striking confirmation of the above conclusions, and, *moreover, it shows that they hold good even in the case of very concentrated solutions.*

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CONCERNING THE CORRECTION OF THE APPARENT WEIGHT OF A SALT TO THE VACUUM STANDARD.

BY THEODORE W. RICHARDS AND GREGORY P. BAXTER.

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The tendency to adsorb gases possessed by finely divided carbon is well known, and there can be no question that other substances also possess, although to a much smaller degree, this same tendency. Therefore the possible effect of adsorbed gases upon the weights of the substances entering into very precise determinations, such as those concerning the atomic weights, is worthy of careful consideration. The idea is by no means new, for Marignac nearly seventy years ago investigated several salts with regard to the possibility of such adsorption, and found in most cases very slight, if any, evidence of an appreciable effect.[1] The topic has been recently revived by Guye and Zachariadès in a brief paper, in which are recorded, without details, a number of extraordinary results very different from those of Marignac.[2] The new investigators interpret their figures to mean that the error from this source is in many cases a serious one, rendering illusory the weighing of most powdered salts more accurately than to within one one-hundredth of one per cent.

The experiments of Guye and Zachariadès have been repeated, as far as potassium chloride is concerned, by Alexander Scott, with results confirming Marignac's rather than those of the new investigators. Scott was unable to find any important adsorptive effect, even in finely powdered potassium chloride.[3] His discussion of the matter seems to leave little need of further remark, except for the fact that Guye and Zachariadès specifically mention the recent Harvard investigations upon atomic weights, and their paper might convey to some the impression that these authors believe their results to concern the work at Harvard. It is very easy to show, however, upon the basis of the evidence in the paper, that, whether the interpretation by the two investigators at Geneva is correct or not, in any case their results can have no relation whatsoever to the Harvard work, and do not render necessary appreciable corrections in any of the Harvard investigations.

Guye and Zachariadès weighed successively in air and in vacuum a number of materials which, as they say, "were chosen especially as having served in the determinations of atomic weights in the chemical

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[1] Marignac, *Oeuvres Completes*, **1**, 44; also *Bibl. Univ.*, **46**, 373 (1843).

[2] Guye and Zachariadès, *Compt. rend.*, **149**, 593 (1909).

[3] Alexander Scott, *Proc. Chem. Soc.*, **25**, 286 (1909).

laboratory of Harvard College." These twenty-six salts were as follows: The nitrates of potassium and silver; the chlorides of potassium, sodium, magnesium, calcium, manganese, nickel, cobalt, iron, cadmium, barium, strontium, and silver; the bromides of potassium, sodium, zinc, barium, strontium, nickel, cobalt, and cadmium; the sulphates of copper and silver; the chlorate of potassium; the oxide of copper. Two of the substances, however—the chlorides of iron and nickel—have never been used as the basis of accurate work at Harvard. The authors conclude that the adsorptive effect "depend de la densité du sel, de l'hygroscopicité, et, à un haut degré des conditions de l'expérience, notamment de la structure physique du sel pesé." Thus, for example, fused potassium chloride in large pieces showed 5 milligrams of adsorption per 100 grams, in crystals 20 milligrams, in powder 32 milligrams. The other twenty-five substances seem to have been investigated in powdered form alone, and only one among them, namely, potassium nitrate, appeared to show as much adsorption as powdered potassium chloride.

Supposing for a moment that the figures just cited really represent adsorbed air, the quantity corresponding to fused material weighed in large pieces would be only enough to affect the atomic weight of potassium calculated from the molecular weight of potassium chloride, by an unimportant quantity, less than 0.004; and potassium chloride was one of the worst of all the substances investigated by Guye and Zachariadès. Hence, even according to their own showing, fused substances in large pieces may be weighed with considerable accuracy.

Now, of the substances in the list used in the Harvard determinations, all except five were fused and weighed in large pieces. This had been done not only because the expulsion of water from a fused salt is more certain than from a solid, but also because the possibility that the powders might adsorb air had been thought of very early in the prosecution of the Harvard researches. For example, in the case of barium bromide, the salt used in Experiments 4 and 13 was fused in a platinum crucible, and yet gave results for the atomic weight of barium and for the content of crystal water essentially identical with those of similar samples which had been merely heated at a high temperature without fusion, being thus in a highly subdivided, effloresced condition.[1] Two of the specimens of barium chloride (those used in Experiments 37 and 38[2]) were fused in a current of hydrochloric acid gas, but gave results for the atomic weight of barium essentially equal within the limit of error of experimentation to those from the unfused effloresced samples. In the later determinations of the atomic weights of other elements, the other substances mentioned by Guye and Zachariadès were all fused and weighed

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[1] Richards, *Z. anorg. Chem.*, **3**, 470 (1893).

