hence, the conversion to rutile had occurred during measurements at temperatures greater than 1,323°K. Only those results obtained at temperatures less than this figure are given in Table I. All of these measurements had been carried out previous to proceeding to higher temperatures. Correction was made for the SiO_2 and CaO impurities.

Seven determinations of the heat content of rutile were made at temperatures as high as 1,746°K. The heat content of rutile at 1,300°K. is about 1% less than that of anatase. Correction was made for the ZrO_2, SiO_2, CaO, Fe_2O_3, and Al_2O_3 impurities. The experimental results of both anatase and rutile when plotted form smooth curves, and no transition was observed in either substance.

Heat content equations were derived by the method described by Shomate.[11] This method utilizes all the high temperature heat-content data and also the true heat capacity at 298.16°K., if the latter is known and is applicable. The following molal heat capacities[3,4] at 298.16°K. were used in the present derivations: TiO, C_p = 9.55; Ti_2O_3, C_p = 23.27; and TiO_2 (rutile), C_p = 13.49. The heat capacity of anatase at 298.16°K. is not known, and the value for Ti_3O_5 was not applicable because of the unusual behavior between 298.16° and 450°K. The equations follow, the temperature range of validity and the mean percentage deviation from the experimental data being given in parentheses.

TiO(α): $H_T - H_{298.16} = 10.57T + 0.00180T^2 + 186{,}000/T - 3{,}935$ (298–1264°K.; 1%)

TiO(β): $H_T - H_{298.16} = 11.85T + 0.00150T^2 - 4{,}100$ (1264–1800°K.; 0.3%)

Ti_2O_3(α): $H_T - H_{298.16} = 7.31T + 0.02676T^2 - 4{,}559$ (298–473°K.; 1.5%)

Ti_2O_3(β): $H_T - H_{298.16} = 34.68T + 0.00065T^2 + 1{,}020{,}000/T - 13{,}605$ (473–1800°K.; 0.2%)

Ti_3O_5(α): $H_T - H_{298.16} = 35.47T + 0.01475T^2 - 11{,}887$ (298–450°K.; 4%)

Ti_3O_5(β): $H_T - H_{298.16} = 41.60T + 0.00400T^2 - 10{,}230$ (450–1400°K.; 0.2%)

TiO_2(anatase): $H_T - H_{298.16} = 17.21T + 0.00054T^2 + 359{,}000/T - 6383$ (298–1300°K.; 0.5%)

TiO_2(rutile): $H_T - H_{298.16} = 17.14T + 0.00049T^2 + 350{,}000/T - 6328$ (298–1800°K.; 0.2%)

The corresponding specific heat equations are given

TiO(α): $C_p = 10.57 + 0.00360T - 186{,}000/T^2$

TiO(β): $C_p = 11.85 + 0.00300T$

Ti_2O_3(α): $C_p = 7.31 + 0.05352T$

Ti_2O_3(β): $C_p = 34.68 + 0.00130T - 1{,}020{,}000/T^2$

Ti_3O_5(α): $C_p = 35.47 + 0.02950T$

Ti_3O_5(β): $C_p = 41.60 + 0.00800T$

TiO_2(anatase): $C_p = 17.21 + 0.00108T - 359{,}000/T^2$

TiO_2(rutile): $C_p = 17.14 + 0.00098T - 350{,}000/T^2$

No previous high-temperature heat content data exist for any of the titanium oxides except the dioxide. Nilson and Pettersson[12] have reported the only measurements of titanium dioxide at temperatures above 373°K. The highest of their four determinations was made at 713°K., and their values average about 4% less than the present data.

Summary

High-temperature heat contents above 298.16°K. of TiO, Ti_2O_3, Ti_3O_5, and TiO_2 were measured.

Three oxides, TiO, Ti_2O_3, and Ti_3O_5, exhibited transitions and the transition heats and temperatures were determined.

The results have been summarized by algebraic equations and a table was compiled which gives heat content and entropy increments above 298.16°K. at 100° intervals.

BERKELEY, CALIFORNIA RECEIVED FEBRUARY 7, 1946

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(11) C. H. Shomate, THIS JOURNAL, **66**, 928 (1944).

(12) L. F. Nilson and O. Pettersson, *Z. physik. Chem.*, **1**, 27 (1887)

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NATIONAL TSING HUA UNIVERSITY, PEIPING, CHINA]

Generalized Beattie-Bridgeman Equation of State for Real Gases[1]

BY GOUQ-JEN SU[2] AND CHIEN-HOU CHANG

In recent years many authors have correlated the compressibility and related thermodynamic properties of real gases on the basis of the law of corresponding states as proposed by van der Waals in 1881. They[3] showed that the compressibility factor μ (= pV/RT) and the fugacity–pressure ratio and some other thermodynamic properties of real gases are approximately functions of the reduced pressure and the reduced temperature. Keyes[4] deduced a simple reduced equation of state for real gases at low pressures. Maron and Turnbull[5] proposed their reduced equations of state, the constants being deduced from the compressibility data of nitrogen.

