TABLE I

CONCENTRATIONS OF ISOPIESTIC SOLUTIONS OF POTASSIUM CHLORIDE AND SODIUM OR POTASSIUM THIOCYANATE

Sodium Thiocyanate

Molality KCl	Molality NaCNS	Molality KCl	Molality NaCNS	Molality KCl	Molality NaCNS
0.1639	0.1608	0.9447	0.8832	2.896	2.555
.1647	.1616	1.097	1.018	3.122	2.745
.2840	.2757	1.298	1.192	3.124	2.746
.4053	.3911	1.428	1.307	3.373	2.938
.5170	.4923	1.506	1.374	3.717	3.228
.5170	.4930	1.887	1.705	3.895	3.384
.5929	.5627	1.970	1.776	4.229	3.641
.7354	.6910	2.226	1.993	4.249	3.650
.8624	.8045	2.621	2.326	4.622	3.982

Potassium Thiocyanate

KCl	KCNS	KCl	KCNS	KCl	KCNS
0.1639	0.1648	1.033	1.035	3.448	3.597
.3057	.3046	1.701	1.728	3.656	3.846
.5170	.5185	1.887	1.923	3.754	3.936
.5904	.5933	2.121	2.167	4.132	4.371
.6770	.6787	2.442	2.507	4.301	4.562
.8624	.8624	2.915	3.020	4.623	4.925

There do not appear to be any data with which the results on sodium thiocyanate may be compared. Data on the potassium salt are also meager; Gibson and Adams[6] have made direct vapor pressure measurements over the concentration range 4.589 to 17.328 M at 20.28°. Redlich and Rosenfeld[7] have calculated activity coefficients from their results with reference to a value of $\gamma = 1$ at 4.589 M. Referred to $\gamma = 0.531$ at this concentration the data of Gibson and Adams lead to activity coefficients which decrease almost linearly with the concentration

(6) R. E. Gibson and L. H. Adams, THIS JOURNAL, **55**, 2679 (1933).

(7) Landolt-Börnstein, "Tabellen," Dritter Ergänzungsband, p. 2146.

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF SODIUM AND POTASSIUM THIOCYANATE

m	NaCNS φ	NaCNS γ	KCNS φ	KCNS γ
0.1	0.937	0.787	0.926	0.769
.2	.934	.750	.911	.716
.3	.935	.731	.904	.685
.5	.943	.715	.898	.646
.7	.954	.710	.896	.623
1.0	.969	.712	.896	.600
1.5	.998	.725	.894	.574
2.0	1.029	.751	.896	.558
2.5	1.061	.784	.901	.548
3.0	1.093	.820	.908	.542
3.5	1.126	.860	.913	.537
4.0	1.160	.911	.918	.533
4.5	...	...	.923	.531
5.0	...	...	.927	.529

to a value of $\gamma = 0.486$ at 17.328 M. It may be shown graphically that the present data and those of Gibson and Adams are consistent.

The activity coefficient curves of these two thiocyanates are not symmetrical with those of the alkali halides. The curve given by potassium thiocyanate is lower than that for potassium chloride and intersects the curve for rubidium chloride at about 3.3 M. The curve for sodium thiocyanate is lower than that for sodium iodide and intersects the curve for sodium bromide at about 3 M.

Summary

Solutions of sodium and potassium thiocyanate have been compared with potassium chloride at 25° by isopiestic vapor pressure measurements and the activity coefficients have been evaluated.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 13, 1940

[CONTRIBUTION NO. 202 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF TEXAS]

The Pressure–Volume–Temperature Relations of n-Hexane and of 2-Methylpentane

BY EDWARD A. KELSO[1] WITH W. A. FELSING

Object of the Investigation.—The increasing utilization of petroleum hydrocarbons for diversified purposes is demanding a more extended knowledge of the properties of the individual members. Numerous contributions have appeared in the chemical literature in the last few years on individual hydrocarbons. It was, therefore, one object of this investigation to determine the compressibilities of the hexanes; a report on n-hexane and 2-methylpentane is being made; work on 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane is being carried on now and will be reported later. It is hoped, at that time, to correlate structure with properties for all of the hexanes.

Method and Apparatus.—The apparatus for this investigation has been patterned after that described by Beattie.[2] The mercury injector was thermostated in a

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(2) Beattie, *Proc. Am. Acad. Arts Sci.*, **69**, 389 (1934).

kerosene-bath at 35° and, as a consequence, it was necessary to use molded neoprene packing washers. These washers gave excellent service throughout.

