ber of operations. The actual time for the fusion, dilution and comparison is short. With a standard prepared the actual working time of the method is less than an hour. The only process requiring time is for the sulfuric acid to cool to room temperature and this can be facilitated by use of a constant temperature bath.

The sample of the titanium-bearing substance is usually most conveniently brought into solution by fusing with potassium acid sulfate. The fusion can be taken up in concentrated sulfuric acid and, after adding an excess of thymol in sulfuric acid, diluted to a definit volume and the color compared in a colorimeter with a standard titanium solution.

MADISON, WIS.

NORMAL AND ABNORMAL CASES OF SPECIFIC VOLUME OF BINARY LIQUID MIXTURES.

BY H. S. VAN KLOOSTER.

Received December 11, 1912.

A recent communication of Mr. A. L. Hyde,[1] concerning the specific gravity of paranitrotoluene dissolved in carbon bisulfide, led me to look for some cases of normal and abnormal specific volumes. A close inspection of the available data led me to the conclusion that the case of paranitrotoluene and carbon bisulfide cannot be qualified as an abnormal one, as was suggested by Mr. Hyde.

It is well known that the properties of aqueous solutions are highly influenced by electrolytic dissociation and probably by the formation of hydrates. To eliminate these factors in studying the properties of mixed liquids it is desirable to choose, for examination, such pairs of substances as do not show such abnormal behavior. One of the first investigators in this field of research seems to have been Guthrie,[2] who studied the volume changes and thermal effects attending mixtures of some organic liquids. He also determined the vapor pressures of binary mixtures and thereby anticipated the most valuable work of Konowalow, Young, Kuenew, Lawidsky, and others. The experiments of Lawidsky[3] form the starting point for the accurate and very interesting determinations of specific volume at different temperatures of binary organic liquids, executed by Hubbard.[4] His results are discussed in the light of Dolezalek's theory of chemical reactions between the two components.[5] The experiments were executed on substances that are not closely related to each other, such as carbon bisulfide and methylal, acetic acid and benzene,

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[1] THIS JOURNAL, 34, 1507 (1912).

[2] *Phil. Mag.*, [5] 18, 495 (1884).

[3] *Z. physik. Chem.*, 35, 129 (1900).

[4] *Ibid.*, 74, 207 (1910).

[5] *Ibid.*, 64, 727 (1908).

and others. In all these cases the relation between specific volume and concentration by weight is *not* linear. On the other hand, this will be the case if the volume change in mixing is insignificant. A strictly linear relation is found especially with homologous substances. Thus a close proportionality between specific volume and concentration can be calculated from the specific gravities of mixtures of methyl and ethyl iodides as determined by Lam[1] and from the data given by Reid[2] for mixtures of methyl and ethyl benzoates.

The same will be the case for closely related substances as bromobenzene and chlorobenzene, where Young[3] observed no change of volume in mixing these liquids in equimolecular proportions. In most cases, however, there occur volume (and thermal) changes in the process of mixing, which involve corresponding changes in specific volume, in such a way that the observed specific volumes are more or less *higher* than the values calculated from the stated rule of mixtures. A large number of these cases are studied by Guthrie[4] and more completely by Hubbard.[4] The latter plotted graphically the difference between observed and calculated specific volumes (at temperatures of 25°, 35°, 17° and 50°) Δv against the concentration by weight as abscissas and obtained curves showing a maximum (with the exception of the curve for acetone chloroform). These curves were compared with similar curves referring to vapor pressure and refractive index in their dependence from concentration. As to the Δv-curves, they arrive at a higher maximum by raising the temperature. In the case of acetone chloroform the observed minimum went farther down with rising temperature. It is highly regrettable that Hubbard did not extend his determinations over a larger range of temperature, especially as there seem to be indications of the case of maximum turning into a minimum with falling temperature (carbon tetrachloride and benzene). So far as can be judged now, it must be considered too wide a generalization to derive from the deviations of the strictly additive properties the existence of intermediate compounds as Guthrie, for instance, did from the abnormal vapor-pressure curve of mixtures of chloroform and carbon bisulfide. Indeed the specific volume curve, which I determined[5] for mixtures of these liquids, only shows a small deviation (in maximo 0.005) from the rectilinear decline and no indication is found for the proposed compound $CS_2.CHCl_3$.