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(1) This paper is in part abstracted from a thesis submitted in July, 1939, to the Faculty of the National Southwestern Associated University, Kunming, China, by Chien-Hou Chang, Shao-Twan King and Chi-Hsun Wang in partial fulfillment of the requirement for the degree of Bachelor of Engineering.

(2) Present address: c/o Dr. Paul Kolachov, Joseph E. Seagram & Sons, Inc., Louisville 1, Kentucky.

(3) J. D. Cope, W. K. Lewis and H. C. Weber, *Ind. Eng. Chem.*, **23**, 887 (1931); G. G. Brown, M. Souders, Jr., and R. L. Smith, *ibid.*, **24**, 515 (1932); W. K. Lewis and C. D. Luke, *ibid.*, **25**, 725 (1933), *Oil Gas J.*, **32**, No. 40, 114 (1934); W. K. Lewis, *Ind. Eng. Chem.*, **28**, 257 (1936); R. H. Newton, *ibid.*, **27**, 302 (1935); R. H. Newton and B. F. Dodge, *ibid.*, **27**, 577 (1935); K. M. Watson and R. L. Smith, *National Petroleum News*, **28**, No. 27 (1936).

(4) F. G. Keyes, THIS JOURNAL, **60**, 1761 (1938).

(5) S. H. Maron and D. Turnbull, *Ind. Eng. Chem.*, **33**, 408 (1941); **34**, 544 (1942); THIS JOURNAL, **64**, 44, 2195 (1942).

The object of this paper is to present the Beattie–Bridgeman equation of state in the generalized reduced form with the same constants for all real gases.

We shall call the ideal critical volume[6] the volume which would be occupied by one mole of an ideal gas at its critical pressure and critical temperature, *i.e.*, $V_{c_i} = RT_c/p_c$. The ratio of the molar volume to the ideal critical volume will be called the ideal reduced volume, $\varphi = V/V_{c_i}$.

The use of the term ideal critical volume eliminates the critical volume, a quantity often not reported and in any event difficult to measure more accurately than either the critical pressure or the critical temperature. Any uncertainty introduced in the value of the critical volume is thus avoided by the use of the ideal critical volume which is defined in terms of the critical pressure and the critical temperature only.

Designate the reduced pressure $\pi = p/p_c$ and the reduced temperature $\theta = T/T_c$. The generalized Beattie-Bridgeman equation of state will take the following form, as previously stated by one of the authors,[6] the primes being added to the generalized constants, as to be differentiated from the constants in the original Beattie–Bridgeman equation of state:[7]

$$\pi = \frac{\theta(1 - \epsilon')}{\varphi^2}\,[\varphi + B'] - \frac{A'}{\varphi^2} \qquad (1)$$

where

$$\begin{aligned} \epsilon' &= c'/\varphi\theta^3 \\ A' &= A_0'(1 - a'/\varphi) \\ B' &= B_0'(1 - b'/\varphi) \end{aligned}$$

The five generalized constants A_0', a', B_0', b' and c' will be evaluated on the reduced basis.

In order to determine the constants of Beattie–Bridgeman equation of state, it is best to arrange the experimental data in the form of isometrics. A few years ago one of the writers[6] presented a system of reduced isometrics based on data on seven hydrocarbons (methane, ethane, ethylene, propane, *n*-butane, isopentane and *n*-heptane). These isometric values have been shown to hold for the seven hydrocarbons studied with an over-all average deviation of 1.0%. They have been tested also with data on nitrogen, carbon dioxide and steam, the agreement being of the same order as in the case of the hydrocarbons. Based on these isometric data, the values of the constants in the generalized equation (1) have been determined. The method of determination of the constants as presented by Beattie and Bridgeman[7] has been followed in the present evaluation of the generalized constants (Table I).

Since these generalized constants are on the reduced basis, they are dimensionless and are the same for all gases for whatever consistent set of units are employed.

