The authors desire to express their appreciation to the Committee of the Cyrus M. Warren fund for assistance in this work.

Summary

The solubilities of the hydrated bromates of lanthanum, praseodymium, neodymium, samarium, gadolinium and terbium of the type $M(BrO_3)_3 \cdot 9H_2O$ have been determined, using water as solvent.

The work upon the remaining bromates is being carried out.

Durham, New Hampshire

[Contribution from the Chemical Laboratories of the Ohio State University]

THE INFLUENCE OF CENTRIFUGAL FORCE ON RATE OF EVAPORATION

By Edward Mack, Jr.

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In his consideration of the mechanism of evaporation, Langmuir[1] has pointed out the probability that crystalline surfaces like those of iodine or naphthalene, when undergoing reversible evaporation, are partially covered with an amorphous layer. The amorphous layer is formed on the surface by the deposition of irregularly placed and loosely held molecules by condensation from the vapor phase. Such molecules stick where they strike and are somewhat slow to rearrange themselves to fit into the regular lattice structure of the crystalline surface. This view is strongly supported by experimental evidence brought forward in the present paper, based on the effect which centrifugal force has on the rate of evaporation of solid iodine.

Experimental Part

A small, high-speed centrifuge has been constructed, driven by a compressed-air turbine, 7.5 cm. in diameter, mounted on a vertical steel spindle pointed at the lower end, and arranged to spin like a top in an agate bearing. The upper part of the spindle turns in a ball-bearing socket. The spindle carries a steel frame, from which hang two tubes, like buckets, which assume horizontal positions when the centrifuge is in motion. The shape and dimensions of the buckets are indicated in Fig. 1. The entire centrifuge is mounted inside a large barrel with heavy concrete walls. The turbine is impelled by four nozzles, placed 90° apart and connected through control valves with a high-pressure air line. When the two buckets are loaded with water a speed somewhat greater than 9000 r.p.m. may be attained and when lighter buckets are attached, or none at all, a much greater speed has been reached.

The manner in which the rate of evaporation of iodine was determined is shown in Fig. 1.

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[1] Langmuir, This Journal, **38**, 2221 (1916).

The cylindrical bucket *B*, made of duralumin,[2] was suspended from the steel frame *F*. A glass cup *C* fitted closely into the bottom of the bucket, and held a layer of absorbent charcoal. The inverted glass lid *L*, carrying a cake of solid iodine, rested on the top of the cup *C*. Both *L* and *C* were made from the same piece of glass tubing, of internal diameter 1.39 ± 0.01 cm., and their contact edges were ground together with fine emery powder. This arrangement for the evaporation and diffusion of the iodine through the air space to the charcoal was in every way similar to that already described in another paper.[3]

The iodine cake was prepared by pouring molten iodine into the glass lid; when it had solidified it was rubbed to a smooth, flat surface with very fine sand paper. The iodine surface soon became visibly crystalline. A platinum wire, looped at both ends, had been sealed into the glass, as indicated, and the solidification of the iodine around the lower loop helped retain the iodine cake, although its adhesion to the glass was also an important factor in its retention in the glass lid. The lid with the iodine was lifted from the cup with forceps and was weighed in a glass-stoppered weighing bottle. The weighings were made with weights calibrated by the Bureau of Standards, and with a sensitive assay balance mounted in a constant temperature room.

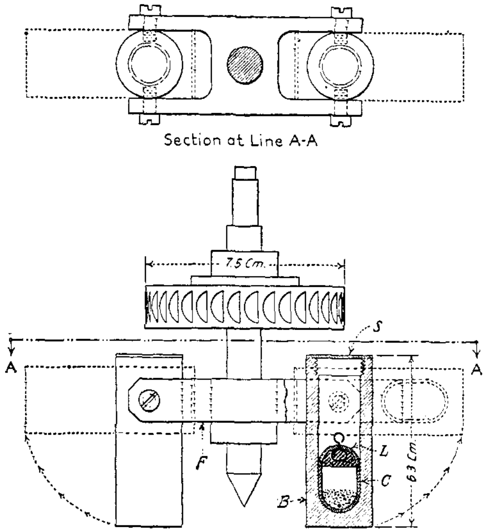

Fig. 1.

