Table IV the critical constants obtained in this investigation are compared with the results of other workers. The agreement of our values with those of Benedict,[6] who used the disappearance of the meniscus method, is striking.

TABLE IV

COMPARISON OF THE CRITICAL CONSTANTS OF ISOBUTENE FROM THIS INVESTIGATION WITH THE VALUES OF OTHER AUTHORS

Source	t_0, °C. (Int.)	p_c(normal atm.)	d_c (g./cc.)
This investigation	144.73 ±0.05	39.48 ±0.05	0.234 ±0.002
Coffin and Maass[3]	143.5		
Scheeline and Gilliland[4]	148.9	39.7	
M. Benedict[6]	144.6 ±0.6	39.5 ±0.2	

The prosecution of this work was greatly aided by a fellowship from the Polymerization Process Corporation. We wish to thank the M. W. Kellogg Company for the gift of the isobutene.

(6) Manson Benedict, private communication.

Summary

The vapor pressure of isobutene was measured from 30 to 125°. The equation $\log_{10} p$(atm.) $= 4.3759_2 - (1163.34/T)$ represents the results well and also computes a vapor pressure at 0° in good agreement with that measured by Lamb and Roper.

The critical constants of isobutene determined by the compressibility method are: $t_c = 144.73 \pm 0.05$°C. (Int.); $p_c = 39.48 \pm 0.05$ normal atmosphere; $v_c = 0.240$ liter/mole (4.28 cc./g.); $d_c = 4.17$ mole/liter (0.234 g./cc.). The uncertainty in the critical volume and density is 1%. The critical pressure and temperature given above are in excellent agreement with those determined by Benedict, who used the disappearance of the meniscus method.

The Compressibility of and an Equation of State for Gaseous Isobutene

BY JAMES A. BEATTIE, HENRY G. INGERSOLL AND WALTER H. STOCKMAYER

In earlier papers from this laboratory[1] the compressibilities of methane, ethane, propane, n-butane, and n-heptane have been reported. The properties of the last four substances have been measured in the same compressibility apparatus which has been described elsewhere.[2] We have determined vapor pressures and critical constants of isobutene using a bomb with the glass liner.[2] The compressibility of the same isobutene sample was then measured from 150 to 275° and to densities of 1.5 to 2 times the critical.

The rate of polymerization of isobutene in a glass-lined bomb above 330° has been measured by Krauze, Nemtzov and Soskina.[3] Calculations made from their equations extrapolated to lower temperatures showed that in the time required for a complete compressibility run at one temperature—about ten hours—the effect of the polymerization at 225° would be of the order of the reproducibility of the compressibility measurements. Actually we measured the 250 and 275°

(1) For the last report on this work see J. A. Beattie, G.-J. Su, and G. L. Simard, THIS JOURNAL, 61, 926–927 (1939).
(2) J. A. Beattie, Proc. Am. Acad. Arts Sci., 69, 389–405 (1934).
(3) M. V. Krauze, M. S. Nemtzov and E. A. Soskina, J. Gen. Chem., 5, 382–387 (1935).

isotherms before the effect of the polymerization became serious. As with the other hydrocarbons we measured the pressure along each isotherm from the lowest to the highest density and then repeated some of the measurements at the lower densities as the pressure was decreased. In Table I are given the pressures for the lowest density—1 mole/liter—before and after each set of isotherms as well as the pressure at 150° before and after the complete series of runs. It will be seen that up to 250° the effect of polymerization is small, while at 275° it may have affected the results by as much as 0.5%.

The constants of the Beattie–Bridgeman equation of state for isobutene determined from the compressibility measurements up to the critical density (4.17 mole/liter) are given in Table II and a comparison of the calculated with the observed pressures in Table III. The variation of the c constant of the equation of state with density, which has been noticed for other substances, is quite evident in the case of isobutene. The change in curvature of the isometrics from negative at low density to positive at high density takes place at a density between 3.5 to 4.0 mole/

TABLE I

EFFECT OF POLYMERIZATION OF ISOBUTENE ON THE COMPRESSIBILITY MEASUREMENTS
All values are for a density of 1 mole/liter

Temp., °C.	150	175	200	225	250	275	150
			Pressure, normal atmospheres				
Before isotherm	25.668	28.407	31.087	33.713	36.298	38.836	25.668
After isotherm	25.662	28.409	31.083	33.707	36.284	38.764	25.573[a]
$-\Delta p\%$	0.02	−0.01	0.01	0.02	0.04	0.19	0.37

[a] After the 275° isotherm.

