, 53, 1627 (1931).

² Baxter, Tani and Chapin, *ibid.*, 43, 1080 (1921); 44, 328 (1922).

³ Hopkins and Driggs, *ibid.*, 44, 1927 (1922).

⁴ Aston, *Nature*, 113, 856 (1924).

⁵ Baxter and Ishimaru, THIS JOURNAL, 51, 1730 (1929).

The silver was a portion of that purified by Professor S. Ishimaru in connection with an earlier research on the atomic weight of meteoric nickel.⁶ Standard methods of purification were used and the product has been found in other investigations to be exactly similar to other samples similarly prepared.

Nitrogen was obtained by passing air through concentrated ammonia in L (Fig. 1), over hot copper catalyst in M, through dilute sulfuric acid in N, and over silver nitrate solution, potassium hydroxide solution, fused potassium hydroxide, concentrated sulfuric acid and resublimed phosphorus pentoxide in O and P. It contained argon and hydrogen (from catalytic decomposition of ammonia in M). Air was purified and dried by passing over similar reagents in Q and R.

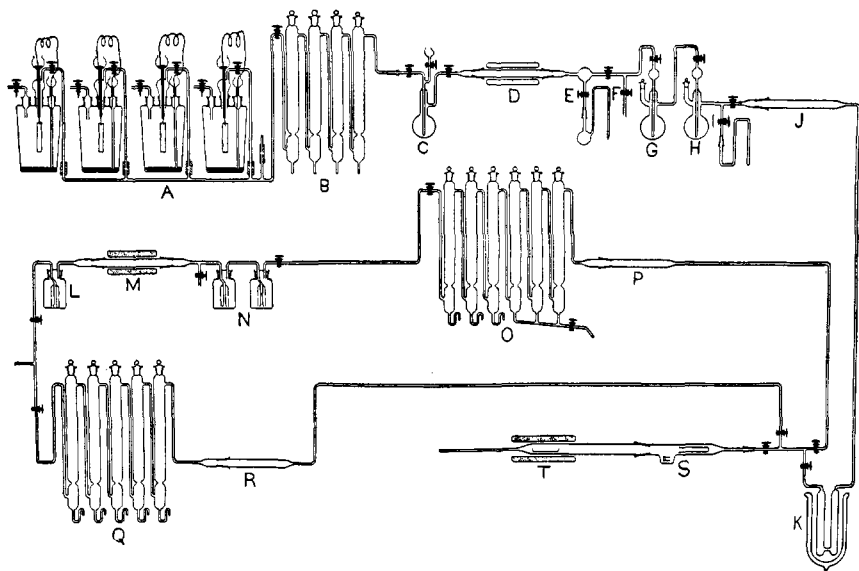


Fig. 1.

The Purification of Lanthanum Material.—The starting point in the purification was two series of less soluble fractions obtained by Chapin and by Tani in the fractional crystallization of lanthanum ammonium nitrate. This is one of the most favorable cases of purification of a rare earth by fractional crystallization because lanthanum tends to concentrate alone in the least soluble fraction, with cerium, praseodymium, neodymium and other rare earth elements following in the more soluble fractions in that order.⁷ Fractions from the two series of estimated similar purity were combined, and the crystallization as double ammonium nitrate was continued.

⁶ Baxter and Ishimaru, *THIS JOURNAL*, 51, 1730 (1929).

⁷ Auer v. Welsbach, *Sitzungsb. Acad. Wiss. Wien*, 112, 1043 (1903).

In the fractionation by Chapin, ninety-six series of crystallizations were carried out, involving 2300 fractions. The final series contained 39 fractions. In that carried out by Tani also ninety-six series of crystallizations, involving 1100 fractions, were completed. In the final series there were twelve fractions. Rejection of the least soluble fraction was more liberally adopted in the latter fractionation, which permitted the greater limitation of the number of fractions.

The combination of the fractions of the two final series is indicated in the following table, in which the less soluble fractions are given the lower numbers.

