Our value of 93.50 kcal. for ΔH_0^0 compares with the values, 78.3 kcal., obtained by Baur and Brunner[2]; 80 kcal., reported by Wagman, Rossini, Evans, Levine and Joffe[6]; and 88.8 kcal., given by Kelley.[5] The latter value is based on a single measurement at the boiling point.

Table III gives ΔH_0^0 values for the sublimation heats of the first series of transition elements. These values differ considerably from those in the table given by Seitz,[7] which were based on older data, but still support the contention that cohesive forces are higher for metals with partially filled d shells than for those with completed d shells. Chromium fits reasonably well into the general scheme.

Least square treatment of the vapor pressure data for chromium yields the equation

$$\log P_{\text{atm}} = -(20{,}473/T) + 7.467$$

Summary

The vapor pressure of chromium has been measured over the temperature range 1283 to 1561°K. by determining the rate at which the metal surface evaporates into a vacuum. The ΔH_0^0 values have been calculated from the individual vapor pressure points and show no appreciable temperature trend, the average value being 93.50 ± 0.18 kcal. By combining this value of ΔH_0^0 with Kelley's free energy functions for solid and gaseous chromium, the vapor pressure equation $\log P_{\text{atm}} = -(20{,}434/T) + 7.415$ is obtained. Like the other transition elements of similar crystal structure with unfilled d shells, chromium has a relatively high energy of sublimation.

TABLE III

ΔH_0^0 VALUES FOR THE SUBLIMATION HEATS OF THE FIRST SERIES OF TRANSITION ELEMENTS

Atomic no.	Element	Electronic structure						ΔH_0^0, kcal.
22	Ti[8]	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3d^2$	$4s^2$	111.0
23	V[9]	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3d^3$	$4s^2$	106.0
24	Cr	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3d^5$	$4s^1$	93.5
25	Mn[12]	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3d^5$	$4s^2$	...
26	Fe[10]	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3d^6$	$4s^2$	96.0
27	Co[9]	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3d^7$	$4s^2$	93.0
28	Ni[11]	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3d^8$	$4s^2$	101.1
29	Cu[10]	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3d^{10}$	$4s^1$	80.7
30	Zn[5]	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3d^{10}$	$4s^2$	31.1

[6] D. D. Wagman, F. D. Rossini, W. H. Evans, S. Levine and I. Joffe, National Bureau of Standards (1949) Series I, Table 49-1.

[7] F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 3, 427–429.

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[9] S. Dushman, "High Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949.

[10] A. L. Marshall, R. W. Dornte and F. J. Norton, THIS JOURNAL, **59**, 1161 (1937).

[11] H. L. Johnston and A. L. Marshall, *ibid.*, **62**, 1382 (1937).

[12] The heat of sublimation of manganese is not listed here since its crystal structure is considerably different than that of the other elements in this list.

COLUMBUS 10, OHIO RECEIVED MARCH 17, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Compressibility of and an Equation of State for Gaseous 1-Butene

BY JAMES A. BEATTIE AND STANLEY MARPLE, JR.

In a recent paper[1] we presented measurements of the vapor pressure, orthobaric liquid volume and critical constants of 1-butene made in 1941. The same loading (6.7122 g.) of the sample was used to determine the compressibility[2] of 1-butene from 150 to 250°. The substance was confined in a bomb with a glass liner.[2]

Roper[3] measured the volumetric behavior of 1-butene at low pressures from −75° to +70° from which he derived an equation for the second virial coefficient for the range −30 to +60°. Aston[4] and co-workers computed the second virial coefficient for the temperature range −71 to −6° from measurements of vapor pressures, heats of vaporization, and orthobaric liquid volumes. In the range −31 to −6° these values were in good agreement with those computed from Roper's equation. Olds, Sage, and Lacey[5] measured the compressibility of 1-butene from 38 to 171° and to about 700 atmospheres.