With the arrangement just described, the iodine evaporated, diffused downward through the air column and was absorbed by the finely powdered (80–100 mesh) charcoal. An activated coconut charcoal, which was employed in the determinations, gave the same results as a charcoal taken from a German gas mask,[4] and also the same results as soda lime (when the centrifuge was at rest and up to 1200 r.p.m.). *The fact that all three absorbents yielded the same results made it extremely probable that the iodine vapor was absorbed just as rapidly as it was supplied to the absorbent;* at least, this was true when the diffusion occurred with the tubes at rest, and also under small centrifugal forces. The charcoal was packed into a very compact layer, and it is not likely that the packing was affected

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[2] Thanks are due the Aluminum Company of America for the gift of the duralumin.

[3] Mack, This Journal, **47**, 2468 (1925).

[4] The author is indebted to Mr. A. C. Fieldner of the U. S. Bureau of Mines, Experiment Station at Pittsburgh, for the German canister from which this sample was taken.

during centrifuging, or that any appreciable alteration was produced in the distance of the iodine from the charcoal layer. This distance was 1.00 ± 0.01 cm. The diffusion of the iodine occurred, then, under a pressure gradient equal to the vapor pressure of the iodine.

The rate of evaporation was determined with the centrifuge in motion at the several speeds indicated in Table I; also at rest, with the tubes immersed in a water thermostat. All temperatures were checked on a thermometer with a Bureau of Standards certificate, and the barometric pressures were read with a barometer calibrated by the Bureau of Standards. The centrifuge speed was measured with a revolution counter and stop watch.

Table I

Rate of Evaporation of Iodine in Centrifuge

The temperature was 25.0 ± 0.2°

1 Speed, r.p.m.	2 Measured barometric press., mm.	3 No. of detns.	4 Observed av. rate of evap'n g./sq. cm./hr.	5 Corrected rate of evap'n at 760 mm., g./sq. cm./hr.	6 Increase in rate of evap'n. due to centrifugal force, g./sq. cm./hr.	7 Centrifugal force acting at iodine surface unit = gravity
At rest	752.6	8	0.00161 ±1.8%	0.00159	......	....
200 ±2%	740.8	2	.00167 ±3%	.00163	0.00004	2.5
400 ±2%	748.7	1	.00179	.00176	.00017	10.0
600 ±2%	748.7	2	.00201 ±1%	.00198	.00039	22.5
800 ±2%	740.7	4	.00229 ±0.5%	.00223	.00064	40.0
1000 ±1.6%	743.4	6	.00268 ±1.5%	.00262	.00103	62.5
1200 ±1.6%	740.5	4	.00318 ±5%	.00310	.00151	90
2000 ±1%	745.6	4	.00421 ±1.2%	.00413	.00254	250
			[.00559]	[.00548]	[.00389]	250
4000 ±1%	740.1	4	.00676 ±0.5%	.00658	.00499	1000
			[.00768]	[.00748]	[.00589]	1000
6000 ±1%	737.9	4	.00768	.00746	.00587	2250

The brackets [ ] indicate the results obtained with moist soda lime as the absorbent instead of charcoal.

In each experiment, the buckets were closed hermetically by a glass cover-slip, *S*, sealed with paraffin as shown in Fig. 1. The pressure of the confined volume of air would become smaller at the inner end of the bucket and greater at the outer end, during centrifuging, and this air at greater pressure, spreading into the diffusion space of Cup *C*, would affect somewhat the rate of diffusion of the iodine vapor. This alteration in the air pressure, however, is so slight even at the higher centrifuge speeds, that it may be neglected without introducing appreciable error.

In order to make possible a comparison among the evaporation losses at the various speeds, the experimental values of Col. 4 have been corrected to give the values of Col. 5, so that these corrected values will represent the losses which would have occurred, if the average pressure in the diffusion space had been 760 mm. The correction is based on the assumption that at these pressures, the rate of diffusion, and consequently the rate of evaporation also, are inversely proportional to the air pressure.