	Tani	Chapin	Baxter and Behrens
	1	1 } 2 }	1
	2 } 3 }	3 } 4 }	2
	4	5 } 6 }	3
	5	7 } 8 }	4
	6	9 } 10 }	5
	7	11 } 12 }	6
	8	13 } 14 }	7
	9	15 } 16 }	8
	10	17 } 18 }	9
	12	19 } 21 }	10

None of the fractions even in concentrated solution in a 5-cm. layer showed any indication of absorption bands so that the essential absence of praseodymium and neodymium was assured at the outset. Detectable amounts of cerium, however, were contained in the more soluble fractions, and it was for the removal of these that the purification process was intended.

The fractionation scheme which was carried out is understood best from Fig. 2 in which the lowest number in a series represents the least soluble fraction. Rejected mother liquors are shown at the right of a series by diagonal lines unconnected with any number. When the least soluble fraction became small it was set aside to be combined later with a least soluble fraction of a subsequent series as indicated by lines in the diagram. Thirty series of fractional crystallizations were completed, the total number of individual crystallizations being 383. Thirteen fractions resulted in the final series, numbered 371 to 383. The final series of fractions was tested for cerium by boiling the solutions with ammonium persulfate,⁸ with the addition of enough ammonium hydroxide to keep the solution barely on the acid side of neutrality. The precipitates formed always contained a small amount of lanthanum hydroxide colored yellow by the ceric hydroxide when cerium was present.

The most soluble fraction, 382, yielded a small amount of cerium. Fraction 379 yielded a trace. The mother liquor of fraction 376 gave no visible indication of cerium. The arc spectra of fractions 371, 372, 376 and 379, after removal of cerium as described, were carefully compared, using pure graphite electrodes and a Féry quartz spectrograph. No differences could be detected, and the arc lines of cerium were not detectable in the spectrograms. Since even 1% of cerium would raise the apparent

⁸ Witt and Thiel, *Ber.*, 33, 1315 (1900).

the crystals were centrifugally drained and washed and then were three times recrystallized in platinum. The crystals were preserved in quartz dishes over fused potassium hydroxide.

The Dehydration of Lanthanum Bromide.—Owing to the danger of the formation of basic salt, the drying of the lanthanum bromide was carried out with the greatest care. Matignon⁹ first pointed out that in the dehydration of the rare earth chlorides a neutral product could only be obtained by a thorough preliminary dehydration followed by fusion in an atmosphere of dry hydrogen chloride. Baxter and Chapin,¹⁰ and Baxter and Stewart¹¹ applied this principle successfully in the preparation of neodymium and praseodymium chloride and the procedure has since been followed by others. It is especially important that as much as possible of the water of crystallization be eliminated by efflorescence before any attempt is made to fuse the salt.

In view of this experience the following method was employed. The hydrated crystals were placed in a weighed platinum boat contained in the quartz tube of a Richards bottling apparatus (T and S, Fig. 1) and the tube was heated to about 110° by means of an aluminum block oven,¹² while at the same time a current of nitrogen containing a small amount of hydrogen bromide was passed through the tube. Since the inversion temperature of the heptahydrate was found experimentally to be 117°, there was no danger of melting. The crystal water evaporated slowly, a period of eight to ten hours being necessary before there was visible evidence of the end of the first stage in the dehydration. Judging from analogy with the chlorides, one molecule of crystal water still remained. Pure hydrogen bromide was then passed through the tube and the temperature was maintained at about 160° until the residual crystal water had evaporated. Again the temperature was raised, to 300°, for some time. Next the aluminum oven was removed and replaced by an electrically heated sleeve. The temperature was raised to dull redness for a short time and finally the salt was fused, at bright redness, as rapidly as possible. Experience with praseodymium chloride has shown that prolonged fusion is highly undesirable, probably because of traces of water in the gas stream. As soon as fusion was complete the salt was allowed to solidify the hydrogen bromide was displaced by nitrogen and this in turn by air. The boat was then transferred to the weighing bottle in which it had originally been weighed, by means of the bottling apparatus, the stopper was inserted and the weighing bottle and contents were placed in a desiccator preparatory to weighing.

⁹ Matignon, *Compt. rend.*, **133**, 289 (1901).

¹⁰ Baxter and Chapin, *THIS JOURNAL*, **33**, 17 (1911).

¹¹ Baxter and Stewart, *ibid.*, **37**, 529 (1915).

¹² Baxter and Coffin, *Proc. Am. Acad.*, **44**, 184 (1909).

