

NOTES.

Changes in Volume during Solution. III.—A request for information as to the change in volume occurring during the solution in water of a certain substance for which experimental evidence is lacking, led to the devising of the following method, which, while it offers no new idea, still may be of interest:

The principle involved¹ is that the "apparent" volume of a salt in solution, *i. e.*, the difference between the volume of the water and volume of the solution, at high dilution is made up of two quantities determined by the nature of the ions of the salt. Although it is not possible to determine with certainty either of the two separately, the two together may be variously found, for instance by subtracting the change in volume when the salt dissolves from the volume of the salt. If the "apparent" volume concerned refers to equivalent amounts of material and is known for two pairs of ions, *i. e.*, potassium chloride and sodium bromide, as well as for one of the other two possible combinations, *i. e.*, sodium chloride, the "apparent" volume for the fourth combination, *i. e.*, potassium bromide, may be found by difference. Knowing the "apparent" volume in solution of potassium bromide as well as the molecular volume of potassium bromide, by subtraction one may find the change in volume during solution of potassium bromide.

In the following specimen calculations the data are taken from the paper of Baxter and Wallace² on changes in volume during the solution of the salts of the alkalis in water. The quantities are given in cc. and refer to gram molecular quantities of material at 25°.

POTASSIUM BROMIDE.

	KCl.	NaBr.	NaCl.
Molecular volume.....	37.5	33.1	27.0
Change in volume during solution at infinite dilution....	—10.4	—7.9	—9.6
"Apparent" volume of salt in solution.....	27.1	25.2	17.4
"Apparent" volume of potassium bromide in solution = 27.1 + 25.2 — 17.4 = 34.9.			
Change in volume during solution of potassium bromide at infinite dilution = 34.9 — molecular volume = 34.9 — 43.3 = —8.4.			
The observed value is — 8.8.			

Lithium Iodide.

	LiCl.	CsI.	CsCl.
Molecular volume.....	20.5	57.6	42.4
Change in volume during solution of infinite dilution....	— 2.9	0.5	— 2.4
"Apparent" volume of salt in solution.....	17.6	58.1	40.0
"Apparent" volume of lithium iodide in solution = 17.6 + 58.1 — 40.0 = 35.7.			
Change in volume during solution of lithium iodide at infinite dilution = 35.7 — molecular volume = 35.7 — 33.0 = 2.7.			
The observed value is 3.0.			

The agreement of the calculated and observed values is satisfactory,

¹ Valson, *Compt. rend.*, 73, 441 (1871); and others.

² THIS JOURNAL, 38, 70 (1916).

in view of the fact that the values at infinite dilution are all obtained by extrapolation. Furthermore it is worth while to call attention to the negative value obtained in the case of potassium bromide while lithium iodide yields a positive value.

At higher concentrations the method gives somewhat less satisfactory, although fairly accurate results. Since the "apparent" volume of a dissolved salt varies with the concentration, usually increasing with increasing concentration, it is necessary to use the appropriate values for the change in volume during solution.

The particular case at point is that of calcium carbonate, the solubility of which is so low as to preclude obtaining experimental evidence.

CALCIUM CARBONATE AT 25°.

	CaCl ₂ .	Na ₂ CO ₃ .	2NaCl.
Molecular volume.....	51.6 ¹	41.9 ²	54.0
Change in volume during solution at infinite dilution...	-32.2 ³	-23.5 ⁴	-19.2
"Apparent" volume of salt in solution	19.4	18.4	34.8
"Apparent" volume of calcium carbonate in solution =	19.4 + 18.4 - 34.8 = 3.0.		
Change in volume during solution of calcium carbonate at infinite dilution =	3.0 - molecular volume = 3.0 - 36.9 ⁵ = -33.9.		

This value for the contraction during solution is over 90% of the volume of the solid salt. Apparently the large contraction is about equally due to the calcium and the carbonate ions.

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Lecture Experiment on Vapor Pressure of Solutions.—The well-known fact that the vapor pressure of a liquid is lowered by a dissolved solid—provided the solid itself has no perceptible vapor pressure and the vapor consists of the pure solvent—is usually demonstrated *at room temperature*, by introducing the solutions and the solvent in the Torricellian vacuum of different barometer tubes. By mounting the tubes within a jacket, connected with a distilling flask, the phenomenon can be shown for any desired temperature, by choosing a suitable distilling liquid for keeping the tubes at the required temperature.

A very simple apparatus, by which it is possible to demonstrate the lowering of the vapor pressure at the *boiling point* (under atmospheric pressure) of the solvent—thus directly connecting with the ebullioscopic methods for molecular-weight determinations—is the following: A cylin-

¹ Richards and Hönigschmid, THIS JOURNAL, 33, 32 (1911).

² Richards and Hoover, *Ibid.*, 37, 105 (1915).

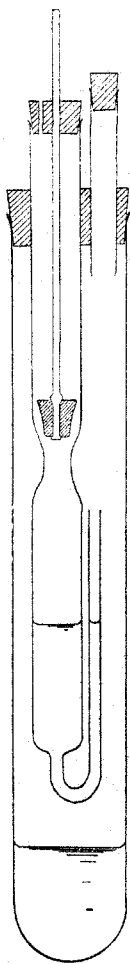
³ Unpublished result by Baxter and Goode.