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[1] *Z. angew. Chem.*, 1898, 125.

[2] *Amer. Chem. J.*, **45**, 496 (1911).

[3] *Stoichiometry*, 1900, p. 257.

[4] *Loc. cit.*

[5] The determinations of the specific gravity were made with a Westphal balance and a specific gravity bottle at the constant temperature of 15°, based on water of 15° as unit.

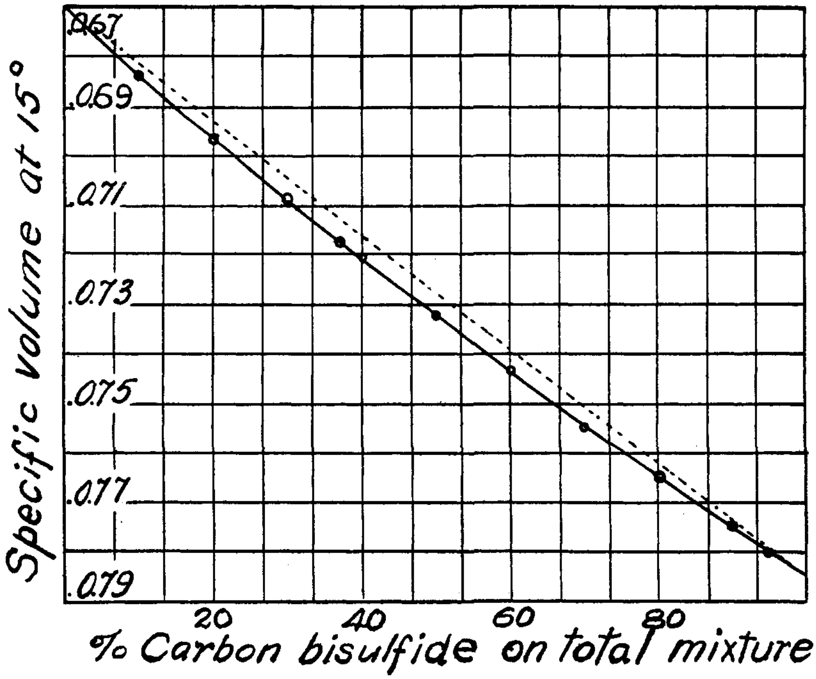

Fig. 1.

TABLE I.—SPECIFIC GRAVITY AND SPECIFIC VOLUME OF MIXTURES OF CARBON BISULFIDE AND CHLOROFORM AT 15°.

% CS_2 by weight.	d^{15}_{15}.	Corresponding spec. vol. v.	Calculated spec. vol. v_c.	$\Delta v = v - v_c$.
0	1.492	0.670	0.670	0.000
10	1.462	0.684	0.681	0.003
20	1.435	0.696^5	0.693	0.003^5
30	1.410^5	0.709	0.705	0.004
37	1.393^5	0.717^5	0.712^5	0.005
40	1.387^5	0.720^5	0.715^5	0.005
50	1.365	0.732^5	0.727^5	0.005
60	1.345	0.743^5	0.739	0.004^5
70	1.324^5	0.755	0.750^5	0.004^5
80	1.307	0.765	0.762	0.003
90	1.289^5	0.775	0.773^5	0.001^5
95	1.280	0.780	0.779^5	0.000^5
100	1.273	0.785	0.785	0.000

A similar behavior is shown by a totally different substance, paranitrotoluene, when dissolved in carbon bisulfide. Here the difference between observed and calculated specific volume Δv is equally positive and amounts in maximo to 0.003. This is the case studied by Mr. Hyde. Now the paranitrotoluene is under normal circumstances a solid with a specific gravity of 1.2860 (Hyde[1]), melting at 54° (Schiff,[2] Neubeck[3]). The density in the liquid state is much smaller: $d_{54} = 1.123$ (Schiff[1]). Calculating from the formula of Schiff, based on the densities in the liquid state, which run from 54° to 66°, the value 1.147 for d_{20}. Taking into account both the observations of Schiff and those of Neubeck, who executed determinations of the specific gravity in the range of 177° to 239°, a smooth curve can be drawn, by plotting specific volume against temperature, from which, by extrapolating graphically for 20°, the value 0.867[5] is derived, giving 1.152 for d_{20}, a value that differs only slightly from the above calculated one.