Except in two preliminary exploratory experiments in which the technique had not been perfected, the fused salt gave a perfectly clear solution when dissolved in a minimum amount of water. We interpret this to mean the absence of basic salt, although if the latter possesses appreciable solubility the conclusion is not justified. In order to throw more light on this important question, after the first two analyses the drying of the hydrogen bromide was made more complete. Baxter and Warren¹³ have shown that fused calcium bromide leaves 0.2 mg. of moisture per liter in air which has been passed over it at room temperature. Most of the better drying agents such as phosphorus pentoxide and sulfuric acid contaminate the hydrogen bromide with decomposition products. We therefore attempted to increase the efficiency of calcium bromide by lowering its temperature. This was done by inserting in the hydrogen bromide train the U-tube K filled with fused calcium bromide and cooling this tube with solid carbon dioxide-alcohol mixture. In a following section is given experimental evidence that this expedient is highly successful in increasing the efficiency of the drying. Since the later experiments with lanthanum bromide showed no difference from the earlier ones, it seems likely that residual water in the hydrogen bromide did not affect the early experiments.

The Analysis of Lanthanum Bromide.—The analysis of the bromide followed conventional lines. The solution was diluted to a volume of 1000 to 1500 ml. so that the concentration was less than 0.05 normal. Baxter and Greene¹⁴ have recently pointed out that a concentration as low as this is desirable to avoid occlusion by silver bromide. A quantity of silver very nearly equivalent to the bromide was carefully weighed and dissolved in nitric acid with especial precautions to avoid loss of spray, and the solution was diluted to a volume of about one liter. The silver solution was then added in small portions with gentle agitation to the bromide solution in a glass-stoppered flask, and the mixture was occasionally shaken for a week. A nephelometric test for excess of bromide or silver was then made. Any deficiency found was made up by adding hundredth normal solution, and the shaking and testing repeated until the exact endpoint was reached. All the analyses were then allowed to stand undisturbed during the summer months and then were again shaken and tested. In the first and fifth analyses a change amounting to only 0.1 mg. of silver was observed. The others remained unchanged.

In order to determine the silver bromide an excess of a few mg. of silver was added to each analysis to reduce the solubility of silver bromide and after standing for some time the precipitates were thoroughly washed and collected on weighed platinum sponge crucibles. In analyses 6 to 8 the washing liquid contained 2 mg. of silver per liter and the precipitate was

¹³ Baxter and Warren, *THIS JOURNAL*, 33, 340 (1911).

¹⁴ Baxter and Greene, *ibid.*, 53, 611 (1931).

transferred to the crucible with pure water. In analyses 9 and 10 the washing as well as the transference was done with water. Drying at 300° for eighteen hours was followed by weighing. In analyses 6 to 8 the crucibles and contents were again heated just above the melting point of the silver bromide. A slight loss in weight was presumably due to retained moisture. In analyses 9 and 10 the bulk of the silver bromide was transferred to a quartz crucible and the loss in weight on fusion determined. The moisture determinations made in the latter way showed no difference from those made in the former.

The solubility of silver bromide in the filtrate and silver nitrate washings was assumed to be negligible but a correction of 0.1 mg. per liter was applied for the aqueous washings. The precipitating flask was rinsed with ammonia to collect silver bromide which had escaped transference and the bromide content of this solution determined nephelometrically. This correction amounted to 0.1 mg. per analysis on an average. A negative correction was applied for any bromide added during the adjustment of the end-point.

Weighings were made on a balance sensitive to 0.01 mg. with weights which had been carefully standardized. All weighings were made by substitution, with the use of similar counterpoises in the case of the weighing bottles and crucibles. Electrostatic charges were eliminated by means of a small amount of radium salt in the balance case. Vacuum corrections were applied as follows:

	Specific gravity	Vacuum correction per g., mg.
Weights	8.3	
Silver	10.49	-0.031
Silver bromide	6.47	+0.041
Lanthanum bromide	5.06	+0.091

The determination of the density of lanthanum bromide is described in a later part of this paper.