TABLE I

VALUES OF GENERALIZED CONSTANTS OF EQ. (I) AS DETERMINED FROM COMPRESSIBILITY DATA

A_0'	a'	B_0'	b'	c'
0.4758	0.1127	0.18764	0.03833	0.05

The reduced constants of Table I have been used to compare the observed reduced pressures with those computed at corresponding values of φ^{-1} and θ, and the results are presented in Table II. The average deviation up to nearly the critical density is 0.7%. The average ideal reduced density at the critical point which is equal to the critical ratio, $r_c = RT_c/p_cV_c$ is about 3.7. The foregoing comparison in Table II is made to the highest ideal reduced density of 3.5. It is believed that the proposed generalized equation will reproduce the compressibility of the hydrocarbons up to nearly the critical density with an over-all average deviation of the order of 1%.

To test the validity and accuracy of Eq. (1) further, detailed calculation and comparisons have been made, using the above constants determined from the compressibility of hydrocarbons, for ten gases, namely, neon, oxygen, carbon dioxide, nitrogen, air, methane, ethyl ether, hydrogen, helium and oxygen. The compressibility data for these ten gases employed in the present calculation are exactly those used previously by Beattie and Bridgeman.[7] Table III shows the results of calculations. The average deviation for these ten gases is 0.6%, which is of the same order of magnitude as that for the seven hydrocarbons. The present generalized equation is believed to be of sufficient accuracy to be employed in many problems, theoretical and *practical*, involving the compressibility and related thermodynamic properties.

In the calculations, the values for the critical pressures and temperatures for ethane, propane, *n*-butane and *n*-heptane as determined by Beattie and co-workers[8] have been used. For hydrogen and helium, as done by Newton,[3] the pseudo-critical pressure (p_c') and the pseudo-critical temperature (T_c') are used, *i.e.*, $p_c' = p_c + 8$, $T_c' = T_c + 8$, when p_c and T_c are expressed in atmospheres, and in degrees Kelvin, respectively.

Discussion

It is of interest to note the relation between these generalized constants and the original Beattie–Bridgeman equation of state constants which are specific for specific gases. This relation may be easily obtained by substituting into the original Beattie–Bridgeman equation of state the reduced quantities: $p = p_c{\cdot}\pi$, $T = T_c{\cdot}\theta$, $V = V_{c_i}{\cdot}\varphi$ and

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[6] G. J. Su, Thesis, Mass. Inst. Tech., June, 1937; note the same quantity was therein named pseudo-critical volume.

[7] J. A. Beattie and O. C. Bridgeman, *Proc. Am. Acad. Arts Sci.*, **63**, 229 (1928).

[8] J. A. Beattie, G. J. Su and G. L. Simard, THIS JOURNAL, **61**, 924 (1939); J. A. Beattie, N. Poffenberger and C. Hadlock, *J. Chem. Physics*, **3**, 96 (1935); J. A. Beattie, G. L. Simard and G. J. Su, THIS JOURNAL, **61**, 24 (1939); J. A. Beattie and W. C. Kay, *ibid.*, **59**, 1586 (1937).

TABLE II

COMPARISON OF THE REDUCED PRESSURES CALCULATED WITH REDUCED PRESSURES OBSERVED IN THE GENERALIZED ISOMETRICS

$1/\varphi$	θ	1.00	1.10	1.20	1.30	1.40	1.60	2.00	2.40
		Reduced Pressures							
0.25	Obs.	0.229	0.256	0.283	0.310	0.336	0.389	0.493	0.598
	Obs. −calcd.	− .001	.000	.000	.000	.000	.000	.002	−0.001
0.5	Obs.	.417	.477	.535	.593	.649	.759	.975	1.193
	Obs. −calcd.	− .003	.000	.002	.004	.004	.003	− .001	−0.003
1.0	Obs.	.693	.832	.959	1.088	1.212	1.450	1.920	2.390
	Obs. −calcd.	− .006	.004	.006	0.010	0.014	0.006	−0.002	−0.008
1.5	Obs.	.863	1.092	1.303	1.509	1.712	2.100	2.856	3.636
	Obs. −calcd.	− .002	0.012	0.015	0.016	0.018	0.009	−0.014	−0.004
2.0	Obs.	.950	1.280	1.591	1.882	2.172	2.732	3.820	4.982
	Obs. −calcd.	.000	0.019	0.024	0.018	0.016	0.006	−0.016	0.046
2.5	Obs.	.990	1.425	1.839	2.236	2.625	3.385	4.860	
	Obs. −calcd.	.009	0.011	0.009	0.003	0.000	−0.005	−0.016	
3.0	Obs.	.999	1.548	2.066	2.586	3.108	4.089		
	Obs. −calcd.	.013	−0.003	−0.024	−0.029	−0.005	−0.003		
3.5	Obs.	.994	1.667	2.310	2.967	3.626	4.900		
	Obs. −calcd.	− .006	−0.049	−0.080	−0.074	−0.041	0.026		
Av. % diff.		.633	0.872	1.10	0.857	0.607	0.276	0.309	0.357

Total average % deviation = 0.7.

