THE
REVIEW OF PHYSICAL CHEMISTRY
OF JAPAN

Founded in 1926

CONTENTS

THE PHYSICO-CHEMICAL SOCIETY OF JAPAN

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN

(Butsuri-Kagaku no Shinpo)

Found in 1926

The Review of Physical Chemistry of Japan

CONTENTS

No. 1

No. 2

STUDIES ON THE *P-V-T* RELATIONS OF FLUIDS AT HIGH PRESSURE III

The Compressibilities of Argon-Ammonia and Nitrogen-Ammonia Gaseous Mixture Systems

BY KAORU DATE*

The measurements of the compressibility factors for three kinds of argon-ammonia gaseous mixtures and for three kinds of nitrogen-ammonia gaseous mixtures were made at 50°C and up to 50 atm within the experimental error of 0.2% by the constant volume method, respectively. The results were presented in tabular form of the compressibility factors at round pressures and densities. The results were also presented in the power series of density and pressure respectively, and their experimental second virial coefficients were compared with those calculated theoretically assuming the Lennard-Jones (12–6) and the Stockmayer potential functions to each intermolecular force pertinently. Both the experimental and the theoretical second virial coefficients were in agreement within the uncertainties inherent in the experimentals.

Introduction

There are few experimental works for the *P-V-T* relations of polar fluids and of the mixtures containing polar fluids. Therefore, the theories on their *P-V-T* relations have not been proved satisfactorily and the estimations of their *P-V-T* values have still some uncertainties at present.

To study the *P-V-T* relations of polar fluids at high pressure, the author had already measured the compressibility factors of gaseous and liquid ammonia in the range from 25 to 125°C and up to 500 atm[1]. In addition, the *P-V-T* values of ammonia in the neighborhood of the critical point had been measured and the critical values of ammonia had been determined from the above experimental *P-V-T* data[2]. In this paper, for the study of the *P-V-T* relations of binary mixtures containing polar fluid, the compressibility factors of argon-ammonia mixtures and those of nitrogen-ammonia mixtures were measured at 50°C and up to 50 atm for three different compositions, respectively.

Other experimental works of the *P-V-T* relations for these binary mixtures, had been only reported by Kazarnowsky *et al.*[3] for a nitrogen-ammonia mixture from 150 to 300°C and up to 1640 atm. The data in this work could not be compared with their data because of the different experimental conditions of pressure and temperature.

1) K. Date, *This Journal*, **43**, 1 (1973)
2) K. Date, *ibid.*, **43**, 17 (1973)
3) J. S. Kazarnowsky, G. B. Simonov and G. E. Aristov, *Zhur. fiz. Khim.*, **14**, 774 (1940)

Experimental

Method and apparatus

The constant volume type apparatus and method used to measure the values of *P-V-T* relations of the mixtures were the same as those for the gaseous ammonia in the previous work reported in detail[1]. It is believed that the compressibility factors of the mixtures would be obtained experimentally within the maximum error of 0.2% as well as for the gaseous ammonia in the previous work.

Materials

Both argon and nitrogen used were above 99.99% grade of purity, respectively. Commercial ammonia was purified by repeated distillation and dehydrated by metallic sodium. The ammonia obtained was sufficiently more than 99.9% of purity from the result of gas adsorbing analysis. The binary gas mixtures of the desired compositions were prepared in the storage vessels by mixing these gases. They were analyzed within the error of 0.1 mol% by the method of gas adsorption.

Results

Argon-ammonia system

The compressibility factors, $Z=PV/RT$, were measured at 50°C and up to 50 atm for three kinds of the binary mixtures of argon-ammonia as below :

        91.8 mol% Ar— 8.2 mol% NH_3,

        83.9 mol% Ar—16.1 mol% NH_3,

        63.5 mol% Ar—36.5 mol% NH_3.

A large number of the experimental values of *Z* were plotted in a large graph against pressures or densities. The smoothed curves were drawn through each experimental point for each mixture. The values of *Z* read from the curves were in agreement with the experimental values within the deviation of 0.2%. These smoothed values of *Z* at round pressures and at round densities are shown in Table 1. In the table, the values of pure ammonia in the previous work[1] and the values of pure argon in the previous work[4] were also represented.

The experimental equations of state were obtained to develop the experimental values of *Z* in the power series of density and pressure, respectively, by the use of the least square method. The results are shown in Table 2. The values of *Z* calculated by these equations were in agreement with the experimental values within the deviation of 0.2%.

---

4) K. Date, G. Kobuya and H. Iwasaki, *Bull. Chem. Res. Institute of Non-Aqueous Solutions, Tohoku Univ.*, **12**, 33 (1963)

Table 1   Compressibility factor of argon-ammonia system   at 50°C

P, atm	$Z=PV/RT$				
	Composition, mol%				
	Ar 100.0 NH_3 0.0	Ar 91.8 NH_3 8.2	Ar 83.9 NH_3 16.1	Ar 63.5 NH_3 36.5	Ar 0.0 NH_3 100.0
0	1.0000	1.0000	1.0000	1.0000	1.0000
2	0.9992	0.9985	0.9981	0.9962	0.9856
4	0.9984	0.9973	0.9964	0.9925	0.9704
6	0.9975	0.9960	0.9947	0.9888	0.9544
8	0.9967	0.9949	0.9931	0.9852	0.9372
10	0.9960	0.9937	0.9916	0.9816	0.9188
12	0.9951	0.9925	0.9900	0.9780	0.8993
14	0.9943	0.9915	0.9885	0.9744	0.8793
16	0.9935	0.9904	0.9870	0.9708	0.8592
18	0.9928	0.9894	0.9855	0.9674	0.8385
20	0.9923	0.9883	0.9840	0.9640	
22	0.9915	0.9872	0.9826	0.9606	
24	0.9907	0.9863	0.9812	0.9572	
26	0.9900	0.9854	0.9800	0.9538	
28	0.9894	0.9845	0.9786	0.9505	
30	0.9888	0.9836	0.9773	0.9471	
40	0.9856	0.9798	0.9714		
50	0.9827	0.9767	0.9663		

Table 1   (continued)

$1/V$, mol/l	$Z=PV/RT$				
	Composition, mol%				
	Ar 100.0 NH_3 0.0	Ar 91.8 NH_3 8.2	Ar 83.9 NH_3 16.1	Ar 63.5 NH_3 36.5	Ar 0.0 NH_3 100.0
0	1.0000	1.0000	1.0000	1.0000	1.0000
0.2	0.9978	0.9967	0.9955	0.9903	0.9595
0.4	0.9957	0.9934	0.9913	0.9810	0.9195
0.6	0.9937	0.9905	0.9872	0.9719	0.8798
0.8	0.9917	0.9878	0.9835	0.9632	0.8393
1.0	0.9899	0.9853	0.9799	0.9548	
1.2	0.9881	0.9831	0.9766	0.9468	
1.4	0.9865	0.9810	0.9736		
1.6	0.9849	0.9792	0.9707		
1.8	0.9835	0.9776	0.9681		
2.0	0.9820	0.9763	0.9657		