TABLE II

VALUES OF THE CONSTANTS OF THE BEATTIE–BRIDGEMAN EQUATION OF STATE FOR GASEOUS ISOBUTENE, $(CH_3)_2C=CH_2$

$$p = [RT(1-\epsilon)/V^2][V+B] - A/V^2$$
$$A = A_0(1-a/V) \quad B = B_0(1-b/V) \quad \epsilon = c/VT^3$$

R	A_0	a	B_0	b	c	Mol. wt.

Units: normal atmosphere, liter per mole, °K. ($T°K. = t°C. + 273.13$)

| 0.08206 | 16.9600 | 0.10860 | 0.24200 | 0.08750 | 250×10⁴ | 56.0616 |

variation of A, have produced a new equation of state that represents the compressibility of hydrocarbons to twice the critical density.

The relation of the second virial coefficient B_v to intermolecular forces has been the subject of many investigations.[5] The parameter B_v is defined by the relation

$$pV = RT\left(1 + \frac{B_v}{V} + \cdots\right)$$

TABLE III

COMPARISON OF THE PRESSURES CALCULATED FROM THE EQUATION OF STATE WITH THE OBSERVED PRESSURES FOR GASEOUS ISOBUTENE

For each temperature the first line gives the observed pressure and the second gives the observed minus the calculated pressure. The calculated pressures are computed from the equation given in Table II. The critical constants of isobutene are: $t_0 = 144.73°C.$ (Int.), $p_0 = 39.48$ normal atmosphere, $v_0 = 0.240$ liter/mole, $d_0 = 4.17$ mole/liter.

Density, mole/liter Temp., °C. (Int.)	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	8.0	9.0
					Pressure, normal atmospheres								
150 obsd.	25.67	32.92	37.51	40.19	41.62	41.84	42.80	43.19	43.78	47.86	65.66	122.27	254.09
obsd. − calcd.	−0.20	−0.25	−0.15	+0.12	+0.42	−0.02	−0.13						
175 obsd.	28.41	37.49	44.14	49.02	52.74	55.78	58.58	61.58	65.33	78.60	111.26	189.42	
obsd. − calcd.	−0.12	−0.10	+0.05	+0.26	+0.38	+0.10	−0.96						
200 obsd.	31.09	41.88	50.52	57.53	63.52	68.99	74.43	80.48	87.78	110.55	157.54		
obsd. − calcd.	−0.07	−0.07	+0.10	+0.25	+0.25	−0.13	−1.22						
225 obsd.	33.71	46.24	56.76	65.88	74.14	82.11	90.39	99.57	110.58	143.20	204.70		
obsd. − calcd.	−0.07	−0.02	+0.10	+0.22	+0.19	−0.16	−0.96						
250 obsd.	36.30	50.48	62.86	74.06	84.61	95.14	106.26	118.76	133.63	176.16			
obsd. − calcd.	−0.08	−0.06	+0.02	+0.13	+0.14	−0.03	−0.47						
275 obsd.	38.84	54.64	68.86		94.98		122.03		156.56	209.07			
obsd. − calcd.	−0.12	−0.14	−0.11		+0.14		+0.19						
Av. dev. (atm.)	0.11	0.11	0.09	0.20	0.25	0.09	0.66						
Av. % dev.	0.36	0.27	0.18	0.35	0.45	0.13	0.88						

Total average deviation (atm.), 0.218; total average % deviation, 0.380.

liter, considerably below the critical, as is to be expected. Benedict, Webb and Rubin,[4] by expressing c as a function of density by use of two new constants and introducing a third new constant to express more accurately the density

TABLE IV

VALUES OF THE SECOND VIRIAL COEFFICIENTS OF GASEOUS ISOBUTENE DETERMINED FROM THE EXPERIMENTAL DATA

$$B_v = \lim_{1/V \to 0} V\left(\frac{pV}{RT} - 1\right) \quad (T = \text{constant})$$

Temp., °C. (Int.)	B_v, liter/mole
150	−0.2920
175	− .2576
200	− .2260
225	− .1988
250	− .1760
275	− .1568

We have determined B_v for isobutene from plots of our experimental data. These are given in Table IV.

We thank the M. W. Kellogg Company and Dr. Manson Benedict for the gift of the pure sample of isobutene, and the Polymerization Process Corporation for a fellowship which greatly aided this investigation.

Summary

Measurements of the compressibility of gaseous isobutene, $(CH_3)_2C=CH_2$, are reported from 150 to 275° and from a density of 1.0 to 9.0 mole/liter, the maximum pressure being 250 atm.

In a glass-lined bomb isobutene did not poly-

(4) M. Benedict, G. B. Webb and L. C. Rubin, J. Chem. Phys., 8, 334–345 (1940).