The complete apparatus was carefuly calibrated with mercury. The piston was calibrated by the method of Bridgeman,[3] employing liquid carbon dioxide at 0°, where its vapor pressure is 26,144.7 mm. The average millimeter equivalent of 1 g. on the piston is 2.00107.

The thermostat was constructed similarly to the one described by Beattie.[4] Instead of knife-blade type of heaters, bare wire heaters were installed immediately above the three stirrer tubes; all oil circulated was drawn through these heaters. At the bottom of each stirrer tube there was inserted a centrifugal stirrer, which improved greatly the effectiveness of the stirring, especially at lower temperatures where the oil was fairly viscous. The thermoregulator contained about 400 cc. of mercury and actuated a supersensitive relay; temperatures could be maintained constant at any given temperature to within at least 0.002°. A platinum resistance thermometer, calibrated by the National Bureau of Standards, was used in temperature measurements. The bath fluid was a special high flash-point oil furnished by the Gulf Refining Company.

The Materials Used. (a) ***n*-Hexane.**—This material was prepared in the laboratory by treating purified propyl iodide with small quantities of metallic sodium. After the sodium had slowly reacted, the solid sodium iodide was dissolved by adding water and the aqueous layer was removed. The resulting propyl iodide–hexane mixture was dried with calcium chloride and again treated with a limited quantity of metallic sodium. The process of removing the sodium iodide, drying, and treating with sodium was repeated until an excess of sodium had been added. The final mixture, containing only traces of propyl iodide, was allowed to stand in contact with an excess of metallic sodium for twenty-four hours, after which it was distilled off this excess. It was then treated repeatedly with concentrated sulfuric acid, aqueous sodium carbonate, and with distilled water. After each series of treatments, the hexane was dried by contact with calcium chloride and then distilled off metallic sodium. The final product boiled at 68.72 ± 0.02° (760 mm.), had a density of 0.6594 g./ml. and a refractive index, $n^{20}D$, of 1.3750; these constants agree well with those listed.[5]

(b) **2-Methylpentane.**—Two samples from different sources were employed. One sample was obtained from Dr. Johannes H. Bruun,[6] designated Sample I, and the other from Dr. M. R. Fenske,[7] designated Sample II.

Sample I had a normal boiling point of 60.19 ± 0.05°, a density at 20° of 0.6527 g./ml. and a refractive index, $n^{20}D$, of 1.3711; for Sample II these quantities were 60.25°, 0.6534 g./ml., and 1.3712. Egloff[8] has given a résumé of published physical constants for this substance.

(3) Bridgeman, THIS JOURNAL, **49**, 1174 (1927).

(4) Beattie, *Rev. Sci. Instruments*, **2**, 458 (1931).

(5) (a) Sheppard, Henne and Midgley, THIS JOURNAL, **53**, 1948 (1931); (b) J. H. Bruun and M. M. Hicks-Bruun, *Bur. Standards J. Research*, **6**, 877 (1931); (c) Cramer and Mulligan, THIS JOURNAL, **58**, 374 (1936); (d) Dornte and Smyth, *ibid.*, **52**, 3546 (1930).

(6) Bruun, Hicks-Bruun and Faulconer, *ibid.*, **59**, 2356 (1937).

(7) Pennsylvania State College, State College, Pa.

(8) Egloff, "Physical Constants of Hydrocarbons," Reinhold Pub. Corp., New York, N. Y., Vol. I, p. 37.

The Data.—The experimental results are presented in Tables I and II. The compressibilities of the hexanes in the liquid state were determined at convenient pressure intervals. In the gas phase the pressures were measured at exact densities.

TABLE I

COMPRESSIBILITY OF LIQUID *n*-HEXANE AND 2-METHYLPENTANE

Molecular weight, 86.172. Pressures are in normal atmospheres. Temperatures are on the International Temperature Scale.[a]