TABLE I
THE ATOMIC WEIGHT OF LANTHANUM

		Series I. $\text{LaBr}_3 \cdot 3\text{Ag}$					
		Ag = 107.880			Br = 79.916		
No. of analysis	Frac- tion	Weight of LaBr_3 in vacuum, g.	Wt. of Ag in vacuum, g.	Wt. of Ag added or subtracted, g.	Corr. wt. of Ag in vacuum, g.	Ratio $\text{LaBr}_3:3\text{Ag}$	Atomic weight of lanthanum
1	376	4.01090	3.42980	-0.00179	3.42801	1.170037	138.923
2	379	5.19186	4.43757	-0.00030	4.43727	1.170057	138.929
3	372	6.57727	5.62165	-0.00032	5.62133	1.170056	138.929
4	371	6.38414	5.45632	-0.00020	5.45612	1.170088	138.939
5	372	6.91830	5.91257	+0.00030	5.91287	1.170061	138.931
6	371	6.19359	5.29319	+0.00020	5.29339	1.170041	138.924
Average						1.170057	138.929

TABLE I (Concluded)
 Series II. $\text{LaBr}_3 : 3\text{AgBr}$

No. of analysis	Fraction	Weight of LaBr_3 in vacuum, g.	Wt. of AgBr in vacuum, g.	Dissolved AgBr , g.	Loss in wt. on fusion, g.	Corr. wt. of AgBr in vacuum, g.	Ratio $\text{LaBr}_3:3\text{AgBr}$	At. wt. of lanthanum
7	376	4.01090	5.96768	0.00000	0.00025	5.96743	0.672132	138.923
8	379	5.19186	7.72480	.00000	.00005	7.72475	.672107	138.909
9	372	6.57727	9.78513	.00035	.00000	9.78548	.672146	138.931
10	371	6.38414	9.49818	.00030	.00005	9.49843	.672126	138.920
11	372	6.91830	10.29255	.00040	.00010	10.29285	.672146	138.931
Average							.672131	138.923
Average of Series I and II								138.926

Below the results are arranged by fractions of the lanthanum material.

	$\text{LaBr}_3:3\text{Ag}$	$\text{LaBr}_3:3\text{AgBr}$	Average
371	138.939	138.920	
	138.924		138.928
372	138.929	138.931	
	138.931	138.931	138.931
376	138.923	138.923	138.923
379	138.929	138.909	138.919

The extreme difference in the experimental ratios amounts to 0.005% in both series, corresponding to 0.25 mg. of silver and 0.40 mg. of silver bromide. Although there is a slight apparent trend downward with increasing solubility of the double nitrate fractions, it is doubtful whether this represents a real difference in the material especially since the most probable impurity, cerium, would raise, not lower, the observed atomic weight.

The ratios of silver used to silver bromide obtained in the same analysis fall within the experimental limit to be expected in analyses of this type and indicate that the silver bromide was reasonably free from contamination.

Analysis	$\text{Ag}:\text{AgBr}$
1 and 7	0.574453
2 and 8	.574422
3 and 9	.574456
4 and 10	.574423
5 and 11	.574464
Average	.574444
Theoretical	.574453

The results of the recent analyses of lanthanum halides are summarized below.

Baxter, Tani and Chapin	$\text{LaCl}_3:3\text{Ag}$	138.916 ^a
	$\text{LaCl}_3:3\text{AgCl}$	138.915 ^a
Hopkins and Driggs	$\text{LaCl}_3:3\text{Ag}$	138.89
Baxter and Behrens	$\text{LaBr}_3:3\text{Ag}$	138.929
	$\text{LaCl}_3:3\text{AgBr}$	138.923

^a Corrected for the new specific gravity of lanthanum chloride found as described in a later part of this paper, 3.842.

The average value obtained in the two investigations in this Laboratory, 138.92, is higher than the International value by 0.02 unit.

II. THE SPECIFIC GRAVITIES OF LANTHANUM CHLORIDE AND BROMIDE

For the purpose of finding the buoyant effect of the air on anhydrous lanthanum bromide in the preceding investigation, a knowledge of the density of this salt was necessary. Since the evidence concerning the density of the anhydrous chloride is conflicting, the densities of both salts were determined, by displacement of toluene.

