It is to be noted that quite aside from this disagreement, the values of r_C, r_H, r_o, etc., are not constant. The calculation of average values of atomic refraction cannot be accepted as a satisfactory solution of the question before us.

In another paper I shall compare these results with the thermochemical data. In comparison I shall attempt to justify the selection of the 8 hydrocarbons as a basis for the calculation of the average values r_{CH_2}, r_C and r_H.

WARSAW, POLAND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY.]

THE EXPLANATION OF AN APPARENT ANOMALY OUTSTANDING IN THE RESULTS OF MEASUREMENT OF DISSOCIATION PRESSURES.

BY ALAN W. C. MENZIES.

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After brief reference to the nature of the anomaly in question and to the various explanations offered to account for it, it is proposed to adduce experimental results, supported by results of a parallel nature drawn from the work of others, to show that this apparent anomaly is disposed of by a knowledge of the real facts of the case.

The Nature of the Anomaly.—In 1888, Tammann,[1] applying a form of the gas-current saturation method to the measurement of the dissociation pressures of salt hydrates near 35°, obtained results which, while somewhat erratic,[2] were uniformly higher by from 2 to 5% than the results obtained by Frowein[3] with the tensimeter. This anomaly was confirmed by Schottky,[4] working under Nernst's guidance, who found that the initial dissociation pressures developed in tensimetric measurements were higher than the equilibrium values. In 1911, Partington[5] added further confirmation, again using the gas-current saturation method, although not in a form identical with Tammann's.

Explanation of the Anomaly.—Thoughtful elucidations and critical discussions have been offered by Tammann,[6] Nernst,[7] Partington,[6] Brereton Baker,[8] and Campbell,[9] those of Nernst and of Campbell being especially instructive. Lack of space forbids their outlining or consideration here.

[1] Tammann, *Ann. Physik.*, **33**, 322 (1888).

[2] Cf. Menzies, THIS JOURNAL, **42**, 978 (1920).

[3] Frowein, *Z. physik. Chem.*, **1**, 5 (1887).

[4] Schottky, *ibid.*, **64**, 415 (1908).

[5] Partington, *J. Chem. Soc.*, **99**, 466 (1911).

[6] *Loc. cit.*

[7] Nernst, *Z. physik. Chem.*, **64**, 425 (1908).

[8] Baker, *Ann. Rep. Progress Chem.*, **8**, 34 (1912).

[9] Campbell, *Trans. Faraday Soc.*, **10**, 195 (1914).

Possible Sources of Experimental Error in Earlier Measurements.—Because it will be shown below that the real facts exhibit no anomaly, it seems desirable, for the sake of progress, to take space to indicate very briefly a few points at which error might have entered into the experimental work of the previous investigators. References to Tammann's work may be omitted[1] for brevity, because he himself was not satisfied with his results. With regard to Schottky's tensimetric results, it will be shown below that considerable pressures of permanent gas, which may be referred to as air, occasionally develop in Bremer-Frowein tensimeters after exhaustion. Schottky must have suspected this, for he allowed his tensimeters to lie in the horizontal position, with the opposite sides in free communication, for 12 hours prior to erection for observation. When, after erection, one bulb of the tensimeter is raised to the higher temperature, as was done in his work, not only will the dissociation pressure on that side increase but so also will the air pressure. But air is soluble in paraffin oil, which Schottky used, as well as in all common manometric liquids except mercury. One would, therefore, predict, in accordance with Henry's law, that Schottky should find, in the presence of air, exactly what he did find, an initial excess of pressure that slowly fell off to the true equilibrium value as the air pressures on opposite sides slowly became equalized by the mechanism of solution and diffusion of air in the oil. With regard to Partington's work, it is suggested that glasswool plugs[2] should not be used to filter rather small volumes of air of 100% humidity, if the humidity is later to be assumed as 100%. Partington does not state whether he corrected for the error that so long escaped the vigilance of Berkeley,[3] who pointed it out some years after Partington's work; nor even whether the more obvious correction for change of air pressure due to the head of water in his saturator was duly applied. Frowein assumed perhaps too lightly the absence of permanent gas from his tensimeters. Campbell points out that the observed static vapor pressure of water in air is less than in a vacuum; while this may be true, the difference in work like Tammann's is not such as to allow his results to be harmonized with Frowein's, as will appear from the evidence given below.

A Re-investigation of the Facts.—In view of notorious precedent in the case of Charles II and the Royal Society of London, it seemed worth while, despite the weight of triple authority cited above, to seek a still simpler explanation of the anomaly than those hitherto offered by once again critically examining the experimental facts. The dissociation pressure of the same sample of cupric sulfate pentahydrate was accord-

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[1] *Vide* ingenious criticism by Campbell, *loc. cit.*

[2] Cf. Menzies, *loc. cit.*

[3] *Nature*, **95**, 54 (1915).

ingly measured, near 25°, by both the gas-current saturation method and by the tensimetric method.