Moles/liter	Press., atm.	Moles/liter	Press., atm.
A. *n*-Hexane (C_6H_{14})			
100.00°		125.00°	
6.750	5.60	6.412	5.60
6.771	13.50	6.441	13.50
6.858	48.91	6.554	48.90
6.970	101.52	6.695	101.51
7.068	154.07	6.815	154.06
7.155	206.71	6.915	206.69
7.232	259.36	7.006	259.36
7.303	311.81	7.089	311.81
150.00°		175.00°	
6.068	13.50	5.639	16.11
6.226	48.90	5.831	48.90
6.409	101.51	6.108	101.50
6.553	154.06	6.288	154.05
6.675	206.69	6.434	206.68
6.783	259.36	6.556	259.35
6.877	311.80	6.667	311.79
200.00°		225.00°	
5.189	26.62	4.494	31.89
5.437	48.88	4.906	48.84
5.783	101.49	4.441	101.45
6.012	154.04	5.733	153.99
6.185	206.66	5.945	206.62
6.330	259.32	6.116	259.29
6.454	311.77	6.257	311.73
B. 2-Methylpentane			
100.00°		125.00°	
6.658	5.59	6.301	5.59
6.683	13.49	6.335	13.49
6.776	48.90	6.463	48.90
6.900	101.51	6.620	101.51
7.003	154.05	6.745	154.05
7.094	206.68	6.854	206.68
7.175	259.35	6.951	259.35
7.250	311.80	7.040	311.80
150.00°		175.00°	
5.939	13.49	5.464	16.11
6.124	48.90	5.740	48.89
6.327	101.50	6.018	101.50
6.483	154.05	6.214	154.05
6.613	206.68	6.371	206.68
6.726	259.35	6.502	259.34
6.829	311.80	6.617	311.79

[a] Burgess, *Bur. Standards J. Research*, **1**, 635 (1928).

TABLE I (*Concluded*)

Moles/liter	Press., atm.	Moles/liter	Press., atm.
200.00°		225.00°	
4.953	26.64	4.288	37.21
5.278	48.90	4.664	48.90
5.683	101.51	5.316	101.51
5.933	154.05	5.640	154.06
6.120	206.68	5.868	206.68
6.274	259.35	6.047	259.35
6.403	311.80	6.195	311.80

The density data on these liquid hexanes are believed to be accurate to 0.05% at the lower pressures and temperatures to 0.1 to 0.2% at the higher pressures and temperatures. The uncertainty in the measurement of pressures is less than 0.03%, in the determination of mass less than 0.01%, and in the measurement of volume from 0.05 to 0.1%. Temperature measurements are correct at least to 0.01°.

TABLE II

PRESSURE–VOLUME–TEMPERATURE DATA ON GASEOUS *n*-HEXANE AND 2-METHYLPENTANE

Density, moles/liter	Pressure, atm.	Density moles/liter	Pressure, atm.
	A. *n*-Hexane, 250.00°		B. 2-Methylpentane, 250.00°
1.0	25.56 (T. and Y.)[a]	1.5	34.13
2.5	36.63	2.0	37.73
3.0	38.17	2.5	40.26
3.5	40.85	3.0	42.78
4.0	47.04	3.5	46.66
4.5	62.59	4.0	55.20
5.0	97.48	4.5	73.33
5.5	167.66	5.0	111.72
6.0	297.78	5.5	187.68
	275.00°		275.00°
1.0	29.76 (T. and Y.)[a]	1.5	39.40
2.5	47.06	2.0	45.40
3.0	51.62	2.5	50.50
3.5	58.29	3.0	56.12
4.0	70.35	3.5	64.11
4.5	94.01	4.0	78.56
5.0	139.69	4.5	104.77
5.5	225.36	5.0	153.85
		5.5	243.25

[a] The pressures for a density of one mole/liter are from the data of Thomas and Young, *J. Chem. Soc.*, **67**, 1071 (1895). These values agree well with the values of this investigation within the limits of the experimental accuracy claimed.

In Table III are presented for comparison some results obtained with the two samples of 2-methylpentane in the gas phase. The first five values at the two temperatures for this material, given in Table II (B), are the averages of the values obtained for the two samples as listed in Table III.

TABLE III

COMPARISON OF THE TWO SAMPLES OF 2-METHYLPENTANE

(Pressure in atmospheres)

Moles/liter	Run no. 1 Sample no. 2	Run no. 2 Sample no. 1	Run no. 3 Sample no. 2
		250.00°	
1.5		34.08	34.18
2.0		37.68	37.77
2.5		40.22	40.29
3.0		42.76	42.79
3.5	46.68	46.64	46.66
		275.00°	
1.5		39.33	39.46
2.0		45.36	45.44
2.5		50.48	50.52
3.0		56.13	56.11
3.5	64.07	64.16	64.09

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Summary

1. The compressibilities of liquid *n*-hexane and 2-methylpentane have been determined at 25° intervals from 100 to 225°.

2. The pressure–volume–temperature relations for gaseous *n*-hexane and 2-methylpentane have been determined at different molar volumes at 250 and 275°.

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