Toluene was dried over sodium and fractionally distilled, with rejection of the first and last fifth, although the boiling point was constant within a degree. Its density was determined at 25° both with an Ostwald pycnometer and also with the special pycnometer for solids described by Baxter and Hines.¹⁵ The latter consisted of a weighing bottle provided with two stoppers, one of which was of ordinary shape and was used during the weighing of the dry substance. Into the other were sealed two glass capillaries which served to fill the bottle with liquid. When the bottle was filled with liquid the joint was made tight with weighed amounts of sirupy phosphoric acid or grease.

Lanthanum bromide was dehydrated and fused in a platinum boat as described in the preceding paper, and was weighed in the pycnometer bottle with the ordinary stopper. The salt was then quickly covered with toluene and placed in a vacuum desiccator in which the pressure was reduced until the toluene boiled gently. As soon as air had thus been expelled from the salt the pycnometer stopper provided with a weighed amount of sirupy phosphoric acid as lubricant was inserted and the pycnometer was filled with toluene at 25°. From the weight of the pycnometer filled with toluene and containing the boat and salt, and the weight similarly determined with the empty boat, the toluene displaced was found.

Lanthanum chloride was prepared from the oxide of fraction 376 and was several times crystallized. It was dehydrated and fused as described by Baxter, Tani and Chapin,¹⁶ and its density found as described above with the bromide.

The following vacuum corrections have been applied:

	Density	Vacuum correction per gram
LaBr ₃	5.06	+0.00009
LaCl ₃	3.84	+0.00017
Toluene	0.8613	+0.00126
Water	0.9971	+0.00106

¹⁵ Baxter and Hines, *Am. Chem. J.*, 31, 220 (1904).

¹⁶ Baxter, Tani and Chapin, *THIS JOURNAL*, 43, 1080 (1921).

OSTWALD PYCNOMETER			
	Weight of water in vacuum, g.	Weight of toluene in vacuum, g.	Density of toluene 25°/4°
	9.85588	8.51362	
	9.85584	8.51347	
Average	9.85586	8.51355	0.86129
SPECIAL PYCNOMETER			
	11.55863	9.98437	
	11.55863	9.98408	
	11.55863	9.98438	
Average	11.55863	9.98428	0.86127
	Weight of LaBr ₃ in vacuum, g.	Weight of toluene displaced in vacuum, g.	Density of LaBr ₃ 25°/4°
	2.3703	0.4036	5.058
	2.1244	0.3619	5.056
			Average 5.057
	Weight of LaCl ₃ in vacuum, g.	Weight of toluene in vacuum, g.	Density of LaCl ₃
	1.6061	0.3600	3.843
	1.5146	0.3396	3.841
			Average 3.842

Earlier determinations of the density of lanthanum chloride are:

Matignon, ¹⁷ displacement of nitrobenzene	18°/4°	3.947
Bourion, ¹⁸ displacement of amyl benzoate	0°/4°	3.79
Kleinheksel and Kremers, ¹⁹ displacement of air	25°/4°	3.82

III. THE INCREASED EFFICIENCY OF CALCIUM BROMIDE AS A DRYING AGENT AT LOW TEMPERATURES

In the preceding investigation on the atomic weight of lanthanum a current of dry hydrogen bromide was necessary. This gas reacts with concentrated sulfuric acid and with phosphorus pentoxide²⁰ and therefore has frequently been dried by fused calcium bromide. This substance, though rapid in its effect, leaves 0.2 mg. of moisture in air passed over it.²¹ We therefore adopted the expedient of chilling the calcium bromide with carbon dioxide snow and alcohol. Although the temperature was thus lowered to the neighborhood of the boiling point of the hydrogen bromide, no condensation actually took place, owing doubtless in part to the fact that the hydrogen bromide was diluted with a small percentage of hydrogen.

In order to determine the efficiency of this method we carried out the following experiments. Pure calcium bromide was freshly fused and

¹⁷ Matignon, *Compt. rend.*, 140, 1339 (1905).

¹⁸ Bourion, *Ann. chim. phys.*, 21, 65 (1910).

¹⁹ Kleinheksel and Kremers, *THIS JOURNAL*, 50, 963 (1928).

²⁰ Bailey and Fowler, *Chem. News*, 58, 22 (1888); Baxter and Hines, *THIS JOURNAL*, 28, 779 (1906).