Table 2   Experimental equations of state for argon-ammonia system   at 50°C

Composition, mol% Ar — NH₃	$Z = 1 + B(1/V) + C(1/V)^2 + D(1/V)^3$,			$1/V$, mol/l
	B	C	D	Range of $1/V$
100.0 — 0.0	−0.01124	0.00113	——	up to 2.0
91.8 — 8.2	−0.01748	0.00282	——	up to 1.9
83.9 — 16.1	−0.02296	0.00291	——	up to 1.89
63.5 — 36.5	−0.04397	0.00420	——	up to 1.16
0.0 — 100.0	−0.2172	0.0628	−0.0566	up to 0.9
Composition, mol% Ar — NH₃	$Z = 1 + B'P + C'P^2 + D'P^3$,			P, atm
	$B' \cdot 10^3$	$C' \cdot 10^6$	$D' \cdot 10^6$	Range of P
100.0 — 0.0	−0.417	1.44	——	up to 50
91.8 — 8.2	−0.667	4.05	——	up to 49
83.9 — 16.1	−0.883	4.19	——	up to 48
63.5 — 36.5	−1.869	3.38	——	up to 29
0.0 — 100.0	−7.477	−34.6	−2.90	up to 19

Nitrogen-ammonia system

The compressibility factors were measured at 50°C and up to 50 atm for three kinds of the binary mixtures of nitrogen-ammonia as below :

87.3 mol% N_2 — 12.7 mol% NH_3,

77.0 mol% N_2 — 23.0 mol% NH_3,

62.3 mol% N_2 — 37.7 mol% NH_3.

The smoothed values of Z were obtained by the same method as in the case of the above argon-ammonia mixtures.   They were in agreement with the experimental values within the deviation of 0.2%.   They are shown in Table 3.   In the table, the values of pure ammonia in the previous work[1] and the values of pure nitrogen in the previous work[5] were also represented.

The experimental equations of state were obtained in the same manner as in the case of argon-ammonia systems.   The results are shown in Table 4.   The values of Z calculated by these equations were in agreement with the experimental values within the deviation of 0.2%.

Consideration on the second virial coefficients of the mixtures

The values of B in Tables 2 and 4 can be looked upon as the experimental second virial coefficients of the mixtures though they are not so accurate because they were obtained only from the experimental P-V-T data at higher pressures than several atmospheres.

5)   K. Date and H. Iwasaki, *Annual Report of the Asahi Glass Foundation for the Contribution to Industrial Technology*, **11**, 65 (1965)

Table 3   Compressibility factor of nitrogen-ammonia system   at 50°C

P, atm	$Z=PV/\boldsymbol{RT}$				
	Composition, mol%				
	N_2 100.0 NH_3 0.0	N_2 87.3 NH_3 12.7	N_2 77.0 NH_3 23.0	N_2 62.3 NH_3 37.7	N_2 0.0 NH_3 100.0
0	1.0000	1.0000	1.0000	1.0000	1.0000
2	1.0000	0.9994	0.9984	0.9965	0.9856
4	0.9999	0.9988	0.9968	0.9930	0.9704
6	1.0000	0.9982	0.9952	0.9896	0.9544
8	1.0000	0.9976	0.9937	0.9865	0.9372
10	1.0000	0.9971	0.9922	0.9834	0.9188
12	1.0001	0.9965	0.9908	0.9805	0.8993
14	1.0001	0.9960	0.9894	0.9777	0.8793
16	1.0002	0.9955	0.9880	0.9751	0.8592
18	1.0002	0.9950	0.9867	0.9725	0.8385
20	1.0004	0.9944	0.9854	0.9701	
22	1.0005	0.9940	0.9842		
24	1.0006	0.9935	0.9830		
26	1.0007	0.9931	0.9818		
28	1.0010	0.6626	0.9807		
30	1.0012	0.9922	0.9796		
40	1.0023	0.9903			
50	1.0038	0.9886			

Table 3   (continued)

$1/V$, mol/l	$Z=PV/\boldsymbol{RT}$				
	Composition, mol%				
	N_2 100.0 NH_3 0.0	N_2 87.3 NH_3 12.7	N_2 77.0 NH_3 23.0	N_2 62.3 NH_3 37.7	N_2 0.0 NH_3 100.0
0	1.0000	1.0000	1.0000	1.0000	1.0000
0.2	0.9999	0.9984	0.9958	0.9909	0.9595
0.4	1.0000	0.9969	0.9919	0.9828	0.9195
0.6	1.0003	0.9955	0.9882	0.9757	0.8798
0.8	1.0005	0.9941	0.9849	0.9696	0.8393
1.0	1.0009	0.9929	0.9818		
1.2	1.0015	0.9918			
1.4	1.0021	0.9907			
1.6	1.0028	0.9898			
1.8	1.0036	0.9889			
2.0	1.0045				

Table 4   Experimental equations of state for nitrogen-ammonia system   at 50°C

Composition, mol%	$Z = 1 + B(1/V) + C(1/V)^2 + D(1/V)^3,$			$1/V$, mol/l
N_2 — NH_3	B	C	D	Range of $1/V$
100.0 — 0.0	-0.00037	0.00131	——	up to 3.0
87.3 — 12.7	-0.0082	0.00114	——	up to 1.8
77.0 — 23.0	-0.0219	0.0034	——	up to 1.07
62.3 — 37.7	-0.0479	0.0123	——	up to 0.7
0.0 — 100.0	-0.2172	0.0628	-0.0566	up to 0.9

Composition, mol%	$Z = 1 + B'P + C'P^2 + D'P^3,$			P, atm
N_2 — NH_3	$B' \cdot 10^3$	$C \cdot 10^6$	$D' \cdot 10^6$	Range of P
100.0 — 0.0	-0.022	1.98	——	up to 100
87.3 — 12.7	-0.038	1.6	——	up to 48
77.0 — 23.0	-0.829	5.0	——	up to 28
62.3 — 37.7	-1.828	16.8	——	up to 18
0.0 — 100.0	-7.477	-34.6	-2.90	up to 19

They were compared with the values calculated theoretically as follows.   The Lennard-Jones (12–6) potential function,

$$\varphi(r) = 4\varepsilon[(r_o/r)^{12} - (r_o/r)^6], \tag{1}$$

was adopted on the intermolecular forces between argon and argon, argon and ammonia, nitrogen and nitrogen, and nitrogen and ammonia.   The Stockmayer potential function,

$$\varphi(r, \theta_1, \theta_2, \phi_2 - \phi_1) = 4\varepsilon[(r_o/r)^{12} - (r_o/r)^6] - (\mu^2/r^3)\, g(\theta_1, \theta_2, \phi_2 - \phi_1), \tag{2}$$

was adopted on the intermolecular forces between ammonia and ammonia.   The figures of the parameters in the functions were given by Hirschfelder et al.[6] as below :