(5) See J. A. Beattie and W. H. Stockmayer, Reports on Progress in Physics, 7, 195–229 (1940).

merize seriously during a ten-hour period until 275° was reached.

The constants of an equation of state of gaseous isobutene were determined from the data up

to the critical density; and the values of the second virial coefficients determined from the experimental data are given from 150 to 275°.

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Activity Coefficients of Rubidium and Cesium Sulfates in Aqueous Solution at 25°[1]

BY HERSCHEL H. CUDD[2] WITH W. A. FELSING

Introduction

In a previous paper[3] an experimental modification of the isopiestic method of determining activities of electrolytes was presented. In order to test the apparatus and technique still further and to gain information on the activity coefficients of two of the rarer alkali sulfates, rubidium and cesium, this investigation was undertaken.

No data on the activity coefficients for these salts were found in the literature.

Experimental

Method and Apparatus.—The method employed was the familiar isopiestic method, using the apparatus described by Phillips, Watson and Felsing.[3] The procedure in this investigation differed only in the simultaneous use of 12 solution cups instead of the usual nine; this lengthened considerably the time required for vapor pressure equilibration.

Sodium sulfate was selected as the reference salt.

Purification of Materials. Sodium Sulfate.—The salt was crystallized four times as the decahydrate and was dehydrated according to the procedure of Ephraim.[4] The mass was finally dried at 140°, ground to a fine powder, and re-dried in a vacuum oven at 140° for seventy-two hours. It was stored in a desiccator over Anhydrone. **Rubidium and Cesium Sulfates.**—C. P. samples of these salts were purified according to the directions of Archibald.[5] In addition, each salt was recrystallized twice from conductivity water, dried, and stored over Anhydrone. **Water.**—All water used had a specific conductance of 0.6–0.7 × 10⁻⁶ reciprocal ohms as delivered from the still; as used, its conductance was approximately 1 × 10⁻⁶ mhos.

Preparation of Solutions.—The dry salts were weighed directly from weighing bottles into weight burets by difference. To the weight buret and its contents was added a calculated amount of water.

(1) Constructed from a portion of a thesis presented to the Graduate Faculty of the University of Texas by Herschel H. Cudd in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1941.

(2) Present address: E. I. du Pont de Nemours & Co., Buffalo, N. Y.

(3) Phillips, Watson and Felsing, THIS JOURNAL, 64, 244 (1942).

(4) Ephraim, "Textbook of Inorganic Chemistry" (translated by Thorne), Gurney and Jackson, London, 1934.

(5) Archibald, "Preparation of Pure Inorganic Substances," John Wiley and Sons, New York, N. Y., 1932.

The solutions were weighed from the weight burets directly into the tared solution cups; the weights were checked by weighing the cups and their contents. The precision in weighing was better than one part in 5000, varying with the size of sample; samples ranged from 1.5 to 6.0 g.

The Data Obtained

The isopiestic solutions investigated extended over the concentration range of approximately 0.4 to 1.9 molal. The upper limit was determined by the solubility of rubidium sulfate; the lower limit, as a practical matter, was determined by the times required for the attainment of equilibrium. The data are listed in Table I. The columns M(obs.) − M(calcd.) are the differences between observed values and values calculated from the smoothed curve.

TABLE I

MOLALITIES OF SOLUTIONS OF RUBIDIUM AND CESIUM SULFATES ISOPIESTIC WITH SOLUTIONS OF SODIUM SULFATE AT 25°

Sodium sulfate	Rubidium sulfate		Cesium sulfate	
	M(obs.)	M(obs.) − M(calcd.)	M (obs.)	M(obs.) − M(calcd.)
0.433	0.422	+0.002	0.418	+0.006
.612	.601	+ .017	.565	± .000
.780	.748	+ .008	.715	+ .003
.916	.858	− .005	.811	− .016
1.031	.968	± .000	.923	± .000
1.198	1.118	± .000	1.068	+ .007
1.488	1.383	+ .014	1.303	± .000
1.610	1.486	+ .010	1.412	+ .008
1.715	1.570	+ .003	1.488	− .002
1.800	1.640	− .002	1.563	+ .003
1.875	1.707	± .000	1.631	+ .008

Treatment of Results

From the observed isopiestic molalities there was determined for each salt the isopiestic ratio, $M(\text{Na}_2\text{SO}_4)/M(\text{Rb}_2\text{SO}_4)$ and $M(\text{Na}_2\text{SO}_4)/M(\text{Cs}_2\text{SO}_4)$. These ratios were then plotted against the observed molalities of rubidium and cesium sulfate. From the smooth curve (passing to the origin), there were read off values of the isopiestic ratio at rounded values of the molalities