Résumé of Experimental Results.—It will be seen from Cols. 6 and 7 of Table I that the increase in rate of evaporation of the iodine is directly proportional to the centrifugal force, within the limit of the experimental error, at values as high as 90 times gravity, but at 250 times gravity and higher, while the rate of evaporation increases rapidly with increasing centrifugal force, it falls short of being directly proportional to the centrifugal force, at least when charcoal is used as absorbent. This is certainly due to the failure of the charcoal at the higher speeds to absorb the iodine vapor as rapidly as it arrives at the charcoal surface; for, when moist soda lime, which proved a more effective absorbent than moistened potassium iodide powder, is substituted for the charcoal, all other conditions being kept the same, the rate of evaporation is proportional to the centrifugal force at 2000 r.p.m., as shown by the values in brackets. At higher speeds, even with soda lime, the rate does not keep pace with the force.

We may conclude, then, that the increase in rate of evaporation is directly proportional to the centrifugal force up to about 250 times gravity, and there is no reason to doubt that it would still be directly proportional in the case of much greater forces, if only a sufficiently rapid absorber for iodine could be employed.

Theoretical Part

When the centrifuge is in motion the confined air is concentrated somewhat at the outer ends of the buckets under the influence of centrifugal force. There is, however, a limit to the concentration which can thus be produced, as diffusion of the air tends to occur in the reverse direction, until finally a steady state is set up. The centrifugal force may be assumed to have no further effect on the air during the diffusion of the iodine vapor through it, and we may limit our consideration to the influence of the centrifugal force on the movement of the iodine molecules. The solid iodine which was employed in the experiments was prepared by the method of Foulk and Mills[5] of this Laboratory and was practically *water-free*, and it seems impossible to account for even the smallest losses of weight suffered by the iodine, by assuming that the small quantity of dissolved water was drawn out of the crystal lattice of the iodine under the influence of centrifugal force.

In seeking for an explanation of the observed effect of centrifugal force in increasing the rate of evaporation of the solid iodine, consideration must be given to three possibilities.

1. It is conceivable that the effect of centrifuging might be to speed up the process by which the iodine vapor is absorbed at the charcoal

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[5] Dissertation of W. W. Mills, soon to be submitted for publication.

surface. This would permit iodine vapor to diffuse more rapidly through the air space, and also permit the solid iodine to evaporate more rapidly. Such a view of the matter is, however, almost certainly incorrect since, as has just been pointed out in the Experimental Part, the charcoal surface is already absorbing *all* of the iodine vapor as fast as it arrives; at least, it does so when the centrifuge is at rest and at speeds up to 1200 r.p.m. It is difficult, then, to see how the pressure gradient, under which the diffusion occurs, could be increased by any change produced by centrifugal force in the *absorptive properties of the charcoal.*

Another reason for believing that the charcoal cuts the pressure of the iodine vapor down to zero, in addition to the argument already given of the similar behavior of the three different absorbents, is the fact that the iodine diffusion coefficient, calculated on the assumption that the charcoal *does* lower the pressure to zero, has a very probable value. When the diffusion coefficient, determined in this way, is employed in calculating[3] the average cross-sectional area of the iodine molecule, the latter agrees rather closely (6%) with the value obtained by Rankine by a viscosity method.

2. A second possibility is that the centrifugal force may directly affect the velocity of diffusion. As the iodine molecules are working through the air space on their way to the charcoal surface, they acquire energy from the centrifugal force field. During each free path, that is, during the interval between successive collisions with air molecules, every iodine molecule will acquire from the centrifugal force field a certain acceleration of its velocity component in the direction of the charcoal surface in very much the same manner that the mobility of gaseous ions is altered in an electric field, and in the same way that a freely falling body undergoes acceleration of its velocity in the earth's gravitational field. It only remains to determine whether such an acceleration in the movement of the iodine vapor molecules towards the outer end of the spinning tube will account for the observed increase in the rate of evaporation.