Experimental Procedure.—As comparative and not absolute measurements were contemplated, especial care was not taken to remove traces of impurity from the blue vitriol employed; this was, however, of the highest analytical quality, was free from chloride and contained less than 0.02% of iron. The absolute bath temperature was, however, known with needless accuracy, being measured by averaging the corrected readings of 2 mercurial thermometers graduated to 0.1°, each furnished with Reichsanstalt certificate of corrections rounded to fiftieths. The temperature of the experiments was actually near 24.70°, and the slope of Frowein's *p-t* curve was used in making the necessary small correction to reduce the values to 25.00°

(*A*) *Gas-current Saturation Method.*—In order to test his results, a procedure like Partington's was followed. The water saturators were, however, of the Kahlenberg type,[1] 3 in series, each exposing a surface of about 5 × 25 cm. of water. A gentle agitation of the saturators was provided. Especial care was taken to minimize the surface condensation error.[2]

In view of the known phenomena of induction periods preceding the first loss of water from uneffloresced crystals,[3] the blue vitriol was converted to trihydrate to the extent of a few per cent. by gentle warming in air.[4] Even with crystals powdered so as to pass a 20-mesh sieve, a column 40 cm. long and of 1.1 cm. diameter was not sufficient to saturate at 25° air passing at 250 cc. per hour; while a column 35 cm. long and of 4.8 cm. diameter proved adequate even with somewhat faster air currents. The more important connections were furnished with ground-glass joints, whose lubricant was removed prior to weighing; other joints were of rubber, coated with paraffin wax, which is satisfactory if the weights of vapor transferred are not too small. The water-absorption tubes, containing calcium chloride and phosphorus pentoxide, were weighed against counterpoises of similar total displacement and external surface, containing air at barometric pressure. The complete apparatus was borne by a single ring-stand, and could be submerged beneath the water of a rapidly stirred water-thermostat kept constant to 0.01°. The air stream was not faster than 0.5 liter per hour, and no correction was required for pressure differences due to friction. The necessary correction, referred to above, for difference of volume of air emerging from water and blue vitriol saturator was, of course, applied. Each run occupied over 40 hours.

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[1] *Science*, July 21, 1905.

[2] Cf. Menzies, *loc. cit.*

[2] Cf. Rae, *J. Chem. Soc.*, 109, 1229 (1916).

[4] Cf. Guareschi. *Atti accad. sci. Torino*, 50, 765 (1915).

(*B*) *Tensimetric Method.*—Frowein's procedure was purposely followed rather closely. Instead of sulfuric acid, however, freshly fused potassium hydroxide, coarsely powdered while yet hot, was preferred.[1] A sample of cottonseed oil of density 0.9165 at 25° served as manometric liquid. Evacuation was effected, through a phosphorus pentoxide tube, by a mercury pump, and the pressures before sealing off, always less than 0.01 mm. of mercury, were read on a McLeod gage. A millimeter scale was transferred from a steel standard to the glass arms of the tensimeter by means of a beam compass. The instruments were immersed in the thermostat already referred to, which had 2 opposite sides of glass. Parallax was eliminated by the use of a scale of similar length to that of the tensimeter placed on the distant side of the tank. Equilibrium was reached within 24 hours in the cases reported below, although the tensimeters were allowed to remain in the bath for many days.

After equilibrium had been attained, the pressure of air in the apparatus was approximately determined, and so corrected for, by immersing the blue vitriol bulb in alcohol cooled below —50° by solid carbon dioxide. The value of this correction was as much as 0.3 mm. of mercury. To find whether, perhaps, this air was liberated only when the water of hydration left the blue vitriol in the process of efflorescence, an experiment was tried with but a small weight of slightly effloresced crystals in the tensimeter. This tensimeter showed much less air (0.06 mm. of mercury) after attaining equilibrium. This result points to the persistance of the air, during evacuation, as an adsorbed layer on the blue vitriol. The air liberated from the glass surface during the operation of sealing off is probably, in this case, a negligible factor.[2] Andreae,[3] in his careful comparative work, also encountered to a like extent difficulty with adsorbed air.

Experimental Results.—(A) The only 2 non-preliminary measurements by the gas-current saturation method gave 7.83 and 7.78 mm. of mercury at 0° as the dissociation pressure at 25.00° of the system $CuSO_4$-(5–3)H_2O and vapor: average, 7.80 mm.

(*B*) The only 2 non-preliminary measurements by the tensimetric method gave 7.72 and 7.76 mm.; average, 7.74. Such results are over 5% higher than Frowein's values.

In spite of precautions to avoid condensation of saturated water vapor before reaching the absorption tubes, the results under (*A*) would be expected to turn out too high by a fraction of one per cent., in conformity with the consistent results of Berkeley and Hartley.[4] As the results

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[1] Cf. Baxter and Starkweather, THIS JOURNAL, **35**, 2038 (1916).

[2] Cf. Shrader, *Phys. Rev.*, **13**, 437 (1919).

[3] Andreae, *Z. physik. Chem.*, **7**, 241 (1891).