	$r_o(\text{Å})$	$b_o = (2/3)Nr_o^3$ (cc/mol)	ε/k (K)	μ (debyes)
Ar —Ar	3.405	49.80	119.8	——
Ar —NH_3	3.002	34.14	195.8	——
N_2 —N_2	3.698	63.78	95.05	——
N_2 —NH_3	3.126	38.54	190.5	——
NH_3—NH_3	2.60	22.12	320	1.47

where the force constants between a polar (subscript p) and a non-polar molecule (subscript n) were obtained from the empirical combination laws represented by the following equations :

$$(r_o)_{np} = (1/2)\,[(r_o)_n + (r_o)_p]\,\xi^{-1/6} \tag{3}$$

$$\varepsilon_{np} = (\varepsilon_n\varepsilon_p)^{1/2}\xi^2 \tag{4}$$

6)   J. O. Hirschfelder, C. F. Curtiss and C. B. Bird, "*Molecular Theory of Gases and Liquids*", John Wiley and Sons, New York (1954)

The factor ξ is given by :

$$\xi = 1 + (1/4)[\alpha_n \mu_p^{*2}/(r_o)_n^3](\varepsilon_p/\varepsilon_n)^{1/2}, \tag{5}$$

in which α_n is the polarizability of the non-polar molecule ($\alpha_n = 1.76$ Å^3 for nitrogen and 0 Å^3 for argon) and $\mu_p^* = \mu_p/[\varepsilon_p(r_o)_p^3]^{1/2}$.

The numerical tables of the reduced second virial coefficient B^* had been given in the literature[6] for each potential function by :

$B(T) = b_o B^*(T^*)$,   for the Lennard-Jones (12–6) potential ;

$B(T) = b_o B^*(T^*, t^*)$, for the Stockmayer potential ;

where $T^* = kT/\varepsilon$ and $t^* = 8^{1/2}\mu_p^{*2}$.

The theoretical values of the second virial coefficients for each pure gas were obtained by the use of the above values of the force constants and the tables of B^*.   For the mixtures, they were obtained by the use of the following relation :

$$B_{mix} = x_n^2 B_n + 2x_n x_p B_{np} + x_p^2 B_p \tag{6}$$

where B_{mix} is the second virial coefficient for the mixture, B_n and B_p are the second virial coefficients calculated for each pure component of non-polar or polar molecule, B_{np} is the second virial coefficient in regard to the interaction between non-polar and polar molecules, and x_n and x_p are the mole fractions of non-polar and polar components in the mixture, respectively.

The results for the comparison are shown in Table 5 and graphically in Fig. 1.   There exist the differences between the experimental and the values calculated theoretically for these binary systems from 0.05 to 9.9 cc/mol. However, it was estimated that these values of B_{exp} for the gradients of the isotherms at zero pressure had some uncertainties of which the quantities would be the same order as the above differences.   From this viewpoint, it can be said that both the experimental and the caluated values of the second virial coefficients were in agreement with each other for these binary systems.

Table 5   Comparison of second virial coefficient for argon-ammonia and nitrogen-ammonia mixture systems at 50°C

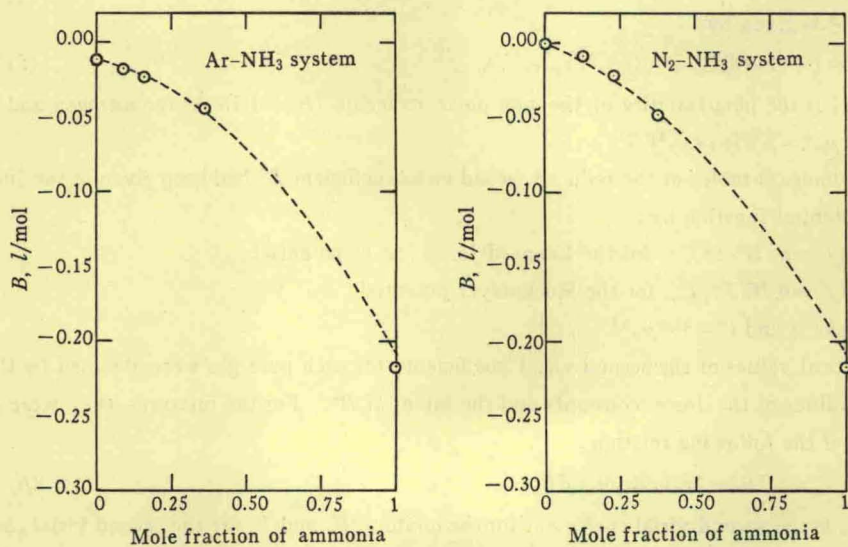| Composition, mol%	B, cc/mol		Difference
	Experimental B_{epx}	Calculated B_{calc}	$B_{exp} - B_{calc}$, cc/mol
100% Ar	− 11.24	− 11.19	0.05
100% N$_2$	− 0.37	− 0.27	0.10
100% NH$_3$	−217.2	−207.3	9.9
91.8% Ar − 8.2% NH$_3$	− 17.48	− 16.13	1.35
83.9% Ar − 16.1% NH$_3$	− 22.96	− 22.33	0.63
63.5% Ar − 36.5% NH$_3$	− 43.97	− 47.67	− 3.70
87.3% N$_2$ − 12.7% NH$_3$	− 8.20	− 11.48	− 3.28
77.0% N$_2$ − 23.0% NH$_3$	− 21.9	− 23.79	− 1.9
62.3% N$_2$ − 37.7% NH$_3$	− 47.9	− 46.35	1.5

Fig. 1   Second virial coefficients of argon-ammonia and nitrogen-
ammonia binary mixture systems both at 50°C

⊙: Experimental   ----: Calculated

Acknowledgment

IONIC SOLUTIONS UNDER HIGH PRESSURES V

Pressure Effects on the Walden Products and Hydration of

Et_4N^+ and ClO_4^- Ions in Water

BY MASARU NAKAHARA AND JIRO OSUGI

The electrical conductivities of aqueous solutions at high pressures up to 5,000 atm have been measured in the concentration range fram 10^{-4} to 10^{-3}N for tetraethylammonium chloride, Et_4NCl at 25 and 40°C and for tetraethylammonium perchlorate, Et_4NClO_4 at 25°C. The equivalent conductances of the electrolytes at infinite dilution have been determined by means of the Onsager equation which was verified to be valid in the dilute solutions at high pressures in the previous papers[1,2]. The limiting equivalent conductances determined at high pressures were separated into the single-ion ones on the basis of the same assumption as used in the previous paper[2]. Although the limiting equivalent conductance of Et_4N^+ has a maximum against pressure at 25°C like other tetraalkylammonium ions, that of ClO_4^-, surprisingly and exceptionally, has no maximum even at 25°C where the viscosity of solvent water has a minimum at about 650 atm[3]. The Walden product of Et_4N^+ decreases slightly with increasing pressure at 25°C and, probably, so at 40°C like that of Me_4N^+. On the other hand, the Walden product of ClO_4^- at 25°C dramatically decreases with increasing pressure. Thus, it is considered that the pressure dependence of the limiting equivalent conductance of the ion in water can not be explained merely in terms of such bulk properties of water as the viscosity and dielectric constant. These differences in the pressure coefficients of the Walden products were ascribed to the differences between the density of the hydration shell and that of the bulk water.

