NOTES

The Heat of Hydrogenation of Diisobutylene

By Bryce L. Crawford, Jr., and George S. Parks

A value for the change in heat content on the hydrogenation of "diisobutylene" to 2,2,4-trimethylpentane was recently needed in connection with a thermodynamic study in this Laboratory. From a critical review of the available combustion data we were able to deduce $\Delta H^\circ_{298} = -28{,}100$ (± 3000) cal. for the reaction involving the diisobutylene and isooctane in the liquid state. In view of the uncertainty in such a value, we decided to attempt also a direct calorimetric measurement for the heat of this reaction.

A 500-cc. Pyrex flask served as the calorimeter proper and the reaction chamber; initially in a determination it contained 150 cc. of liquid diisobutylene, which was gradually hydrogenated to yield a solution of 2,2,4-trimethylpentane in diisobutylene. This reaction flask was fastened to a shaking device and was equipped with a water jacket, adjustable in temperature, so that the calorimetric procedure could be made approximately adiabatic in character. Purified hydrogen was led into it from a gas train through a flexible glass connecting-tube; and the temperature rise, coinciding in time with the adsorption of measured quantities of hydrogen, was determined by a copper–constantan thermocouple in conjunction with a White potentiometer. The temperature relations of the calorimeter and jacket were also determined by a thermocouple and the temperature adjustment of the jacket was made by regulated electrical heating. The hydrogenation process was catalyzed by freshly prepared platinum black, suspended in the olefin in the reaction flask. The process was carried out between 24 and 35°. Calibration of the calorimetric apparatus was made electrically in a series of blank experiments in which pure trimethylpentane was substituted for the olefin, correction being made for the small difference in the heat capacities of these hydrocarbons.

Three series of determinations, involving fifteen "runs," yielded an average value of $\Delta H^\circ_{298} = -28{,}580$ cal. for the reaction

$$C_8H_{16}\,(l) + H_2\,(g) = C_8H_{18}\,(l)$$

on the assumption that the trimethylpentane–diisobutylene solution is approximately perfect. As shown by Fenske, Quiggle and Tongberg [*Ind. Eng. Chem.*, **24**, 414 (1932)], the diisobutylene is really a mixture containing 4 parts of 2,4,4-trimethylpentene-1 and 1 part of 2,4,4-trimethylpentene-2. The heats of hydrogenation of these two olefins may differ by perhaps 500 cal., if we may judge by the very precise results obtained for the isomeric butenes by Kistiakowsky, Ruhoff, Smith and Vaughan [This Journal, **57**, 876 (1935)]. Considering this factor and also the experimental errors incidental to the measurements, we believe that the maximum error in the above ΔH°_{298} value, when this is assigned to the hydrogenation of the 2,4,4-trimethylpentene-1, is within 800 cal. Such a result is considerably more reliable than that obtainable from the combustion data, although at present much less accurate than the hydrogenation values obtained by Kistiakowsky and collaborators with their vapor phase apparatus at 355°K. It might be noted in this connection that our value for diisobutylene is probably most comparable, on theoretical grounds, with theirs for isobutene (about $-28{,}140$ cal. per mole calculated to 298°K.).

Before concluding, we wish to thank Mr. Benjamin Holt and Mr. Harold Scheeline for their help in the measurements.

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The Preparation of the Isomeric Hexanes

By Paul L. Cramer and Maurice J. Mulligan

In connection with the studies in this Laboratory of the aliphatic hydrocarbons, the isomeric hexanes have been prepared in large amounts and of a high degree of purity, and it seemed desirable to indicate the methods of preparation and also to present their physical constants, which in a few instances vary somewhat from previously recorded values, Table I.

The general alcohol–olefin–paraffin method was employed in their syntheses. The alcohols were prepared by the usual methods and their dehydrations were carried out by the procedures indicated in Table I. The main side reaction product

TABLE I

Dehydration of alcohols			Olefins		Hexanes			
Alcohol	T., °C.	Catalyst	B. p., °C.	Yield, %	Name	B. p., °C.	d^{20}_4	n^{20}_D
Ethyl-*n*-propylcarbinol	350	Al_2O_3	63–68	92	*n*-Hexane	68.74–68.78	0.6595	1.3752
Dimethyl-*n*-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 pinacol[1] 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 catalyst[3] 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).

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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 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.