[4] Berkeley and Hartley, *Trans. Roy. Soc. London* (*A*), **209**, 177 (1909); cf. Menzies, *loc. cit.*

stand, therefore, it is obvious that the discrepancy is well within the experimental error of such measurements. And thus the anomaly disappears.

Comparison of the Results of Frowein with Those of Others.—As it would appear from the above that the results of Frowein, on which much reliance has been placed, are too low in this instance, it was thought well to compare his results for other salts with the available values obtained by later workers who have used the static method. This comparison is exhibited in Table I, in which the results of Andreae,[1] E. Cohen[2] Schottky, and Bolte[3] have been utilized. Frowein's values for barium chloride dihydrate and for strontium chloride hexahydrate were obtained by interpolation from the straight line obtained by plotting log p against $1/T$, using his mean experimental values.

TABLE I.

Comparison of Dissociation Pressure Results by Static Method.

A. Hydrate.	B. Temperature, ° C.	C. Press. in mm. Hg acc. to Frowein.	D. Press. in mm. Hg acc. to Andreae.	E. Excess of D over C. %.
$SrCl_2.6H_2O$	19.7	4.88	5.61	15
	25.6	7.77	8.72	12
	29.9	10.8	11.84	10
	34.1	14.7	15.83	8.0
	37.55	18.7	19.86	6.3
$MgSO_4.6H_2O$	...	...	Cohen	..
	30.75	18.35	18.96	3.4
$BaCl_2.2H_2O$	...	...	Schottky	..
	29.95	7.69	7.96	3.5
	34.95	11.38	11.62	2.2
	36.20	12.32	12.99	5.4
$MgSO_4.6H_2O$	...	...	Bolte	..
	30.75	18.35	18.92	3.1

The duplicate measurements of Cohen and of Bolte are very much more concordant than those of Frowein for the same salt; but this means little, for the latter obtains in other cases excellent concordance for duplicates each suffering severely from the same systematic error. It is evident from Table I that the results of Frowein are several per cent. too low for these salts also, and not alone for cupric sulfate.

Summary.

(1) The experimental results of Tammann, Schottky and Partington have been outlined so as to elucidate an anomaly that is outstanding at the present time, namely, that the dissociation pressures of salt hydrates appear higher as measured by the gas-current saturation method than

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[1] *Loc. cit.*

[2] Cohen, *Z. physik. Chem.*, **36**, 517 (1901).

[3] Bolte, *ibid.*, **80**, 338 (1912).

by the tensimetric method; and that early readings in a tensimetric measurement are higher than later ones.

(2) The suggested explanations of Tammann, Nernst, Campbell, Partington and Brereton Baker have been referred to.

(3) A number of criticisms, which it is hoped may be helpful to other workers, have been offered of the experimental work of users of both tensimetric and gas-current saturation methods.

(4) An experimental re-examination of the facts has been described.

(5) It has been shown that the real facts exhibit no anomaly.

(6) Reason has been given for accepting the tensimetric results of Frowein, often regarded as standard, only with caution.

PRINCETON, N. J.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE STABILITY OF ATOMS AS RELATED TO THE POSITIVE AND NEGATIVE ELECTRONS IN THEIR NUCLEI, AND THE HYDROGEN, HELIUM, H_3, H_2 THEORY OF ATOMIC STRUCTURE.

BY WILLIAM D. HARKINS.

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The purpose of this article is to extend the theory presented in the earlier papers[1] of this series, the first of which were published in 1915. Using as a basis the evidence obtained from the electrolysis of solutions, from the positive ray work of Thomson,[2] and from the atomic weights of the elements and of the separate atomic species, insofar as the latter were then known, the writer presented the theory that the nuclei of all atoms are made up of positive and negative electrons, and evidence was presented which indicated that the nuclei of hydrogen atoms are positive electrons. It will be pointed out later in the present paper that in the light nuclei there are in general about half as many negative as positive electrons, and that in no known complex nucleus is the ratio of negative to positive less than one to two.

The theory indicated that the deviation of the atomic weight of helium (3.969 when calculated on the basis of hydrogen as 1) from a whole number, is due to a "packing effect" which amounts to a decrease of mass equal to 0.77%. This theory was based on the idea of Rutherford[3] that the nucleus of the atom is very minute. That there is a decrease of

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[1] THIS JOURNAL, **37**, 1367–1421 (1915); **38**, 186–214 (1916); **39**, 856–879 (1917); **41**, 970–992 (1919); *Phil. Mag.*, **30**, 723–734 (1915); *Science, N. S.*, **46**, 419–427, 443–448 (1917); **50**, 577–82 (1919); *Proc. Nat. Acad. Sci.*, **1**, 276 (1915); **2**, 216–224 (1916); *Phys. Rev.*, **15**, 73–94 (1920); *Z. anorg. Chem.*, **97**, 175 (1916).

[2] Thomsen, "Rays of Positive Electricity," Longmans, Green and Co. (1913).

[3] Rutherford, *Phil. Mag.*, **21**, 669 (1911); **26**, 702 (1913); **27**, 448 (1914).