Introduction

Colladon and Sturm[4] are the first persons to attempt to examine the effect of pressure on the electrical conductivities of electrolyte solutions, when it was not yet known what carries electricity in solution. In 1885, first of all, Fink[5] established that pressure (up to 500 atm) does decrease the electrical resistances of electrolyte solutions ; it was two years before the appearance of the Arrhenius

1) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **42**, 12 (1972)

2) M. Nakahara, *ibid.*, **42**, 75 (1972)

3) J. B. Cappi, Ph. D. Thesis, London University (1964)

4) D. Colladon and C. Sturm, *Ann. Chim. Phys.*, **36**, 231 (1827)

5) J. Fink, *Wied. Ann.*, **26**, 481 (1885)

theory for the behavior of electrolyte solutions. In the 1890's, Röntgen[6], Fanjung[7] and Tammann[8] first found a parallelism between the pressure dependence of the electrical conductivities of aqueous solutions and that of the solvent fluidity measured by Cohen[9]. Strictly speaking, however, those early works were not so much accurate but only phenomenological, even after the eminent Debye-Hückel theory[10] for the strong electrolyte solution was developed in 1923. It seems to the authors that first great efforts to determine accurately the limiting equivalent conductances at high pressures were made in the 1950's by Hamann and his coworkers in particular for the purpose of examining the pressure effect on the ionization of weak electrolytes. In the 1960's, the accourately determined limiting equivalent conductances at high pressures began to be analyzed in terms of the transition state theory[13] by Brummer and Hills[14, 15], Osugi, Shimizu and Takizawa[16], and Adams and Laidler[17], and also in terms of the dielectric relaxation effect by Skinner and Fuoss[18] and Cussler and Fuoss[19].

When we deal with a transport property in solution, there is one fundamental question as to how much the transport property might reflect the equilibrium property of ions in solution. In the case of ionic conductance, however, there would be fairly good correspondence between them for the following reasons. The ions in solution are originally moving very rapidly in a random way colliding with the solvent molecules or with each other, as well-known as Brownian motion. When an external electric field is applied to the system, the ions begin to move preferentially in the direction of the applied field. At this time, if the external perturbation is so weak, as often in the conductance measurement, that it may not disturb the internal field exerted by the ions themselves and polar solvent molecules, the limiting ionic equivalent conductance would minutely reflect the ion-solvent interaction in the equilibrium state. In consequence, the limiting ionic equivalent conductance could be used as a useful probe to study ionic hydration. As a matter of fact, it was previously reported[20] that there are linear correlations between the hydration number calculated from the limiting ionic equivalent conductance and the hydration enthalpy for the alkali metal ions and for the halogen ions at normal pressure.

6) W. C. Röntgen, *Nachrichten der k. Gesellsch. zu Göttingen*, 509 (1893)
7) I. Fanjung, *Z. Phys. Chem.*, **14**, 673 (1894)
8) G. Tammann, *ibid.*, **17**, 725 (1895)
9) E. Cohen, *Wied. Ann.*, **45**, 666 (1892)
10) P. Debye and E. Hückel, *Phys. Z.*, **24**, 185 (1923)
11) S. D. Hamnn, "Physico-Chemical Effects of Pressure", Butterworths, London (1957)
12) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955)
13) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill (1941)
14) S. B. Brummer and G. J. Hills, *Trans. Faraday Soc.*, **57**, 1816 (1961)
15) S. B. Brummer and G. J. Hills, *ibid.*, **57**, 1823 (1961)
16) J. Osugi, K. Shimizu and H. Takizawa, *This Journal*, **34**, 55 (1964)
17) W. A. Adams and K. J. Laidler, *Can. J. Chem.*, **46**, 1989 (1968)
18) J. K. Skinner and R. M. Fuoss, *J. Phys. Chem.*, **71**, 4455 (1967)
19) E. L. Cussler and R. M. Fuoss, *ibid.*, **71**, 4459 (1967)
20) M. Nakahara, K. Shimizu and J. Osugi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sec.*), **92**, 785 (1971)

Expermiental

Tetraethylammonium chloride, Et_4NCl was obtained by using anion exchange resin from its bromide which was first synthesized by the Menschutkin reaction. Et_4NCl salt was three times recrystallized from its methanol solution by adding chilled ether, and dried in vacuum at about 50°C for a week. Tetraethylammonium perchlorate was precipitated by adding excess amount of perchloric acid to the aqueous solution of Et_4NBr*, recrystallized twice from its aqueous solution, and dried in vacuum at room temperature for 3 days after heated up to 100°C for 2 hours with great care to avoid explosion.   The dilute sample solutions were prepared from stock solutions just in the same way as before[1, 21].

The high-pressure apparatus and the conductivity cell were already described elsewhere.

Results and Discussion

Determination of $\Lambda^{\circ(P)}$

The equivalent conductances, $\Lambda^{(P)}$ of Et_4NCl and Et_4NClO_4 in dilute aqueous solution at pressure P were determined, after the corrections for the solvent conductivity and changes in concentration and cell constant with pressure had been made just in the same manner as the previous study[1]. Then, the equivalent conductances at infinite dilution at pressure P, $\Lambda^{\circ(P)}$ were obtained with the aid of Onsager's equation for conductance,

$$\Lambda = \Lambda^{\circ} - (\alpha\Lambda^{\circ} + \beta)\sqrt{C}; \tag{1}$$

that is,

$$\Lambda^{\circ} = \frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}}, \tag{2}$$

from which $\Lambda^{\circ(P)}$ of Et_4NCl at 25 and 40°C and Et_4NClO_4 at 25°C were calculated and given in Tables 1~3. The adequacy of this method to obtain $\Lambda^{\circ(P)}$ from $\Lambda^{(P)}$ in the dilute concentration range would be supported by the approximate constancy of $\Lambda^{\circ(P)}$ around their mean value within the experimental error, which was already found in the previous study on Me_4NCl and Bu_4NCl[2]. However, it was reported[22, 23] that the direct graphical extrapolation of the conductance data of Et_4NCl to infinite dilution with the aid of the theoretical limiting slope was not satisfactory exceptionally. When the conductances of Et_4NCl shown in Table 1 are compared with those measured at a higher concentration by Horne and Young[24], there are rather large discrepancies between them as found

* This salt was kindly supplied by Mr. T. Hori, Laboratory of Analytical Chemistry of our Department.

21) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 1 (1970)

22) A. B. Gancy and S. B. Brummer, *J. Chem. Eng. Data*, **16**, 1763 (1968)

23) S. B. Brummer and A. B. Gancy, "Water and Aqueous Solutions", Chap. 19, Part I, ed. by R. A. Horne, Wiley-Interscience, New York (1972)

24) R. A. Horne and R. P. Young, *J. Phys. Chem.*, **72**, 1763 (1968)

in the cases of Me_4NCl and Bu_4NCl[2].

Table 1 $\Lambda^{\circ(P)}$ (ohm^{-1}·cm^2·equiv^{-1}) of Et_4 NCl in H_2O at 25°C

Sample* Pressure, atm	A	B	C	D	Average
1	108.9	108.9	108.8	108.8	108.9
500	110.9	110.6	110.7	110.8	110.8
1,000	111.4	111.1	111.4	111.1	111.3
1,500	111.2	110.6	110.9	110.2	110.7
2,000	109.9	109.3	109.7	109.1	109.5
2,500	108.3	107.6	107.8	107.1	107.7
3,000	106.2	105.3	105.7	105.1	105.6
3,500	103.3	102.9	103.1	102.8	103.0
4,000	100.8	100.3	100.3	100.1	100.4
4,500	98.3	97.6	97.7	97.5	97.8
5,000	95.6	95.0	94.9	94.6	95.0

* A: 3.866×10^{-4} N,   B: 6.201×10^{-4} N,   C: 8.536×10^{-4} N,   D: 11.598×10^{-4} N at 1 atm

Table 2 $\Lambda^{\circ(P)}$ (ohm^{-1}·cm^2·equiv^{-1}) of Et_4NCl in H_2O at 40°C

Sample* Pressure, atm	A	B	C	D	Average
1	143.9	143.9	143.8	143.9	143.9
500	143.6	143.7	143.7	143.6	143.7
1,000	142.6	142.6	142.6	142.5	142.6
1,500	141.2	141.2	141.0	141.1	141.1
2,000	139.6	139.1	138.9	139.2	139.2
2,500	137.2	136.5	136.4	136.6	136.6
3,000	134.6	133.8	133.5	133.7	133.9
3,500	131.4	130.5	130.3	130.4	130.7
4,000	128.2	127.2	126.9	127.0	127.3
4,500	124.9	123.6	123.4	123.4	123.8
5,000	121.5	120.1	119.9	119.8	120.4

* A: 3.847×10^{-4} N,   B: 5.992×10^{-4} N,   C: 8.495×10^{-4} N,   D: 11.542×10^{-4} N at 1 atm

Obtaining of $\lambda^{\circ(P)}$ from $\Lambda^{\circ(P)}$

The single-ion equivalent conductances at pressure P, $\lambda^{\circ(P)}$ were calculated on the basis of the same postulate used in Ref. (2); it was assumed that the Walden product of Bu_4N^+ is approximately independent of pressure. In the present calculation, the previous[25] interpolations of the values of water viscosity measured by Cappi[3] have been corrected as shown in Table 4, because the interpolation from the direct plot of water viscosity, η° against pressure was found to be less accurate than

25) M. Nakahara, K. Shimizu and J. Osugi, *This Journal*, **40**, 12 (1970)

Table 3 $\Lambda^{\circ(P)}$ (ohm^{-1}·cm^2·equiv^{-1}) of Et$_4$NClO$_4$ in H$_2$O at 25°C

Sample* Pressure, atm	A	B	C	D	Average
1	99.86	99.95	99.82	99.95	99.9
500	98.37	98.71	98.61	98.89	98.6
1,000	95.94	96.49	96.27	96.43	96.3
1,500	93.55	93.82	93.41	93.60	93.6
2,000	90.45	90.69	90.41	90.53	90.5
2,500	87.34	87.46	87.20	87.46	87.4
3,000	84.40	84.38	84.11	84.16	84.3
3,500	81.11	81.11	80.90	80.94	81.0
4,000	77.89	78.02	77.85	77.88	77.9
4,500	74.80	74.99	74.82	74.88	74.9
5,000	71.93	72.08	71.96	72.02	72.0

* A: 4.547×10^{-4} N,   B: 7.276×10^{-4} N,   C: 9.093×10^{-4} N,   D: 10.919×10^{-4} N

that from the plot of log η° against pressure at the high pressures due to the steep dependency of η° upon pressure and the scarcity of the measured points (The corrected values of η° in Table 4 does not make the curve of $\Lambda^\circ(KCl)\cdot\eta^\circ$ vs. pressure at 25°C cross that at 40°C ; see Fig. 4 in Ref. (1)) The obtained values of $\lambda^{\circ(P)}$ at 25°C are summarized in Table 5, where the values of $\lambda^{\circ(P)}$ of other ions so far investigated are also given for comparison after the above correction has been made.   In Table 5, it is seen that the correction does not cause so large alteration in the values of $\lambda^{\circ(P)}$ and the discussion and conclusion in the previous paper might not be amended.

Table 4   The viscosity of water, η°(cP) at 25°C (interpolated by plotting Cappi's data against pressure)

Pressure, atm	Present	Previous[25]
1	0.8937	
500	0.8865	
1,000	0.8905	
1,500	0.9053	
2,000	0.9260	0.9266
2,500	0.9532	0.9534
3,000	0.9853	0.9709
3,500	1.0135	1.0022
4,000	1.0589	1.0392
4,500	1.0895	1.0756
5,000	1.1457	1.1163

M. Nakahara and J. Osugi

Table 5 $\lambda^{\circ(P)}$ (ohm^{-1}·cm^2·equiv^{-1}) of the ions in H_2O at 25°C

Ions Pressure, atm	Bu_4N^+	Bu_4N^+*	Et_4N^+	Me_4N^+	K^+	Cl^-	ClO_4^-
1	19.4	19.4	32.5	44.7	73.5	76.4	67.4
500	19.6	19.6	32.9	45.0	74.7	77.9	65.7
1,000	19.5	19.5	32.5	44.4	74.6	78.8	63.8
1,500	19.2	19.2	31.8	43.8	74.0	78.9	61.8
2,000	18.7	18.7	30.9	42.8	73.0	78.6	59.6
2,500	18.2	18.2	30.0	41.6	71.9	77.7	57.4
3,000	17.6	17.9	29.0	40.3	70.1	76.6	55.3
3,500	17.1	17.3	27.8	38.9	68.4	75.2	53.2
4,000	16.4	16.7	26.8	37.6	66.6	73.6	51.1
4,500	15.9	16.1	26.0	36.1	64.9	71.8	48.9
5,000	15.1	15.5	24.8	34.5	62.4	70.2	47.2

