

TABLE I

Dehydration of alcohols			Olefins		Name	Hexanes		
Alcohol	T., °C.	Catalyst	B. p., °C.	Yield, %		B. p., °C.	d_4^{20}	n_D^{20}
Ethyl- <i>n</i> -propylcarbinol	350	Al ₂ O ₃	63-68	92	<i>n</i> -Hexane	68.74-68.78	0.6595	1.3752
Dimethyl- <i>n</i> -propylcarbinol	122	I ₂	64-66	94	2-Methylpentane	60.22-60.26	.6532	1.3718
Methyldiethylcarbinol	120	I ₂	65-69	95	3-Methylpentane	63.16-63.21	.6642	1.3775
Pinacol	130-150	HBr	70.4	55	2,3-Dimethylbutane	57.82-58.02	.6612	1.3750
Pinacolyl ^a	400	...	40.8-41	96	2,2-Dimethylbutane	49.80-49.82	.6493	1.3692

^a Alcohol converted to the acetate and the ester pyrolyzed to obtain the olefin.

formed in the dehydration of pinacol¹ is pinacolone, which was utilized in the preparation of pinacolyl alcohol. *t*-Butylethylene was prepared by the thermal decomposition of pinacolyl acetate.² Eighty per cent. of the acetate was converted to the olefin and acetic acid by one passage through the reaction tube, packed with glass wool, and the unchanged acetate was recovered in nearly theoretical amounts. The olefins were readily hydrogenated to the corresponding hexanes by means of platinum oxide catalyst³ and the products were finally purified by washing with sulfuric acid and refluxing over sodium.

The fractionation of the hexanes was carried out in a small glass spiral column having an efficiency of twenty theoretical plates, and the boiling points, appropriately corrected, are those of at least 95% of the chemically purified products. The densities were determined by the pycnometric method, and the refractive indices were obtained by means of an Abbe refractometer.

(1) Kyriakides, *THIS JOURNAL*, **36**, 980 (1914).

(2) Whitmore and Rothrock, *ibid.*, **55**, 1106 (1933).

(3) Adams and Shriner, *ibid.*, **45**, 2171 (1923).

RESEARCH DIVISION
GENERAL MOTORS CORPORATION
DETROIT, MICHIGAN

RECEIVED NOVEMBER 2, 1935

The Vapor Pressure of Silicon Tetrachloride

BY K. KEARBY

The vapor pressure of silicon tetrachloride has been measured by Regnault,¹ Becker and Meyer,² and Stock, Somieski and Wintgen.³ The values obtained by the first and last of these investigators are in fair agreement. Those of Becker and Meyer are much higher, namely, by 50% at 0°, 20% at 10° and 10% at 20°. Their measurements were made on a sample of silicon tetrachloride which they considered of excellent quality. The measurements of Stock, Somieski and Wintgen

(1) H. V. Regnault, *Mem. de l'acad. royale des Sciences de l'Institut de France*, **26**, 339 (1862).

(2) W. Becker and J. Meyer, *Z. anorg. allgem. Chem.*, **43**, 261 (1905).

(3) A. Stock, Somieski and Wintgen, *Ber.*, **50**, 1754 (1917).

were made on only 0.3 g. of silicon tetrachloride which they considered pure, but they do not describe the method of purifying it. Thus it is seen that considerable discrepancy exists among the available data.

Recently⁴ the author had occasion to prepare some very pure silicon tetrachloride and make a few vapor pressure measurements on it. Later, with a view of clearing up the above situation, additional measurements were made.

Materials and Apparatus

A kilogram of silicon tetrachloride, 99.3% pure, was refluxed over mercury in a current of pure, dry nitrogen for four hours. It was then fractionally distilled in a series of wetted wall, glass fractionating columns, using large reflux ratios. Three fractionations were made in an atmosphere of pure nitrogen, and three *in vacuo*. The last fraction yielded about 25 cc. of pure silicon tetrachloride which was sealed off in several thin bulbs which were attached to the evacuated system. Freshly distilled mercury was used in the manometer, the pressures on which were read with a cathetometer accurate to 0.1 mm. The manometer and the tube to which it was attached, containing the bulb of silicon tetrachloride, were thoroughly evacuated and torched before breaking the bulb of silicon tetrachloride. This apparatus was placed in a thermostat constant within 0.02°. Temperatures were measured on a calibrated thermometer accurate to 0.02°.

The pressures thus measured, expressed in millimeters of mercury at 0° and a force of gravity of 980.665 cm. per sec. per sec. are given in the table.

TABLE I

Temp., °C.	Pressure, mm.	Temp., °C.	Pressure, mm.
0	77	35	346
5	98	40	419
10	124	45	501
15	153	50	599
20	191	55	709
25	235	60	839
30	287		

These results can be expressed, with a maximum deviation of 1%, by the empirical equation $\log p = 7.6414 - 1572.3/T$. From this equation the

(4) S. S. Kistler and K. Kearby, *Acta Physicochimica (U. R. S. S.)*, **1**, 354 (1934).

boiling point at 760 mm. pressure is found to be 57.0°.