[2] Richards, *Ibid.*, **6**, 121, 122 (1894).

in large pieces except the five already alluded to. Of these five, nickel and cobalt bromides were weighed in the form of crystals of appreciable size, but Guye and Zachariadès found these substances even in a state of powder to show only a slight irregularity. Hence, they could not have been at fault. Copper oxide, another of the five, falls entirely out of consideration, partly because Guye found almost no suspicious effect in this case, and partly because if any air had been adsorbed by copper oxide it would have been determined along with the included nitrogen in the due course of the experiments upon this substance. Copper sulphate was indeed used in a finely powdered condition, but the weight of this substance did not enter into any of the finally accepted values for the atomic weight of copper. Hence the fourth of the unfused substances also falls out of consideration. Cobalt chloride also was used in an effloresced condition, but gave the same results for the atomic weight of cobalt as did the more compact cobalt bromide.

Having thus shown that the results of the European experimenters do not at all concern the Harvard determinations, even if some powdered substances really occlude air, we may perhaps repeat a description of two series of experiments carried out within the last two years in the Harvard laboratory with finely divided substances not in the list given by Guye and Zachariadès. In recent experiments iodine pentoxide and powdered silver phosphate have been used as means of obtaining information concerning the atomic weights of iodine and phosphorus respectively. Bearing in mind the possibility of this error in question (although at that time the paper of Guye and Zachariadès had not been published), Baxter and Tilley[1] and Baxter and Jones[2] carried out experiments with these two substances respectively. Iodine pentoxide had been made by double efflorescence from iodic acid through the compound $I_2O_5HIO_3$ and therefore must have been an extremely porous material with a surface comparable with that of charcoal. In two experiments with 25.8 grams of material, the air actually displaced by the pentoxide was found to be within about 0.0001 gram of that calculated from the density of the substance.

The description of these experiments is given below:

"Two weighing bottles were constructed with long, very well ground stoppers which terminated in stopcocks through which the tubes could be exhausted. These tubes were very closely of the same weight and of very nearly the same internal capacity. The tubes were first exhausted and compared in weight by substitution. Next they were filled with dry air and again weighed, the weighings being carried out with the stopcocks open." Both steps were then repeated with essentially the

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[1] This Journal, 31, 214 (1909).

[2] *Proc. Amer. Acad.*, 45, 155 (1909). This Journal, 32, 298.

same results, the difference in the weight of air contained in the two tubes being found on the average to be 0.00014 gram, the counterpoise being slightly the larger.

"Into one of the tubes was introduced 25.84 grams of carefully dried iodine pentoxide, and both tubes were completely exhausted. When the tube containing the pentoxide was warmed to about 150° no perceptible quantity of gas was evolved. After the difference in weight of the exhausted tubes had been determined, they were again filled with dry air and weighed, and the process of exhausting the tubes and filling them with air was repeated." The difference between the weight of air admitted to the two tubes now averaged 0.00651 gram, corrected to 19° and 758 mm. Subtracting the difference found for the empty tubes (0.00014 gram), the quantity 0.00637 gram is found as the weight of air displaced by the powder, whereas the value calculated from the density of the solid (4.799[1]) is 0.00649. Thus the amount of air adsorbed by nearly twenty-six grams of the very finely subdivided, effloresced iodine pentoxide was only a trifle more than 0.1 milligram—a quantity scarcely greater than the probable error of experiment. In this case the usual method of calculating the correction to the vacuum standard yields a possible error of only 1 in 200,000.

Similar experiments have been made with *precipitated* and dried silver phosphate by Baxter and Jones with similar results.

"In two experiments, when air was admitted, after exhaustion the counterpoise gained 0.00028 and 0.00021 gram respectively (average 0.00025), more than the tube which was later to contain the silver phosphate. After 22.69 grams of pure dry silver phosphate had been placed in the tube, the tube and its counterpoise were exhausted and the difference in weight determined. When dry air at 25° and 766 mm. was admitted to both the tube containing the silver phosphate and the counterpoise, the counterpoise gained 0.00443 gram more than the tube. Therefore the air displaced by the silver phosphate was 0.00443 — 0.00025 = 0.00418 gram. Since 22.69 grams of silver phosphate of density 6.37[2] have a volume of 3.56 cc., the volume of pure air displaced at 25° and 766 mm. should weigh 0.00425 gram.

"The experiment was then repeated. After the air had been exhausted from the tube and its counterpoise, the tube containing the silver phosphate was heated gently. No gas was evolved. The tube and its counterpoise were then weighed by substitution. When dry air at 24.5° and 767 mm. was admitted to both, the counterpoise gained 0.00445 gram more than the tube containing the silver phosphate. Therefore the air displaced by the silver phosphate was 0.00445 — 0.00025 =

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[1] Baxter and Tilley, This Journal, **31**, 213 (1909).