Recently[4] 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

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(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, 251 (1905).

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

(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.

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Note on the Calculation of Activity Coefficients and of Molal Volumes

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

Recently Pearce and Blackman[1] 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 Randall[2] 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 electrolytes[3]; 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 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 FUR PHYSIKALISCHE CHEMIE
AN DER TECHNISCHEN HOCHSCHULE
WIEN

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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);

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(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).

(4) The activity coefficients of $LiNO_3$, NaCl, NaBr, KI, $HClO_4$, 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.

"I. C. T.," Vol. V, p. 123]. Concerning the reliability of Marignac's data, *cf.*, *e. g.*, T. W. Richards and A. W. Rowe [THIS JOURNAL, **43,** 776 (1921)].

NOVEMBER 20. 1935

OTTO REDLICH
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The Vapor Pressures and the Activity Coefficients of Aqueous Solutions of Calcium and Aluminum Nitrate at 25° (Correction)

BY J. N. PEARCE

Shortly after the publication of the paper[1] on "The vapor pressures and the activity coefficients of aqueous solutions of calcium and aluminum nitrate," two of my students discovered an unfortunate error in the activity coefficients of the ions of these salts. This error arose through the use of an erroneous conversion factor for planimeter readings. All of these data have been recalculated and replotted independently by these students, and the results have been checked by the writer. The corrected data are given in the accompanying tables.

TABLE I

VAPOR PRESSURE, ACTIVITY AND FREE ENERGY DATA OF AQUEOUS SOLUTIONS OF CALCIUM NITRATE AT 25°

m	p, mm.	a_1	$h/m^{1/2}$	$\gamma_\pm$	$-\overline{\Delta F}_1$, cal.	$-\Delta F_2^{0,1}$, cal.
0.0	23.752	1.0000	1.365	1.0000	....	...
.1	23.659	0.9961	0.8686	0.3894	2.32	...
.2	23.566	.9922	.6075	.3250	4.72	911
.4	23.373	.9841	.4043	.2754	9.53	1849
.6	23.160	.9751	.2861	.2585	14.96	2458
.8	22.915	.9647	.1902	.2574	21.26	2962
1.0	22.638	.9531	.1109	.2644	28.48	3406
1.5	21.868	.9207	− .0159	.2940	48.98	4316
2.0	21.002	.8843	− .0979	.3381	72.88	5077
2.5	20.042	.8438	− .1626	.3971	100.7	5759
3.0	19.107	.8044	− .1976	.4556	129.0	6328
3.5	18.118	.7628	− .2306	.5290	160.5	6868
4.0	17.098	.7198	− .2603	.6171	194.9	7379
5.0	15.008	.6319	− .3125	.8441	272.1	8334
6.0	13.062	.5499	− .3446	1.1240	354.5	9167
7.0	11.260	.4741	− .3677	1.4688	442.4	9917
8.0	9.603	.4043	− .3869	1.9034	536.8	10616
8.3601[a]	9.041	.3806	− .3950	2.0957	572.5	10865

[a] Saturated. $a_2 = 4(\gamma m)^3$.

TABLE II

VAPOR PRESSURE, ACTIVITY AND FREE ENERGY DATA OF AQUEOUS SOLUTIONS OF ALUMINUM NITRATE AT 25°

m	p, mm.	a_1	$h/m^{1/2}$	$\gamma_\pm$	$-\overline{\Delta F}_1$, cal.	$-\Delta F_2^{0,1}$, cal.
0.0	23.752	1.0000	2.895	1.000	....	...
.1	23.648	0.9956	1.2315	0.1970	2.60	...
.2	23.500	.9894	0.5790	.1711	6.33	1311
.4	23.235	.9782	.3723	.1291	13.05	2285
.6	22.860	.9624	.1474	.1355	22.69	3363
.8	22.405	.9433	− .0146	.1517	34.61	4313
1.0	21.911	.9224	− .1202	.1718	47.88	5137
1.5	20.386	.8583	− .3382	.2587	90.61	7065
2.0	18.561	.7814	− .5034	.4102	146.2	8845
2.5	16.678	.7013	− .6088	.6382	210.3	10422
3.0	14.860	.6256	− .6762	.9599	278.0	11823
3.1607[a]	14.370	.6050	− .6786	1.0608	297.8	12183

[a] Saturated. $a_2 = 27(\gamma m)^4$.