The 1-butene used in the present investigation was furnished by the Linde Air Products Company through the courtesy of Dr. J. M. Gaines, Jr. The increase of vapor pressure with decrease in vapor volume and the slope of the isotherms in the two phase region near the critical point indicated[1] the presence of a moderate amount of impurity which did not seem to be a permanent gas.

Above 200° 1-butene polymerizes rather rapidly. As is the usual procedure we measured the pressures along each isotherm for increasing densities starting with 1 mole per liter. After the completion of the isotherm we remeasured the

[1] J. A. Beattie and S. Marple, Jr., THIS JOURNAL, **72**, 1449 (1950).

[2] For the last paper in this series see J. A. Beattie, S. Marple, Jr., and D. G. Edwards, *J. Chem. Phys.*, **18**, 127 (1950). For a description of the apparatus and method see J. A. Beattie, *Proc. Am. Acad. Arts and Sci.*, **69**, 389 (1934).

[3] E. E. Roper, *J. Phys. Chem.*, **44**, 835 (1940).

[4] J. G. Aston, H. L. Fink, A. B. Bestul, E. L. Pace and G. J. Szasz, THIS JOURNAL, **68**, 52 (1946).

[5] R. H. Olds, B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **38**, 301 (1946).

lowest density. At and above 200° the work was carried on continuously until the 250° isotherm had been completed and the time allowed for equilibrium to be attained after each change in density was reduced to 25 minutes at 225° and 20 minutes at 250°. In addition about one hour was required to increase the temperature of the thermostat 25° and establish thermal equilibrium. The measurements presented in Table I indicate that at 200° the effect of polymerization is very small, at 225° the pressure dropped 0.027 atm. during the four hours of the run, and at 250° the pressure dropped 0.083 atm. during a three-hour period. The values of the vapor pressure at 125° determined before the sample had been above this temperature and after the completion of all of the measurements also indicate the formation of a less volatile substance.

TABLE I

EFFECT OF POLYMERIZATION OF 1-BUTENE DURING THE COMPRESSIBILITY MEASUREMENTS

1. Pressure at a density of 1 mole per liter at the start of an isotherm and after completion of the same isotherm.

Temp., °C. (int.)	150	175	200	225	250
	Pressure, normal atmosphere				
Pressure at start	25.603	28.353	31.028	33.652	36.204
Press. after completion	25.601	28.351	31.021	33.625	36.121
Δp	−0.002	−0.002	−0.007	−0.027	−0.083

2. Vapor pressure at 125° before and after the compressibility measurements

Vapor volume, ml.	78.3	68.4	2.1
	Pressure, normal atmosphere		
Pressure before	27.784	27.787	27.853
Pressure after	27.312	27.438	27.770
Δp	−0.472	−0.349	−0.083

TABLE II

VALUES OF THE CONSTANTS OF THE BEATTIE–BRIDGEMAN EQUATION OF STATE FOR 1-BUTENE

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

Units: normal atmospheres, liters per mole, °K. (T°K. = t°C. + 273.13°)

R = 0.08206
A_0 = 16.6979
a = 0.11988
B_0 = 0.24046
b = 0.10690
c = 300 × 10^4
Mol. wt. = 56.0616

TABLE III

COMPARISON OF THE PRESSURES CALCULATED FROM THE EQUATION OF STATE WITH THE OBSERVED PRESSURES FOR GASEOUS 1-BUTENE

For each temperature the first line gives the observed pressure and the second line gives the observed pressure minus the pressure calculated by the equation given in Table I. The critical constants of 1-butene are t_c = 146.4°C. (Int.), p_c = 39.7 normal atm., d_c = 4.15 moles per liter.