* From Ref. (2)

The postulate introduced to obtain the single-ion equivalent conductances at infinite dilution at high pressures has been justified in Ref. (2) by comparing the calculated transference numbers of K^+ in KCl,

$$t^{\circ(P)}(K^+) = \frac{\lambda^{\circ(P)}(K^+)}{\Lambda^{\circ(P)}(KCl)}, \tag{3}$$

with those directly measured up to 2,000 atm at 25°C. In order to estimate the values of $\lambda^{\circ(P)}$ at 40°C, it was additionally assumed that

$$\tau^{\circ(P)}(K^+) = \frac{t^{\circ(P)}(K^+)}{t^{\circ(1)}(K^+)} \tag{4}$$

Table 6 Walden products of the ions in H_2O at 40°C
(ohm^{-1}·cm^2·$equiv^{-1}$·cP)

Ions Pressure, atm	Et_4N^+	Me_4N^+	K^+	Cl^-
1	28.5	41.1	63.0	66.0
500	27.4	39.8	63.7	67.9
1,000	27.9	40.2	64.4	68.5
1,500	27.8	40.9	65.4	70.3
2,000	27.5	39.8	66.2	72.0
2,500	27.5	39.8	67.1	73.2
3,000	27.5	39.8	67.9	74.3
3,500	27.5	39.8	68.7	75.5
4,000	27.2	39.5	69.4	76.8
4,500	27.2	39.5	70.0	77.5
5,000	27.0	39.1	70.3	79.0

is nearly independent of temperature, because in our laboratory[26] it has been recently shown that $\tau^{\circ(P)}(K^+)$ decreases by only 0.7% with the increase in temperature from 15 to 25°C or from 25 to 40°C both at 1,000 and at 1,500 atm. By using the values of $\tau^{\circ(P)}$ at 25°C calculated from the ionic equivalent conductance values in Table 5, $\varLambda^{\circ(P)}$ (Et$_4$NCl) in Table 2, $\varLambda^{\circ(P)}$ (KCl) in Ref. (1), $\varLambda^{\circ(P)}$ (Me$_4$NCl) in Ref. (2) and $t^{\circ(1)}$ (K$^+$) at 40°C in Ref. (27), the single-ion values of the limiting equivalent conductances at 40°C at high pressures were obtained and used for the calculation of the Walden Products in Table 6.

Pressure dependence of $\lambda^{\circ(P)}$

The relative variation of the limiting equivalent conductances of the ions with pressure is shown in Fig. 1. It is to be noted that the pressure dependence of $\lambda^{\circ(P)}$ of tetraalkylammonium ions such as Bu$_4$N$^+$, Et$_4$N$^+$ and Me$_4$N$^+$ are somewhat similar to each other and, moreover, to that of the viscosity of solvent water. On the other hand, the pressure dependence of $\lambda^{\circ(P)}$ of K$^+$, Cl$^-$ and, above all, ClO$_4^-$ are quite different with each other. Furthermore, it is surprising that ClO$_4^-$ ion has no maximum conductance against pressure at 25°C, although all other ions so far studied have a maximum conductance against pressure at the same temperature. These facts would suggest that the limiting ionic equivalent conductance at high pressure can not be interpreted only by such a macroscopic property of the solvent as viscosity, in spite of the early finding and statement by Röntgen, Fanjung and Tammann.
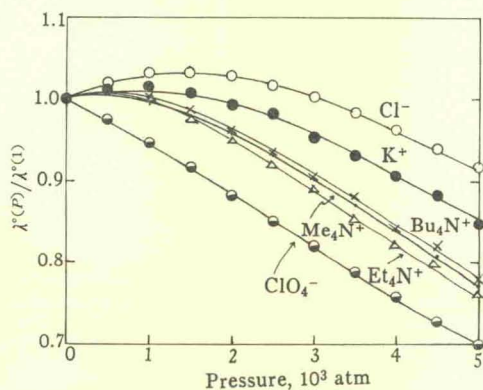

Fig. 1 $\lambda^{\circ(P)}/\lambda^{\circ(1)}$ vs. pressure at 25°C

Variation of the Walden product with pressure

In order to deduct the pressure influence on the macroscopic viscosity of water from that on the ionic conductance, the Walden products, $W=\lambda^{\circ(P)}\cdot\eta^{\circ(P)}$ of the ions at 25°C are calculated by using the values of $\lambda^{\circ(P)}$ in Table 5 and $\eta^{\circ(P)}$ in Table 4 and given in Table 7, and their relative variations with pressure are shown in Fig. 2. There, we see that the pressure coefficient of the Walden product, $\partial W/\partial P$ at 1 atm and 25°C is positive, slightly negative and remarkably negative for Cl$^-$ and K$^+$ ions,

26) Y. Matsubara, K. Shimizu and J. Osugi, *This Journal*, **43**, 24 (1973)
27) R. W. Allgood, D. J. LeRoy and A. R. Gordon, *J. Chem. Phys.*, **8**, 418 (1940)

Table 7   Walden products of the ions in H_2O at 25°C
$(ohm^{-1} \cdot cm^2 \cdot equiv^{-1} \cdot cP)$

Ions Pressure, atm	Et_4N^+	Me_4N^+	K^+	Cl^-	ClO_4^-
1	29.0	39.9	65.7	6.83	60.2
500	29.2	39.9	66.2	69.1	58.2
1,000	28.9	39.5	66.4	70.2	56.8
1,500	28.8	39.7	67.0	71.4	55.9
2,000	28.6	39.7	67.6	72.8	55.2
2,500	28.6	39.7	68.5	74.1	54.7
3,000	28.6	39.7	69.1	75.5	54.5
3,500	28.2	39.4	69.3	76.2	53.9
4,000	28.4	39.8	70.5	77.9	54.1
4,500	28.3	39.3	70.7	78.2	53.3
5,000	28.4	39.5	71.5	80.4	54.1

tetraalkylammonium ions and ClO_4^- ion, respectively. Comparing Fig. 2 with Fig. 3[28, 29], we notice that $\partial W/\partial P$ at 25°C and 1 atm does not correlate with $\partial W/\partial T$ at 1 atm 25°C for these ions. The possible view-points for the interpretation of the pressure and temperature coefficients of the ionic Walden product are summarized in Table 8, where all the view-points but the first one are relevant