⁴ Lamb and Lee, THIS JOURNAL, 35, 1685 (1913). (A small correction has been applied, since the experiments were made at 20°.)

⁵ Landolt-Börnstein-Roth.

drical vessel, 30 cm. long with an inner bore of 5 cm.,¹ in which the solvent is boiled, serves as a constant temperature bath. This jacket is closed by a two-hole cork stopper, carrying a tube (inner bore 2 cm.) with a constriction half-way down and ending in a narrow tube (inner bore 5 mm.), bent upward as indicated in the figure. A short piece of glass tubing (inner bore 1 cm.) serving as outlet for the escaping vapor is run through the other hole in the stopper.

The inner tube can be shut off in the constricted part by a cork stopper, tightly held by a glass rod, which is loosely run through another cork, so as to allow an easy upward and downward movement of the rod. A



ground-glass stopper affords a certain advantage, but is not absolutely necessary, provided gas-tight corks can be obtained. Pure solvent is poured in the outer jacket and also in the inner tube, filling both the wide and the narrow limb of the U-tube to a height of about 7 cm. above the bend. A trace of some anilin dye can be safely added in order to make any difference in level better visible at a distance. Owing to capillarity the liquid stands a little higher in the narrow (gage) tube. The difference in level may be neglected in a qualitative experiment of this kind, since it usually does not amount to more than two or three mm. The solvent in the jacket is then slowly heated over a small Bunsen or Teclu burner, suitably provided with a chimney, while the stopper is removed from the outlet tube. As soon as the vapor condenses on the walls of the outlet tube and escapes in the open, the air is removed and the outlet is closed. The vapor of the solvent then enters into the gage tube, heats the liquid in the test tube up to its boiling point, and escapes through the constricted neck, expelling at the same time the remaining air. After the vapor has bubbled through for a few minutes, the cork stopper—about 3 mm. above the neck—has been sufficiently heated and is pushed down, while at the same time the stopper is removed from the outlet tube, thus allowing the vapor to escape directly, as before in the open. The liquid in the inner tube ceases to boil, but is kept at constant temperature (the boiling point of the solvent) and is in equilibrium with its vapor. It will be seen that the level in the gage tube is practically the same as inside the test tube. The neck stopper is then removed and a weighed quantity, perhaps 0.3 g.,

¹ The exact dimensions may be derived from the figure, which includes a scale in cm. divisions.

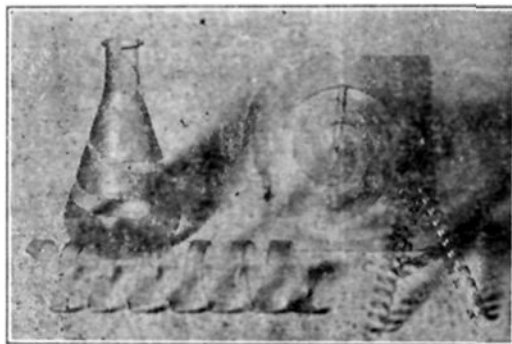
of some solid, easily dissolved in the chosen solvent, is introduced, preferably in the form of a tablet, and the operation is repeated. After equilibrium has been established, a difference in level of two or more cm. will be observed, the liquid standing at a lower level in the gage tube. On adding the same quantity of solute once more and repeating the above operation, the fall of the level in the narrow tube will be, on reaching equilibrium, about twice as much as before. A good solvent for a lecture demonstration is carbon tetrachloride, on account of its low boiling point (76°) its low surface tension (the capillary ascension being negligible) and its non-inflammability. As solute naphthalene or any other organic compound which can be compressed in tablets and dissolves readily in this solvent may be used.

The above-described method of heating the solution by means of the vapor of the solvent has been used by a great many investigators on ebullioscopic molecular-weight determinations: Sakurai, Landsberger, Walker and Lumsden, Ladenburg, Eykman, Smits, Beckmann, McCoy, and lately Menzies.¹ The last-named devised an apparatus similar to the one described here though more complicated, allowing quantitative measurements of molecular weights, solely based on the observed pressure differences, without any thermometer. The apparatus, proposed in this note, does not require for its construction any particular skill in glassblowing, can be easily set up and gives, in the limited time usually available for lecture experiments, very satisfactory results.