Density, moles/liter Temp., °C. (int.)	1.0	1.5	2.0	2.5	3.0	3.5	4.0	5.0	6.0	7.0	8.0
					Pressure, normal atmospheres						
150 obsd.	25.60	32.76	37.21	39.74	41.02	41.63	41.95	42.66	46.22	63.13	117.33
obsd. − calcd.	−0.21	−0.25	−0.13	+0.16	+0.48	+0.53	−0.24				
175 obsd.	28.35	37.34	43.86	48.60	52.16	55.04	57.69	64.04	76.69	108.07	183.55
obsd. − calcd.	−0.14	−0.12	+0.04	+0.29	+0.45	+0.10	−0.92				
200 obsd.	31.03	41.76	50.24	57.11	62.94	68.23	73.51	86.32	108.30	153.70	248.94
obsd. − calcd.	−0.10	−0.08	+0.07	+0.28	+0.37	+0.06	−0.05				
225 obsd.	33.65	46.08	56.47	65.42	73.51	81.29	89.32	108.98	140.68	199.98	
obsd. − calcd.	−0.10	−0.08	+0.05	+0.23	+0.33	+0.14	−0.54				
250 obsd.	36.20	50.27	62.48	73.50	83.84	94.11	104.93	131.47	172.72	245.26	
obsd. − calcd.	−0.16	−0.17	−0.10	+0.09	+0.24	+0.27	+0.05				
Av. dev., atm.	0.14	0.14	0.08	0.21	0.37	0.24	0.54				
Av. % dev.	0.47	0.36	0.17	0.39	0.68	0.44	0.81				

Total average deviation, 0.25 atm.; total average percentage deviation, 0.47%.

The compressibility results of the present investigation are listed in Table III together with the deviations of the pressures computed by the equation of state of Table II from the observed pressures to a density of 4 moles per liter, just below the critical density. The molecular weight of 1-butene (C = 12.00, H = 1.0077) and the value of the ice point (273.13) used are not the most recently accepted values but are employed to conform with the values used in the earlier work of this laboratory on hydrocarbons.

A comparison of our work with that of Roper is hardly possible since his highest temperature is almost 100° below our lowest. At 50° Roper's equation gives for the second virial coefficient −14.0 atm.-liter²/mole²; extrapolation of the equation of state to this temperature yields −12.7. The highest isotherm studied by Olds, Sage and Lacey is 171.11° (340° F.). Our isometrics were interpolated to this temperature and his compressibility factors (pV/nRT) interpolated to our densities. Their pressures are uniformly higher than ours: from a density of 1 to one of 6 moles per liter the agreement is practically within the error of the double interpolation, their pressures being higher than ours by an average of 0.3%; at 7 and 8 moles per liter their pressures are 3.5% higher than ours.

Summary

The compressibility of gaseous 1-butene from 150 to 250° and from 1 to 8 moles per liter has been measured and the results to 4 moles per liter fitted to an equation of state. The constants of the Beattie–Bridgeman equation of

state of 1-butene (molecular weight 56.0616) are: $R = 0.08206$, $A_0 = 16.6979$, $a = 0.11988$, $B_0 = 0.24046$, $b = 0.10690$, $c = 300 \times 10^4$ in units of normal atmospheres, liters per mole, and °K. (T, °K. $= t° + 273.13$).

The polymerization of 1-butene is slow at 200° but becomes quite rapid by 250°.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT BRANCH, OFFICE OF SYNTHETIC LIQUID FUELS, U. S. BUREAU OF MINES]

Partition Studies. V. Partition Coefficients and Ionization Constants of Methyl-substituted Pyridines and Quinolines[1]

BY CALVIN GOLUMBIC AND MILTON ORCHIN

Previous papers in this series[2] dealt with the partition coefficients of phenols and application of this information to the isolation of certain phenolic constituents of coal-hydrogenation oil. In the present work, the partition properties of some alkyl-substituted pyridines and quinolines have been investigated. In addition, practical separations of mixtures of these compounds that can be achieved by countercurrent distribution are illustrated. The compounds chosen for study may be considered as prototypes of the basic constituents of coal-hydrogenation oil.