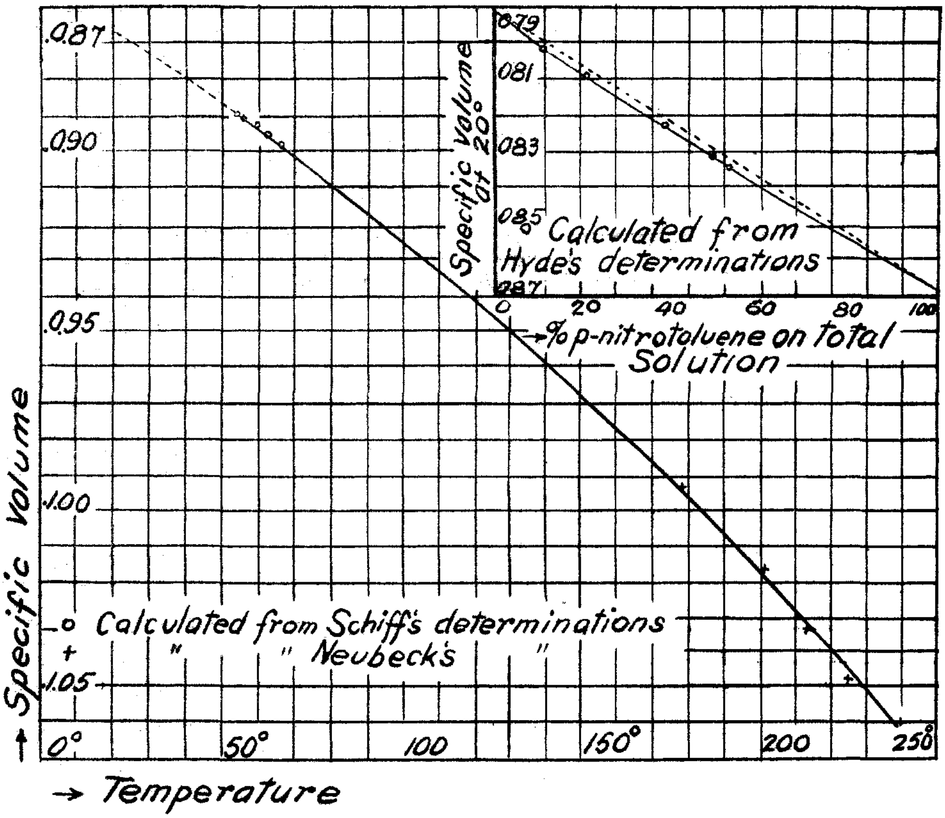

Fig. 2

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[1] *Loc cit.*, p. 1508.

[2] *Ann.*, 223, 261 (1884).

[3] *Z. physik. Chem.*, 1, 659 (1887).

TABLE II.—SPECIFIC GRAVITY AND SPECIFIC VOLUME OF *p*-NITROTOLUENE IN THE LIQUID STATE AT DIFFERENT TEMPERATURES.

Temperature.	Observed sp. gr.	Corresponding spec. vol.
20°	[Calc. 1.152]	0.867^{5}
54°	1.123 Schiff	0.890^{5}
55.4°	1.122^{5} "	0.891
59.3°	1.119 "	0.893
62.3°	1.117 "	0.895
66°	1.113 "	0.898^{5}
177.5°	1.007 Neubeck	0.993
201°	0.984 "	1.017
213°	0.968 "	1.033
225°	0.954^{5} "	1.048
239°	0.943 "	1.060

(Attempts to test this value by undercooling the molten paranitrotoluene failed, as undercooling could not be driven so far beneath the melting point.)

TABLE III.—SPECIFIC GRAVITY AND SPECIFIC VOLUME OF MIXTURES OF *p*-NITROTOLUENE AND CARBON BISULFIDE AT 20°.