Table 8   Prediction of the sign of $\partial W/\partial P$

Point of view	Ref.	Sign of $\partial W/\partial P$
C) Compression effect	20, 21	+
D) Dielectric friction theory	18, 19	+
E) Electrostriction theory		−
P) Pressure-induced dehydration	30	+
S) Structural change of water	28	−, 0, +

to ion-solvent interaction at any rate. Before we correlate the pressure coefficient of the ionic Walden product with the ion-solvent interaction, we now consider the theoretical background of W or $\lambda°$. Although in very dilute electrolyte solutions, λ has been successfully represented in some quantitative forms by Onsager, Fuoss and others, no satisfactory theory for ionic conductance has been established at the two extremes, at infinite dilution and at high concentration.   Owing to this undeveloped stage of the theory for $\lambda°$, we could not make any completely quantitative explanation of the pressure

28) R. L. Kay and D. F. Evans, *J. Phys. Chem.*, **70**, 2325 (1966)

29) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths, London (1957)

30) R. A. Horne, "Advances in High Pressure Research", Vol. 2, Chap. 3, ed. by R. S. Bradley, Academic Press, London (1969)
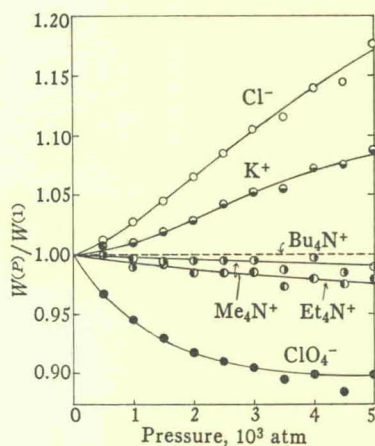
Fig. 2 $W^{(P)}/W^{(1)}$ vs. pressure at 25°C
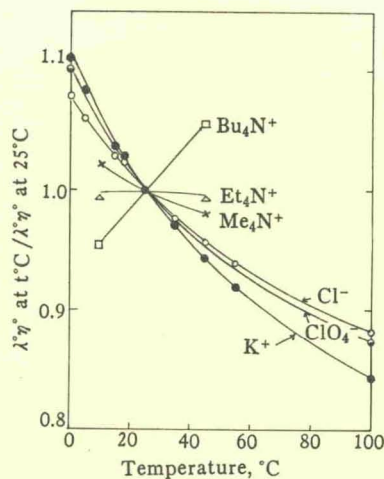
Fig. 3   Variation of the Walden products with temperature at 1 atm λ° of Bu_4N^+, Et_4N^+ and Me_4N^+ are cited from Ref. (28), and λ° of K^+, Cl^- and ClO_4^- from Ref, (29).

coefficient of the ionic Walden product as yet. Then, we want to try some qualitative discussion by using the modified[20,21] Stokes equation,

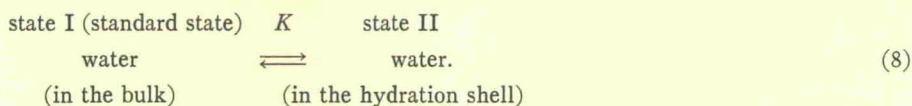$$\lambda^\circ = \frac{|z|\,e\,F}{C\eta^\circ r_e}\,,\tag{5}$$

where z, e, F, C, λ° and r_e are the ionic valence, protonic charge, Faraday constant, hydrodynamic parameter being a function of r_e, solvent viscosity and effective radius of a hydrated ion, respectively. From Eq. (5) we have

$$W = \lambda^\circ \eta^\circ = \frac{|z|\,e\,F}{C r_e}\,.\tag{6}$$

When Eq. (6) is differentiated with respect to pressure, it follows that

$$\frac{\partial W}{\partial P} = -W\frac{\partial r_e}{\partial P}\left(\frac{1}{r_e} + \frac{1}{C}\,\frac{\partial C}{\partial r_e}\right),\tag{7}$$

where the third factor in the right-hand side has a positive value because $\partial C/\partial r_e$ is positive[20,21]. Then, it may be approximated that water exists in the following two states,

state I (standard state) K state II

water $\rightleftarrows$ water.   (8)

(in the bulk)   (in the hydration shell)

For the above equilibrium, we can write

$$K = \frac{a_{II}}{a_I} \doteqdot hm\gamma_{II}\qquad (a_I = 1,\, m \ll 1)\,,\tag{9}$$

where K is the equilibrium constant, a the activity of water, h the hydration number of an ion at infinite dilution, m the concentration of the ion which is arbitrarily very small, and γ_{II} the activity

coefficient of water in the state II.   More than ten years ago, the kinetic aspect of the hydration of ions was discussed by Samoilov[31, 32] especially from the view-point of energetics.   Now, we attempt to discuss the hydration equilibrium in terms of density.   By differentiating the logarithmic form of Eq. (9) with respect to pressure, neglecting the pressure coefficient of γ_{II} and considering the basic thermodynamic relationship, we have

$$\frac{\partial \ln h}{\partial P} = \frac{1}{h} \frac{\partial h}{\partial P} = -\frac{\overline{V}^{\circ}{}_{\mathrm{II}} - \overline{V}^{\circ}{}_{\mathrm{I}}}{RT}, \tag{10}$$

where $\overline{V}^{\circ}{}_{\mathrm{I}}$ and $\overline{V}^{\circ}{}_{\mathrm{II}}$ are the molal volumes of water in each state.   Since we can neglect the compression effect[1] for such weakly hydrated (bulky monovalent) ions as R_4N^+ and ClO_4^-,

$$\text{sign of} \left(\frac{\partial r_e}{\partial P}\right) = \text{sign of} \left(\frac{\partial h}{\partial P}\right). \tag{11}$$

From Eqs. (7) and (10), we have

$$\text{sign of} \left(\frac{\partial W}{\partial P}\right) = \text{sign of} \; (\overline{V}^{\circ}{}_{\mathrm{II}} - \overline{V}^{\circ}{}_{\mathrm{I}}), \tag{12}$$

if $h > 0$.

Eq. (12) means that the density of the hydration shell is larger than that of the bulk water if the Walden product of the ion has a negative pressure coefficient and *vice versa*. As shown in Fig. 2, $\partial W(ClO_4^-)/\partial P$ is strongly negative at 1 atm and comes to be nearly zero at about 5,000 atm. Therefore, we could say the density of the water molecules in the vicinity of ClO_4^- ion is higher than that of the bulk water at the lower pressures and the difference becomes very small at about 5,000 atm. This higher density around ClO_4^- ion could be accounted for by its breaking effect on the water structure which would become weaker at high pressures because pressure would break down the water structure. Furthermore, concerning the two types of molecular models[33, 34] proposed for the orientation of a water molecule with respect to an anion, Buckingham's one that seems to result in the higher density of the hydration shell would be preferred especially for ClO_4^- ion. Judging from Fig. 2 and Table 6, on the other hand, the hydration shells of the tetraalkylammonium ions have slightly higher densities than that of the bulk water ; $\partial W(Bu_4N^+)/\partial P$ really becomes slightly negative, if the directly measured transference number data[26] are used for the estimation of the limiting equivalent conductances of the ions at high pressures instead of the postulate, $\lambda^{\circ(1)}(Bu_4N^+) \cdot \eta^{\circ(1)} = \lambda^{\circ(P)}(Bu_4N^+) \cdot \eta^{\circ(P)}$. Although it is not sufficiently known in terms of both energy and density what kind of structure of water is formed about alkyl chains, the above conclusion drawn from the pressure effect on the Walden products of Me_4N^+, Et_4N^+ and Bu_4N^+ ions seems to be conformed with the following volumetric results : the negative contribution[35] to the partial molal volumes of the hydrophobic hydration