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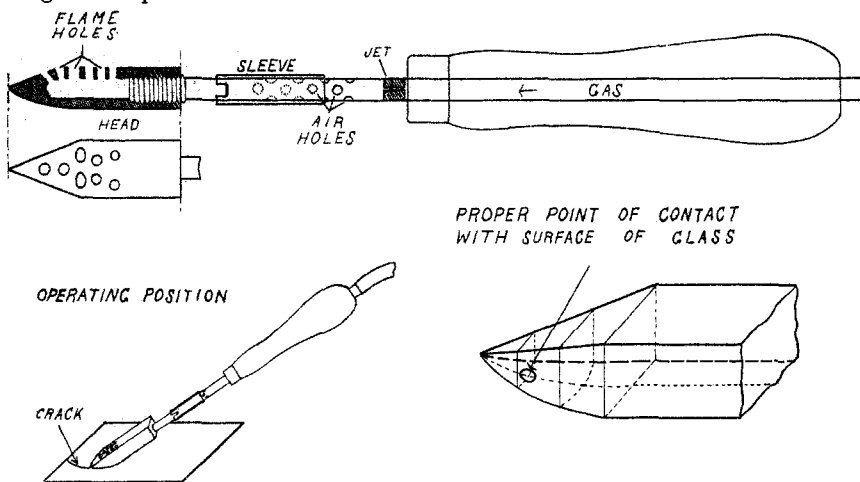
A New Glass-Cutting Tool.—The cutting of large glass tubing with the hot point of a file is a common-place operation in chemical laboratories, but in the case of more complicated forms of apparatus the process is somewhat difficult and uncertain. Description is here given of a tool, constructed in this laboratory, which extends the method to a considerable degree. The fundamental requirement is a point that may be kept hot continuously; a crack once started should be kept moving in the right direction until the cut is completed; the success of the whole method depends upon the sudden, uniform expansion of a small area immediately in front of the crack.



The tool consists of a small, hollow head of brass or copper in which

¹ THIS JOURNAL, 32, 1615 (1910).

ordinary gas is burned, which is brazed or screwed onto a metal tube, through which the gas is supplied. The flow of gas should be regulated so that the flame will "strike back" and burn within the head. The diagram explains itself. The crack is started with a diamond or file



scratch and led in the desired direction with the hot, pointed end of the tool. The shape indicated has given the best results. With the head of the tool constantly red hot, it is an easy matter to cut glass into almost any shape desired, as indicated in the photograph.

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Substituting the Term Adduction for Oxidation.—The August number of *THIS JOURNAL*, page 1619, contains a short article on "Elements neither Free nor Combined. A Third State," in which I referred incidentally to substituting the term adduction for oxidation, giving what appeared to me to be good reasons. This being merely incidental in this article, I did not repeat the history of the term, as that was given by me in the second reference cited at the end as also on page 105 of a recently published book on "Electrochemical Equivalents." It was there acknowledged that this term was apparently first suggested for similar reasons by Dr. M. L. Hamlin in a paper by Nelson and Falk in *THIS JOURNAL*, 35, 1812 (1913), and independently by Dr. Frederick H. Getman in 1916, who had not seen this prior suggestion. I take pleasure in again repeating that the term was first suggested by Dr. Hamlin, and as there are very good reasons for its substitution for the antiquated, inconsistent and irrational term oxidation, I hope this new and rational term will meet with favor.

CARL HERING.

A Method for Preventing Salts from Creeping over the Sides of Evaporating Dishes.—In the course of mineral or soil analysis it is frequently necessary to evaporate saline solutions to smaller volumes or to complete dryness to expel ammonium salts. When, during evaporation, the solution becomes saturated and solids separate on the sides of the dish, the deposited solids, particularly if calcium and magnesium chlorides be present along with ammonium chloride, have a tendency to draw the less concentrated solution further up the sides of the dish and deposit crystals there. If determinations are left to run overnight or unwatched in the daytime, they are frequently ruined in this manner.

Creeping can easily be prevented by painting a strip about $\frac{1}{4}$ inch wide around the inner rim of the dish with collodion. Salts will not creep over this strip. The collodion dries immediately after being put on so there is no time lost in this operation. The film contains no non-volatile residue and can easily be burned off.

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CORRECTIONS.

On p. 1568 of our paper on Heterogeneous Equilibria between Aqueous and Metallic Solutions,¹ the statement is made that by the extrapolation of the logarithmic curve (curve No. 3, Fig. 4, p. 1563), a C_0 value of 2.32 is obtained at an amalgam concentration of 0.225 milli-equivalent per 10 g. of mercury. And this value, 2.32, is subsequently made use of in the paper as the actual C_0 value.

Also, on p. 1569, it is stated that C_0 values at certain other amalgam concentrations are similarly obtained by the extrapolation of curves 1, 2 and 4, in Fig. 6.²

Owing to an unfortunate confusion of the zero point on the (log. total salt concn. $\times 10$) abscissa, Fig. 4, p. 1563, with an actual salt concentration of zero, it was concluded that values of C_0 could be obtained by the extrapolation of the logarithmic curves. This error has just been discovered. The values arrived at are not the C_0 values in question, but the corresponding C_c values for the 0.1 *N* mixed salt solution (since $0 = \log 0.1 \times 10$).

This error will necessitate a new study of the experimental data in the case of the sodium-strontium chloride mixtures; and this we hope to have ready for publication in the near future.

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Nov. 17, 1917.

¹ THIS JOURNAL, 39, 1545 (1917).

² The statement should be "in Fig. 4;" owing to a typographical error, Fig. 6 is mentioned at this point.