% *p*-nitrotoluene by weight.	d_{15}^{20} (Hyde).	Corresponding spec. vol. v.	Calculated spec. vol. v_C.	Δv.
0	1.266	0.790	0.790	0.000
11.4	1.249	0.801	0.799	0.002
20.9	1.237	0.808	0.806	0.002
38.4	1.215^{5}	0.823	0.820	0.003
49.3	1.203^{5}	0.831	0.828	0.003
53	1.199	0.834	0.831	0.003
100	...	...	0.867^{5} *	...

Table III gives the observations of Hyde, the corresponding values of specific volume and the theoretical values for the specific volume, calculated from the specific gravities of carbon bisulfide: $d_{20} = 1.266$ (Hyde) and of molten paranitrotoluene: $d_{20} = 1.152$ (Schiff and Neubeck). The curve shown on the right hand side of Fig. 2 gives a close analogy to that of Fig. 1.

Finally, I wish to call the attention to a really abnormal case (already noticed by Guthrie),[1] *i. e.*, of chloroform and ether. He showed, first, that the rise of temperature on mixing ether and chloroform in different proportions by weight is a maximum for 61.8% $CHCl_3$ (*i. e.*, 1 mol. $CHCl_3$ + 1 mol. $C_4H_{10}O$) and then that exactly at this monomolecular ratio (on mixing at constant temperature various concentrations of both liquids) a maximum contraction takes place. The abnormal viscosity curves, obtained by Thorpe and Rodger[2] are a further support for this conception. The scanty determinations of specific gravity for

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* Extrapolated from Schiff's and Neubeck's values for the sp. gr.

[1] *Loc. cit.*, 508.

[2] *J. Chem. Soc.*, 71, 360 (1897).

mixtures of these two substances by Tsakalotos[1] and by Thorpe and Rodger[2] lead to the surprising result that the difference Δv (observed specific volume — calculated specific volume) for all examined mixtures is *negativ* and reaches for the equimolecular concentration or thereabout a minimum (after Tsakalotos, $\Delta v_{18.2°} = -0.015$, after Thorpe and Rodger, $\Delta v_{0°} = -0.012$) of relatively high value. The case of chloroform-acetone gives also a minimum, though of much smaller values (0.002). It would be highly interesting to extend these determinations of specific gravities, to obtain a good insight into the displacement of this minimum by change of temperature, and to examin whether lowering of the temperature finally leads to a separation of the supposed compound in the solid state. An investigation in this direction by studying the cooling curves of the binary mixtures of *this couple* is planned in this laboratory.

INORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY,
GRÖNINGEN, HOLLAND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UTAH EXPERIMENT STATION.]

SOME FACTORS INFLUENCING THE QUANTITATIVE DETERMINATION OF ARSENIC IN SOILS.[3]

BY J. E. GREAVES.

Received October 22, 1912.

Since it has been announced that arsenic occurs in many virgin soils[4] and that it may, on account of its extensive use as an insecticide, accumulate in soils to such an extent as to become injurious to vegetation,[5] the principles involved in its accurate determination are of considerable practical importance at the present time. Many methods, both qualitative and quantitative, have been proposed for its determination in soil, but even the most modern[6] do not make allowance for the influence of the iron in the soil upon the quantitative determination of the arsenic.

That arsenic is retained by iron when the Marsh method is used for its determination was first shown by Parson and Stewart,[7] and later corroborated by the work of Harkins.[8] These investigators found that the arsenic retained by the iron increased as the iron introduced with the

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[1] *Z. physik. Chem.*, 74, 743 (1908).

[2] *Loc cit.*, p. 370.

[3] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[4] Headden, *Proc. Colo. Scientific Soc.*, 9, 349 (1910).

[5] Headden, Colo. Exp. Sta., *Bull.* 131 and 157.

[6] *Mai. Pharm. Centr.*, 50, 169–200; Headden, *Colo. Sci. Soc.*, 9, 348 (1910); Haywood, U. S. Dept. of Agr., Bur. of Chem., *Bull.* 113 (revised), 58.

[7] Parson and Stewart, THIS JOURNAL, 24, 1905 (1902).

[8] Harkins, *Ibid.*, 32, 518 (1910).