Lenard's equation[6] may be employed to calculate the velocity of drift of the iodine molecules through the air space under the influence of the outside force:

$$v_{\text{drift}} = \frac{F}{S^2\pi\bar{c}d}\left[\frac{\mu + (1-\mu)\,4/\pi}{\sqrt{\mu}} \times \frac{3}{3+\mu}\right] \tag{1}$$

where F is the centrifugal force acting on each iodine molecule; S is the sum of the radii of the iodine[3] molecule and an average air molecule (2.29×10^{-8} cm. + 1.54×10^{-8} cm., respectively); $\bar{c}$ is the average velocity of the air molecules and is equal to $0.921 \times \sqrt{3RT/M}$; d is the density of the air (g. per cc.); and μ is $m/(m + M)$, where m is the molecular weight of iodine, 253.86, and M is the average molecular weight of air,

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[6] Lenard, *Ann. Physik*, **61,** 665 (1920).

28.96. The numerical term in the brackets assumes for iodine and air the value 0.835. At a centrifuge speed of 1200 r.p.m., and at 25° and 760 mm. air pressure, the average velocity of drift of the iodine molecules through the air, due to the influence of the centrifugal force, would then be 0.000121 cm./sec. This drift, calculated from the Lenard equation, is equivalent to a loss of 0.000,000,91 g. of iodine per sq. cm. per hour, and is more than 1600 times smaller than 0.00151 g., the measured loss due to centrifugal force at 1200 r.p.m. (see Col. 6, Table I). We may therefore conclude that the influence of the centrifugal force on the velocity of diffusion of the iodine molecules is wholly inadequate to explain the experimental results.

The same conclusion may be reached in another way. If the centrifugal force really affects appreciably the velocity of diffusion, it would be expected that if the positions of the iodine and charcoal were reversed so that the iodine vapor would thus have to diffuse *against* the centrifugal force field rather than *with* it, the rate of evaporation would be diminished. This experiment was performed. The charcoal was held in a small basket made of a glass cylinder with a piece of silk cloth for its bottom, as already described.[3] As a matter of fact, the rate of evaporation under these conditions was *not* measurably diminished whether the centrifuge speed was 1000, 2000 or 4000 r.p.m., but in each case was the same, within the experimental error, as during normal diffusion with the centrifuge at rest. (An effect of exactly the same sort has been noted also in the case of *p*-dichlorobenzene.)

3. The third possibility is that the centrifugal force may increase the rate of evaporation by exerting its influence *at the surface of the iodine.* It is not likely that the iodine atoms or molecules could actually be torn out of the surface of the solid crystal by the action of the centrifugal force, which at 1200 r.p.m. is only about 8.82×10^4 dynes per gram. The cohesive forces holding together the elements of the iodine crystal are[7] of the order of 10^9 dynes per sq. cm. Neither is it likely that the acceleration acquired from the field by the atoms or molecules of iodine in the crystal surface could be of any material assistance to them in attaining the critical velocity necessary to permit their escape from the surface into the vapor phase; for, if this were so, we should expect a corresponding decrease in the rate of evaporation when the diffusion positions of the iodine and charcoal are reversed.

The probable explanation seems to involve the consideration that the surface of the iodine is in a somewhat amorphous condition, as a result of what Langmuir calls "reversible evaporation." If we picture the surface of the solid iodine as being strewn with loosely-held molecules and small aggregates of molecules, and even extremely minute sub-microscopic

[7] Estimated from the heat of vaporization of solid iodine.

crystal leaflets formed upon the surface by condensation from the vapor, it is not difficult to see how such surface material could be detached and carried into the vapor space by the action of the centrifugal force. The result would be an increase in the effective vapor pressure of the iodine, when the centrifugal force is acting *away* from the iodine surface, and since the velocity of diffusion is directly proportional to the pressure gradient, the increasing rate of evaporation with increasing centrifugal forces could readily be explained. It has been suggested to the author by one of the reviewers of this paper that the small iodine leaflets, once detached from the surface, might travel as solid iodine powder through the air space. This indeed seems quite likely, although it would also probably be true that before this powder could penetrate very far into the air space, each solid particle would evaporate, and become true vapor, since of course an iodine vapor pressure gradient is established between the iodine surface and the charcoal surface, with the pressure falling off toward the charcoal end of the air space. At any rate, when sand was substituted for charcoal as an absorbent in the centrifuge experiments, no measurable evaporation of iodine was observed.