²¹ Baxter and Warren, *ibid.*, 33, 340 (1911).

packed in a U-tube. Into one side could be passed pure air of low humidity. The other side could be connected with a counterpoised U-tube containing phosphorus pentoxide.

A measured volume of air was first aspirated at the rate of two liters per hour through the system with the calcium bromide at 25° (Experiments 1 and 2). The results confirmed those of Baxter and Warren. The experiments were then repeated with the calcium bromide at -72° (Experiments 3 and 4). The calcium bromide was then removed from the U-tube and the experiments repeated (Experiments 5 and 6). In these experiments a mist condensed in the chilled U-tube. Since in Experiments 5 and 6 the removal of the water from the air seemed to be as complete without the calcium bromide as when it was used, and since in none of the Experiments 3 to 6 was the water obtained much greater than the experimental uncertainty, further experiments were then made, with (Experiments 7 to 9) and without (Experiments 10 and 11) the use of calcium bromide at -21° (salt and ice). In these a real increase in efficiency appeared if the calcium bromide was used. The following table gives the experimental data.

Experiment	Temp., °C.	Tube	Volume of air S. T. P., liters	Weight of water, mg.	Weight of water per liter, mg.
1	25	CaBr ₂	7.3	1.2	0.16
2			7.2	0.8	.11
					Average .14
3	-72	CaBr ₂	14.5	.20	.014
4			14.5	.15	.010
					Average .012
5		Empty	14.5	.20	.014
6			14.5	.25	.017
					Average .016
7	-21	CaBr ₂	14.6	.30	.020
8			14.5	.25	.017
9			14.6	.30	.020
					Average .019
10		Empty	14.5	.70	.048
11			14.5	.60	.041
					Average .045

These experiments are of interest in establishing both that calcium bromide is considerably more efficient at low temperatures and that the speed with which it removes residual water from a gas current is sufficiently high. Presumably the efficiency of other drying agents may be similarly increased.

Summary

1. The preparation of anhydrous lanthanum bromide is described.
2. The analysis of this salt by comparison with silver and by weighing the resulting silver bromide is found to yield 138.92 as the atomic weight of lanthanum.

3. The specific gravities of anhydrous lanthanum chloride and bromide at 25° are found by displacement of toluene to be 3.842 and 5.057, respectively.

4. The greater efficiency of calcium bromide as a drying agent at low temperatures is experimentally investigated.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]
ADSORPTION AND REACTIONS AT SURFACES OF ZINC OXIDE

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RECEIVED OCTOBER 23, 1931

PUBLISHED FEBRUARY 5, 1932

The present investigations originated in an attempt to obtain additional experimental data on the decomposition of alcohols at oxide surfaces in order to test two alternative theories for the distribution of decomposition between dehydrogenation and dehydration reactions at such surfaces. The two theories may be described as the Adkins-Burk-Balandin theory of multiple attachment at surfaces having varied spacings which determine the mode of decomposition and the Taylor theory of dual surfaces according to which the mode of decomposition is determined by the ionic charge of the group to which the adsorbed alcohol molecule is attached. There is no necessity to set forth the evidence for and relative merits of the two points of view since this has recently been independently done in detail by Schwab¹ in his recent text on catalysis. It will suffice to summarize the experiments performed with respect to the alternative reactions at various surfaces of zinc compounds, to emphasize the limited nature of the conclusions which may, as yet, be safely drawn from such work, and finally to detail the results concerning the adsorption of water vapor and hydrogen at zinc oxide surfaces, indicating their paramount importance in this problem of alternative reactions at a given surface.

Prior to the adsorption experiments a very large number of experiments were made with the object of obtaining definitive data on the velocity, nature and temperature coefficients of the decomposition of isopropanol on various zinc compound surfaces. As the result of a mass of experimental data obtained over a period of one year with six different types of surface, we are forced to the conclusion that *much of what has previously been deduced as characteristic of such surfaces is based on an entirely too restricted range of experimental measurements*. Our multiplication of such measurements served to show definitely that for even *approximately* reproducible results the most stringent regulation of a variety of experimental details must be arranged. Similar apparently capricious results

¹ Schwab, "Katalyse vom Standpunkt der chemischen Kinetik," Julius Springer, Berlin, 1931, pp. 173, 184-186, 203.