In making these calculations we have assumed that the activity of the solvent, a_1, is equal to the relative humidity, or $a_1 = p_1/p_1^0$. The activity coefficients have been calculated by means of the equation of Randall and White,[2] namely

$$\log \gamma = -h/2.303 - 2/2.303 \int_0^{m^{1/2}} (h/m^{1/2}) \mathrm{d}m^{1/2}$$

where $h = 55.51 \ln a_1/\nu m + 1$. The value of the integral was determined by means of a polar

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[1] Pearce and Blackman, THIS JOURNAL, **57**, 24 (1935).

[2] Randall and White, *ibid.*, **48**, 2514 (1926).

planimeter. The remaining symbols of the tables have their usual significance.

IOWA CITY, IOWA RECEIVED JULY 10, 1935

The Preparation of Glass Helices for Use in Fractionating Columns

BY WILLIAM G. YOUNG AND ZENE JASAITIS

The separation of *cis*- and *trans*-2-butene[1] and of crotyl and methylvinyl-carbinyl bromides[2] by means of a column packed with broken glass helices clearly demonstrates that it is possible to carry out quantitative separations on isomeric mixtures with this type of packing and unless the separation requires the maximum possible efficiency it may be accomplished with an inexpensive fractionating column. However, the preparation of these glass helices[3] has been a slow and tedious process requiring considerable skill.

With the coöperation of National Youth Administration students, Messrs. Roland Icke, Robert Kreiss and Lawrence Richards, we have modified the method of winding and breaking the glass helices so that a satisfactory product may be prepared in one-fifth the time previously required.[3c]

Winding the Helices.—One end of the 3.2 mm. steel rod[3c] is held in a loose metal or wood bearing while the other end is fastened to a variable speed laboratory stirring motor which is clamped on a ring stand. The molten Pyrex or soft glass is fed to the rapidly turning steel rod with the right hand, leaving the left hand free to move the blast-lamp along the rod at a uniform speed. With the rod turning at a rate of 380–400 r. p. m., it is possible to make 36 helices 45 cm. long in one hour. The volume of the unbroken helices amounts to 400–425 ml. compared to 150 ml. previously reported,[3c] while the volume of broken helices obtained equals 60 ml. compared to 15 ml. The fiber diameter of the coils may be varied from 0.2 to 0.9 mm. by regulating the speed of the motor and the temperature of the molten glass as it is fed to the winding form. The helices made in this way are uniform throughout and very closely wound.

Breaking the Helices.—The long spirals which are strung on a No. 18 Chromel wire are brought in contact with the hot wire by rubbing a glass rod from one end of the spiral to the other two or three times. The spirals are then broken by gently rubbing a short section between the thumb and forefinger in a direction parallel to its long axis. The resulting product contains 10.5% of helices of less than one-half turn per coil, 6.2% between one-half and three-fourths turns, 8.6% between three-fourths and one turn, 51.5% of one turn, 15.6% between one and two turns and 7.6% about two turns. The spirals turn slightly as they are rubbed against the wire, thus making it possible for the majority of the helices to be one turn or more. Since the rings cling together it is possible to remove everything below three-fourths of a turn by gently shaking 10–15 ml. at a time. Although the product averages slightly more than one turn per coil and is very satisfactory for most purposes its efficiency may be further increased by carefully sorting out the helices of less than one turn as previously described.[3c]

The following data have been obtained for helices made from 6-mm. soft glass rod as described above:

Fiber size, mm.	0.2–0.3	0.3–0.4	0.5
Total volume, ml.	10[a]	10	10
Number of helices	1700	1600	1100
Glass, g.	2.24	3.24	5.26
Vol. of glass, ml.	0.9	1.3	2.12
Surface area, sq. cm.	140	150	170
% of free space	91	87	79

[a] Volumes were measured in a graduated cylinder 12 mm. in diameter.

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[1] Kistiakowsky and co-workers, THIS JOURNAL, **57**, 876 (1935).

[2] Winstein and Young, *ibid.*, **58**, 104 (1936).

[3] (a) Wilson, Parker and Laughlin, *ibid.*, **55**, 2795 (1933); (b) **56**, 1396 (1934); (c) Roper, Wright, Ruhoff and Smith, *ibid.*, **57**, 954 (1935).