On the other hand, when the centrifugal force is acting *toward* the iodine surface, that is, when the positions of the iodine and charcoal have been transposed, the loosely-held amorphous aggregates would be accelerated *toward* the surface, and they would be largely prevented from escaping into the air space. At the same time the crystalline portion of the surface would manifest its normal vapor pressure, unaffected to any measurable extent by centrifugal forces of the magnitude employed in these experiments.

The author wishes to acknowledge the valuable assistance given by Mr. T. A. Moorman, while a graduate student at the Ohio State University in 1921–1922, in the design and construction of the centrifuge.

Summary

1. A small, high-speed centrifuge is described in which solid iodine is permitted to evaporate and diffuse through an air space under the influence of centrifugal force.

2. It is shown that the effect of the centrifugal force on the rate of evaporation is very large, and is proportional to the force as long as the absorbent, placed at the end of the diffusion space, absorbs all of the iodine vapor as fast as it arrives.

3. The explanation of the influence of the centrifugal force on the rate of evaporation cannot be found in an effect on the absorbent or in an effect on the diffusion velocity. The result is probably due to the somewhat amorphous structure of the solid iodine surface, which loses small molecular aggregates and loosely-held molecules of iodine under the influence of the centrifugal force field.

4. A reversal of the positions of the iodine and absorbent so that the iodine vapor diffuses against the centrifugal force does not decrease the rate of evaporation but gives the same rate of evaporation that is found when normal diffusion occurs in the centrifuge at rest.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE REACTION BETWEEN BROMINE AND CHLORIDE ION IN HYDROCHLORIC ACID. BROMINE MONOCHLORIDE

BY GEORGE SHANNON FORBES AND RAYMOND MATTHEW FUOSS

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In contrast with systems containing chlorine and iodine, those involving chlorine and bromine have received scant attention. This is due, perhaps, to absence of compounds when chlorine is dissolved in liquid bromine, a topic summarized by Abel.[1] On the other hand, the loss of color by bromine when chlorinated in hydrochloric acid, with the action of the product upon ethylene, has led several investigators[2] to assume bromine chloride present, stabilized by complex formation with the acid. The only attempt at an electrochemical study seems to have been made by Brown,[3] who measured between platinum electrodes the decomposition potential E of a solution of bromine chloride, $BrCl.HCl$ (strongly hydrolyzed), and found EF to correspond roughly to the heat of formation of the compound from bromine and chlorine.

The mutual replacement of chlorine and bromine in the presence of their ions, though of obvious importance, has hitherto been completely neglected.

As no quantitative information about this system could be found, we investigated it by methods[4] previously applied in this Laboratory to solutions of iodine and chlorine in hydrochloric acid. We worked in 6 N and 4 N acid partly to avoid hydrolysis, and partly to take advantage of the relation between E and $[Cl_2]$ previously determined in these acids. Further work, in more dilute acids, is projected.

If successive portions of a solid bromide are added to chlorine in hydrochloric acid, the plot of oxidation potential against added bromide has two steeply descending linear portions, recalling the analogous curve for iodine and chlorine. The first of these includes the "bromine monochloride point," as we shall call it, where total bromine equals total chlorine; the other the "bromine point," where added bromide equals initial chlorine, or where pure bromine is dissolved directly in the acid. Using cells of

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[1] See Abegg, *Handbuch der anorganischen Chemie*, 4^2, 294 (1913).

[2] Simpson, *Proc. Roy. Soc.*, **27**, 118 (1878). James, *J. Chem. Soc.*, **43**, 37 (1883). Delépine and Ville, *Bull. soc. chim.*, **27**, 673 (1920).

[3] Brown, *Phil. Mag.*, **31**, 449 (1891).

[4] Forbes, Glass and Fuoss, THIS JOURNAL, **47**, 2893 (1925).