TABLE III

SUMMARY OF THE AVERAGE DEVIATIONS OF THE PRESSURE CALCULATED FROM THE PRESSURE OBSERVED FOR THE GASES

Gas	Max. pressure, atm.	Max. density, moles/liter	Temp. range, °C.	Number of points	Total average deviations Atm.	Total average deviations %
Ne	106	8.5	400 to −218	176	0.296	0.509
O_2	103	9.0	100 to −117	132	.091	.220
CO_2	111	5.5	100 to 0	127	.554	.857
N_2	134	5.5	400 to −149	207	.132	.320
Air	177	8.0	200 to −145	168	.167	.279
CH_4	243	6.0	200 to 0	60	.168	.163
$(C_2H_5)_2O$	90	2.7	325 to 150	64	.666	1.611
H_2	103	10.0	200 to −217	283	.412	1.007
He	101	10.0	400 to −225	170	.394	0.725
A	114	6.0	400 to −150	209	.257	0.672
Grand average					.300	0.628
Total no. of points				1596		

equating the coefficients, setting $V_{c_i} = RT_c/p_c$. It has been shown[6]

$$A_0' = A_0 \Big/ p_c\left(\frac{RT_c}{p_c}\right)^2 \qquad a' = a \Big/ \left(\frac{RT_c}{p_c}\right) \qquad (2)$$

$$B_0' = B_0 \Big/ \left(\frac{RT_c}{p_c}\right) \qquad b' = b \Big/ \left(\frac{RT_c}{p_c}\right)$$

$$c' = c \Big/ T_c^3\left(\frac{RT_c}{p_c}\right)$$

We shall presently see how well the relations in eq. (2) hold, if we substitute the known Beattie–Bridgeman equation of state constants of gases and the critical values of pressure and temperature of the gases concerned. Table IV shows the generalized values calculated by applying the relations in eq. (2). The fact that the constants tend to converge to some generalized values is gratifying in view of the fact that the specific constants of the gases have been derived from compressibility data covering widely different fields of pressures and temperatures. The generalized constants calculated from the specific constants for the first eleven gases listed in Table IV show such a degree of constancy that average values have been computed and listed in the table. These average generalized constants agree surprisingly well with the values directly determined from the compressibility as shown in Table V. For actual

TABLE IV

"GENERALIZED" CONSTANTS CALCULATED FOR "SPECIFIC" CONSTANTS

	A_0'	a'	B_0'	b'	c'
Argon	0.404	0.0902	0.152	0	0.0673
n-Butane	.550	.1307	.265	0.1013	.0491
Carbon dioxide	.587	.2082	.306	.2115	.0688
Ethane	.446	.112	.1795	.0366	.0594
Ethylene	.581	.109	.266	.0789	.0220
Hydrogen	.341	− .0238	.0983	− .205	.0647
Methane	.424	.0542	.163	− .0464	.0539
Neon	.417	.156	.147	0	.0821
Nitrogen	.422	.0846	.1631	− .0224	.0680
Oxygen	.462	.1006	.1813	.01652	.0515
Propane	.545	.1011	.250	.0594	.0328
Average	.471	.102	.197	.0210	.0563
Ammonia	.242	.571	.1146	.641	.241
Ethyl ether	.756	.115	.421	.111	.00304
Helium	.267	.316	.0739	0	1.49
Heptane	.750	.122	.432	.0117	0.0155

TABLE V

COMPARISON OF GENERALIZED CONSTANTS CALCULATED FROM SPECIFIC CONSTANTS AND THOSE DETERMINED FROM COMPRESSIBILITY DATA

	A_0'	a'	B_0'	b'	c'
From specific constants	0.471	0.102	0.197	0.0210	0.0563
From compressibility data	.4758	.1127	.1876	.03833	.050

calculations, however, the constants directly determine from the compressibility data and presented in Table I should be used. It is to be remarked that the constants have compensating effect and that two sets of constants even with appreciable numerical differences may yield similar results so far as the compressibility, not the derivatives of the quantities, is concerned.

Acknowledgment.—The writers are grateful to Professor James A. Beattie and Professor Warren K. Lewis for their suggestions and encouragement.