These results are found to be in fair agreement with those of Stock, but are considered more accurate. The values of Becker and Meyer are clearly too high.

UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED OCTOBER 5, 1935

Note on the Calculation of Activity Coefficients and of Molal Volumes

By O. REDLICH, P. ROSENFELD AND W. STRICKS

Recently Pearce and Blackman¹ published measurements on vapor pressures and specific gravities of aqueous solutions of calcium and aluminum nitrates. On this occasion, they find that the series given by Lewis and Randall² for the activity of the solvent can be represented by the formula $\ln a_1 = \ln [1 - (p_1^0 - p_1)/p_1^0]$. We may add, moreover, that $a_1 = p_1/p_1^0$, this relation being the *origin* of the above mentioned series.

Further, Pearce and Blackman develop the solution volume (*i. e.*, the volume of the quantity containing 1000 g. of water) in a series in terms of the molarity: $V = \alpha + \beta m + \gamma m^2$. On a previous occasion it has been shown that a similar series can by no means account for the behavior of dilute solutions of strong electrolytes³; on the basis of the Debye-Hückel theory it can be proved that a term with $m^{3/2}$ is indispensable. So it is not at all surprising that the differences between observed and calculated values in Tables III and IV show a distinct trend.

The constants α , β and γ are determined by Pearce and Blackman according to the method of least squares. The authors calculate in fact the constant α also from their measurements on solutions of calcium and aluminum nitrate, ignoring completely that this constant representing the volume of 1000 g. of water is determined by the specific gravity of pure water. This quantity, however, is not actually measured by the authors, but forms the basis of their measurements (the

(1) J. N. Pearce and L. E. Blackman, *THIS JOURNAL*, **57**, 24 (1935).

(2) G. N. Lewis and M. Randall, "Thermodynamics," New York, 1923, Chapter XXII, Eqn. (34). A misprint in this equation, reproduced in the German translation (Wien, 1927), was retained by J. N. Pearce, M. D. Taylor and R. M. Bartlett, *THIS JOURNAL*, **50**, 2951 (1928), and was corrected in later papers without a special reference. The series, appropriate only in the case of very dilute solutions, has repeatedly been applied by Pearce and collaborators to rather concentrated solutions.

(3) O. Redlich and P. Rosenfeld, *Z. Elektrochem.*, **37**, 705 (1931); *cf. Z. phys. Chem.*, **A155**, 65 (1931).

volume of the pycnometer being determined by means of it); it cannot be legitimately derived therefore from their results. The procedure applied by them leads to the consequence that the specific volume of water depends on the nature of substances which are dissolved in zero concentration (volume of 1000 g. water = 1002.9621 cc. from calcium nitrate solutions, and 1003.0730 cc. from aluminum nitrate solutions).

Calculating the apparent molal volume of calcium nitrate from the data of Pearce and Blackman and plotting this quantity against square root of concentration (the usefulness of such proceedings being shown in the papers mentioned above), we obtain a curve which is markedly convex toward the $c^{1/2}$ axis for dilute solutions; we do not know any other strong electrolyte of similar behavior. Therefore we evaluated the data given for solutions of calcium nitrate by some former observers and by "I. C. T.," Vol. III; none of these data give a curve of apparent molal volume of similar curvature. The differences between the values of Pearce and Blackman and the older figures are considerable. We have not found adequate data for a comparison in the case of aluminum nitrate.

A paper on the calculation of activity coefficients, to be published shortly in the *Sitzungsber. Akad. Wiss. Wien*, will contain a few additional remarks.⁴

INSTITUT FÜR PHYSIKALISCHE CHEMIE

AN DER TECHNISCHEN HOCHSCHULE

WIEN

RECEIVED JUNE 12, 1935

Addition.—We are much obliged to the Editor for the opportunity of examining the contribution of Professor Pearce, "The Vapor Pressures and the Activity Coefficients of Aqueous Solutions of Calcium and Aluminum Nitrate at 25° (Correction)," before its publication. In view of this contribution we would wish only to state that the activity coefficients of calcium nitrate at 25°, calculated from freezing points and used by us as reference values, are to be published in Landolt-Börnstein, "Tabellen," III. *Ergänzungsband*; the differences between the values at freezing temperature and at 25° have been derived from heats of dilution [E. Lange, H. Streeck, *Z. physik. Chem.*, **A157**, 1 (1931)] and from specific heats [C. Marignac, *Ann. chim. phys.*, [5] **8**, 410 (1876);

(4) The activity coefficients of LiNO₃, NaCl, NaBr, KI, HClO₄, calculated by us from vapor pressures given by Pearce and collaborators, are to be found in Landolt-Börnstein-Roth-Scheel, "Tabellen," III. *Ergänzungsband* (to be published). The differences between the activity coefficients of these authors and our results are considerable.