[2] Baxter and Jones, *Proc. Amer. Acad.*, **45**, 155 (1909).

0.00420 gram, whereas the weight of air displaced, calculated from the density of the salt, is 0.00426 gram.

"The agreement between the experimental results and those calculated from the density of silver phosphate on the assumption that no adsorption takes place is close enough to show that no significant amount of adsorption occurs."

Furthermore, in many cases dried precipitates of silver halides have been weighed both before and after fusion, and, while in some cases the loss has amounted to 0.01 per cent., owing to moisture retained by the dried salt, in many cases the loss in weight has been very slight indeed, showing that the great diminution in surface is without effect upon the apparent weight. This was especially the case in the recent investigations upon the atomic weights of bromine and lithium, wherein silver bromide and chloride dried for a long time at 180° and 250°, respectively, lost sometimes not more than 1 part in 100,000 on fusion. Even this almost negligible loss was probably due to traces of water imprisoned in the unfused substance.[1]

When with these results we rank the similar results of Scott with potassium chloride, one cannot but believe that many substances at any rate adsorb so little air as not to be greatly affected as to their weights thereby, at least when the solids are weighed in any ordinary state of subdivision.

One other case, that of sublimed ammonium chloride, may receive passing mention. This salt seems to exhibit a slight tendency in the opposite direction, as it gains somewhat more weight in vacuum than corresponds to the calculated correction. According to the concordant results of Marignac, Stas, and Richards and Köthner and Tiede[2] the salt gains 0.00080 gram per gram when the air is exhausted, whereas the best value for the density of transparent ammonium chloride (1.525) corresponds to a gain of 0.000793—a result but very slightly less than the observed value.

Sublimed ammonium chloride is, however, a peculiar substance because, on cooling, it suffers transition into a denser form, causing the crystals to be permeated with pores of molecular fineness. The porosity of the solid renders difficult the determination of its true bulk, upon which depends the correction to the vacuum standard. Some of the interstices would undoubtedly fill with air, while others might not; and none of them would probably fill with a liquid. This would account for Stas's uncertainty about the specific gravity of the salt, and for the various

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[1] Baxter, THIS JOURNAL, 28, 1332 (1906). Richards and Willard, *Ibid.*, 32, 29 (1910).

[2] Marignac, *loc. cit.*; Stas, *Untersuchungen*, Aronstein's translation, p. 56 (1867); Richards, Köthner, and Tiede, THIS JOURNAL, 31, 7 (1909).

interpretations which have been put upon the results. Hence ammonium chloride, also, is probably not fundamentally abnormal.

The details given in the recent paper by the Geneva experimenters are so meagre that an explanation of their unprecedented results can hardly be attempted. They make no mention of the degree of purity of the salts or the precautions taken in drying them before the experiment. This is, however, a matter of great importance, for the preparation of many of these salts in a pure state, free from water, is a very difficult matter; indeed it is almost impossible to obtain some of them in a powdered form and yet entirely anhydrous. Hence, as they weighed the salts first in air and then in a vacuum, a loss of weight may have been due simply to loss of moisture, as Scott has pointed out in the criticism already quoted. If the salts had been weighed first in vacuum and then in air, the presence of a trace of moisture could have had no effect on the result. Baxter and Tilley, and Baxter and Jones employed this method, as did also Scott.

After the present paper was sent to the press, another paper by the experimenters at Geneva has come to our notice.[1] In it the magnitudes of all the assumed abnormalities have been somewhat changed, and the corrections have apparently been given the opposite sign in every case. Criticism of this unexpected development will not be attempted here; it is enough to say that the arguments brought forward above concerning the Harvard results are not in any wise affected by the changes. No hasty investigation can throw light upon any matter of this kind. The details, both as regard purity of materials and precautions in treatment, must be as thoroughly worked out as in a most careful determination of an atomic weight in order that the work may have any significance.

The contents of this paper may be briefly summarized as follows: First, the possible adsorption of gases by solids had not been overlooked in the Harvard investigations; secondly, even if the conclusions of Guye and Zachariadès hold under their conditions, these conclusions do not essentially affect the determinations of atomic weights conducted in the chemical laboratory of Harvard College; and thirdly, in the light of other careful work carried out, not only in this laboratory but also by Scott, it seems improbable that either of the interpretations by Guye and Zachariadès of their own results is free from fault.

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[1] Guye and Zachariadès, *Compt. rend.*, 149, 1122 (December. 1909).