Summary

1. A generalized form of Beattie–Bridgeman equation of state is proposed

$$\pi = \frac{\theta(1 - \epsilon)}{\varphi^2}\,[\varphi + B'] - \frac{A'}{\varphi^2}$$

where

$\epsilon' = c'/\varphi\theta^3$

$A' = A_0'(1 - a'/\varphi)$

$B' = B_0'(1 - b'/\varphi)$

$\pi = p/p$, reduced pressure

$\theta = T/T_c$, reduced temperature

$\varphi = V/V_{c_i}$, ideal reduced volume

$V_{c_i} = RT_c/p_c$, ideal critical volume

The constants A_0', a', B_0', b' and c' have the same numerical values irrespective of nature of gas as follows

$A_0' = 0.4758$ $B_0' = 0.18764$ $c' = 0.05$

$a' = 0.1127$ $b' = 0.03833$

2. The proposed generalized equation holds for seventeen gases with an average deviation of 2% or less for each gas up to nearly the critical density. It is believed that the proposed equation may be applied in general to all real gases.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Organosilicon Compounds. V.[1] β-Eliminations Involving Silicon[2]

BY L. H. SOMMER, G. M. GOLDBERG, E. DORFMAN AND F. C. WHITMORE

α-Chloroethyltrichlorosilane with methylmagnesium bromide gives α-chloroethyltrimethylsilane with no attack on the alpha chlorine.[3]

$$CH_3CHClSiCl_3 + 3CH_3MgBr \longrightarrow CH_3CHClSi(CH_3)_3$$

In striking contrast, the corresponding beta chlorine is very reactive. Moreover it induces the splitting of the C–Si bond. β-Chloroethyltrichlorosilane with excess methylmagnesium bromide gives *tetramethylsilane* and *ethylene*. Similarly, ethylmagnesium bromide gave ethylene and tetraethylsilane. Stepwise addition of four equivalents of the Grignard reagent showed that the fission of the C–Si bond and the evolution of ethylene took place mainly as follows

$$ClCH_2CH_2Si(CH_3)_3 + CH_3MgBr \longrightarrow (CH_3)_4Si + CH_2{=}CH_2$$

In earlier work[1,3] we found the amazing reactivity of chlorine beta to silicon as shown by quantitative titration with 0.5 *N* alkali. We now report that this unusual activity is associated with fission of the C–Si bond to give the corresponding olefin. Thus an ether solution of β-chloroethyltrichlorosilane reacts vigorously at room temperature with aqueous alkali.

$$ClCH_2CH_2SiCl_3 \xrightarrow[H_2O]{OH^-} CH_2{=}CH_2 + Si(OH)_4 + 4Cl^-$$

In striking contrast is the action of the ether solution with water alone. Removal of the ether and heating at 170–180° for two hours leaves a clear brittle polymer in 80% yield. This polymer is β-chloroethyl silicone, $ClCH_2CH_2SiO_{1.5}$.[4] It reacts rapidly with dilute alkali to give ethylene.

$$ClCH_2CH_2SiO_{1.5} \xrightarrow[H_2O]{OH^-} CH_2{=}CH_2 + Si(OH)_4 + Cl^-$$

β-Chloro-*n*-propyltrichlorosilane in ether solution reacts vigorously with aqueous alkali at room temperature to give propylene.

$$CH_3CHClCH_2SiCl_3 \xrightarrow[H_2O]{OH^-} CH_3{-}CH{=}CH_2 + Si(OH)_4 + 4Cl^-$$

Acknowledgment.—We thank the Minnesota Mining and Manufacturing Co. and the Miner Laboratories for a grant which made this work possible.

Experimental

Reaction of β-Chloroethyltrichlorosilane with Methylmagnesium Bromide.—A 2-liter three-necked flask was fitted with a reflux condenser, mercury sealed stirrer and dropping funnel; the system was protected from moisture by a sulfuric acid trap. In the flask there was prepared, by the usual method, 3 equivalents of methylmagnesium bromide in 900 cc. of ether. The system was then connected to a trap maintained at −70° by acetone and Dry Ice. Next, a solution of 100 g., 0.5 mole, of β-chloroethyltrichlorosilane in 125 cc. of dry ether was added to the Grignard reagent which was cooled by means of an ice-bath; the time of addition was three hours. The ice-bath was removed and the reaction mixture heated

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[1] Paper IV, Sommer, Dorfman, Goldberg and Whitmore, THIS JOURNAL, 68, 488 (1946).

[2] Presented before the Division of Organic Chemistry at the New York Meeting of the American Chemical Society, September 12, 1944.

[3] Sommer and Whitmore, THIS JOURNAL, 68, 485 (1946) (Paper III).

[4] (a) This polymer contains a three-dimensional network of Si–O–Si bonds; (b) *cf.* Rochow and Gilliam, THIS JOURNAL, 63, 798 (1941).