Relation between Partition Coefficient and Ionization Constant.—Analogous to a previously derived equation relating the partition coefficient and ionization constant of an organic acid,[2a,3,4] the equilibria involved in the distribution of an organic base between an organic solvent and an immiscible acid buffer phase may be described by the equation

$$\log k' = pH + \log k - pKa \qquad (1)$$

where k' is the observed partition coefficient, k is the partition coefficient of the un-ionized base, and pKa is the acidic ionization constant. The equation is limited to those circumstances in which $pH << pKa$ and in which no association occurs in the organic phase.

According to this equation, log k' is directly proportional to pH, and a plot of these variables should give a straight line with a slope of 1. To test the validity of this relation, partition coefficients were measured for the distribution of pyridine, picolines, 2,6-lutidine and 3-aminoquinoline between chloroform and citrate–phosphate buffer and for the distribution of quinoline, isoquinoline, and methyl-substituted quinolines between cyclohexane and citrate–phosphate buffer. The initial concentration of base was 0.5 mg. per ml. At this concentration, association effects are either absent or negligible (see experimental part). Plots of the logarithms of the observed partition coefficients *vs.* pH are presented in Figs. 1 and 2. The partition coefficients are expressed as (concentration in organic phase)/(concentration in aqueous phase). Straight lines are obtained for each monoacid base, and the slopes (m) are all very close to 1 (Table I, column 2). It is interesting to note that the slope of the aminoquinoline curve becomes greater than 1 in the strongly acid range. This is the result to be expected, because 3-aminoquinoline is known to form a di-acid salt in highly acid solutions.[5] Hence, the observed slope should increase from 1 to a limiting value of 2 when the pH has become $<< pK_2$.

A further test of equation (1) was made by employing it for calculation of approximate ionization constants (pKa) of each base studied. In order to do this, the k values had to be measured first. This was accomplished by determining the partition coefficient of each base when distributed between the organic phase and water. Corrections for the "salting-out effect" of the buffer were negligible except in the case of 2,6-dimethylquinoline. When concentrated buffers are employed in distribution, the "salting-out" effect is appreciable.[2a] The experimental k values are listed in Table I, column 3. As was expected, the

TABLE I

PARTITION COEFFICIENTS AND IONIZATION CONSTANTS OF PYRIDINES AND QUINOLINES

Compound	m	k (H_2O)[a]	pKa	pKa literature
Pyridine	0.95	27	5.5	5.35,[b] 5.38,[c] 5.48[d]
2-Picoline	.98	62	6.1	6.02,[b] 6.65,[c] 6.51[d]
3-Picoline	.97	77	5.8	6.04[d]
4-Picoline	.95	75	6.1	6.04[d]
2,6-Lutidine	.98	198	6.9	..
Quinoline	1.00	18	5.0	4.80,[c] 4.94[f]
Isoquinoline	1.00	13	5.4	..
2-Methylquinoline	1.00	44	5.8	5.42[e]
4-Methylquinoline	1.04	34	5.6	5.20[e]
6-Methylquinoline	1.01	52	5.2	4.92[e]
8-Methylquinoline	1.05	164	5.0	4.60[c]
2,6-Dimethylquinoline	1.02	104	6.1	..
3-Aminoquinoline	0.96–1.15	19	4.9	4.95[e]

[a] Measured at 25°. [b] Barron, *J. Biol. Chem.*, **12**, 313 (1937). [c] Goldschmidt and Salcher, *Z. physik. Chem.*, **29**, 114 (1899). [d] Constam and White, *Am. Chem. J.*, **29**, 46 (1903). [e] Felsing and Biggs, THIS JOURNAL, **55**, 3624 (1933). [f] Albert and Goldacre, *Nature*, **153**, 407 (1944).

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(1) Article not copyrighted.

(2) (a) Golumbic, Orchin and Weller, THIS JOURNAL, **71**, 2624 (1949); (b) Golumbic, *ibid.*, **71**, 2627 (1949); (c) Orchin and Golumbic, *ibid.*, **71**, 4151 (1949); Golumbic, Woolfolk, Friedel and Orchin, *ibid.*, **72**, 1939 (1950).

(3) Yabroff, *Ind. Eng. Chem.*, **32**, 257 (1940).

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