31) O. Ya. Samoilov, "Structure of Aqueous Electrolytic Solutions and the Hydration of Ions", Chap. 3, Consultant Bureau, New York (1965)

32) O. Ya. Samoilov, *Discussion Faraday Soc.*, **24**, 141 (1957)

33) J. D. Bernal and R.H. Fowler, *J. Chem. Phys.*, **1**, 535 (1933)

34) A. D. Buckingham, *Discussion Faraday Soc.*, **24**, 151 (1957)

35) F. J. Millero, "Water and Aqueous Solutions", Chap. 13, ed. by R. A. Horne, Wiley-Interscience (1972)

of the tetraalkylammonium ions and the depressing effect[36] of the tetraalkylammonium ions on the temperature of maximum density of water.

Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto, 606
Japan

36) A. J. Darnell and J. Greyson, *J. Phys. Chem.* **72**, 302 (1968)

"VOID" AND "EXPANSION" VOLUME CONTRIBUTIONS
TO REACTION AND ACTIVATION VOLUMES OF
NEARLY NONPOLAR REACTIONS

BY TSUTOMU ASANO* AND WILLIAM J. LE NOBLE

The reaction volume, ΔV, (and the activation volume, $\Delta V^{\neq}$) of nearly non-polar reactions are divided into three terms: i) van der Waals volume change, ΔV_W, ii) void volume change, ΔV_V and iii) expansion volume change, ΔV_E. Each contribution is estimated by means of Bondi's V_W, Miller's V_0 (volume of the hypothetical liquid at $0°K$) and the known densities of hydrocarbons for the reactions of pure liquids. Unexpectedly the results clearly indicate that ΔV_W is a rather minor factor.

Introduction

There is one well-known but very often overlooked fact about liquid, *i. e.*, about one half of the volume is empty. It is easily forgotten especially when we use bulk properties, for instance, dielectric constant. Although the continuum model of solvent is quite often successful[1], it fails also quite often to reproduce the observed phenomena probably because of its basically wrong description of liquids. In this communication, we would like to demonstrate that the discontinuity of liquid is one of the essential factors that must be taken into account in the interpretation of reaction volumes and activation volumes for nearly nonpolar reactions on the basis of the known volume properties of liquids.

Discussion

Nomenclature

Because of the current confusion of the terminology, it is necessary to make the definitions of several terms clear before we start discussion[2]. The following definitions and symbols are adopted in this communication.

1) For example, see E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms", Academic Press, New York (1966)

2) J. H. Hildebrand, J. M. Prausnitz and R. L. Scott, "Regular and Related Solutions", p. 42, van Nostrand Reinhold, New York (1970)

(1) The van der Waals volume : V_W = the volume of the space occupied by the "van der Waals spheres" of one mole of molecules.

(2) The zero-point volume : V_0 = the volume of the space occupied by one mole of hypothetical liquid at 0°K.

(3) The void volume : $V_V = V_0 - V_W$.

(4) The expansion volume : $V_E = V_T - V_0$. V_T ; molal volume of liquid at T°K.

From the above definitions we have Eq. (1) for molal volume and our first aim is to find out the relative importance of the three contributions to V_T.

$$V_T = V_W + V_V + V_E. \tag{1}$$

Estimation of V_W and V_0

There have been a few attempts to estimate the van der Waals volumes of organic and inorganic compounds. Recently Bondi[3] published tables of group contributions to the van der Waals volume of organic compounds calculated from "the most reliable X-ray diffraction data". His work includes a number of elements and functional groups and enables us to calculate the van der Waals volumes of various kinds of organic molecules.

It is proposed by Miller[4,5] that the zero-point volume can be obtained by Eq. (2),

$$V_0 = \left(\frac{ab}{\varepsilon_0} \right)^{1/2}, \tag{2}$$

where a and b are the van der Waals constants, i. e., $a = 27\mathbf{R}^2 T_c^2 / 64 P_c$ and $b = \mathbf{R}T_c / 8P_c$ in terms of the critical constants, and ε_0 is the vaporization energy for the hypothetical liquid at 0°K which, in turn, can be obtained from the B constant of the Frost-Kalkwarf vapor pressure equation, (3), by Eq. (4)[6].

$$\log P = A + \frac{B}{T} + C \log T + \cdots\cdots. \tag{3}$$

$$\varepsilon_0 = -2.3\mathbf{R}B. \tag{4}$$

For n-alkanes the values of V_0 thus obtained are not only in good agreement with the values by Doolittle[7], Eq. (5), but also consistent with Eq. (6)[8],

$$V_0 = Me^{10/M}, \quad M: \text{molecular weight} \tag{5}$$

$$V_0 = \left(\frac{P_c V_c}{\mathbf{R}T_c} \right) V_c, \tag{6}$$

and Miller claims that the Eqs. (2), (4) and (6) are applicable "to a wide variety of polar and non-polar, organic and inorganic liquids, where hydrogen bonding is absent". Table 1 lists the zero-point volumes of saturated hydrocarbons obtained by several methods along with the molal and the van der Waals volumes. The values for olefinic and naphthenic hydrocarbons are given in Table 2. Obviously

3) A. Bondi, *J. Phys. Chem*, **68**, 441 (1964)

4) A. A. Miller, *ibid.*, **69**, 3190 (1965)

5) A. A. Miller, *J. Polymer Sci. A-2*, **4**, 415 (1966)

6) A. A. Miller, *J. Phys. Chem.*, **68**, 3900 (1964)

7) A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951)

8) A. P. Mathews, *J. Phys. Chem.*, **20**, 554 (1916)

Table 1   Volume properties of saturated hydrocarbons   (ml/mole)

Compound	V_T[a]	V_W[b]	V_0			
			c)	d)	e)	f)
Methane	—	17.1	30.1	28.6	—	—
Ethane	—	27.3	42.0	42.1	42.0	—
Propane	89.5[g]	37.6	55.7	55.3	55.4	—
n-Butane	101.5[g]	47.8	69.0	69.9	69.1	—
n-Pentane	116.1	58.0	82.9	83·6	83.0	82.4
2-Methylbutane	117.4	58.0	—	82.5	—	83.1
2,2-Dimethylpropane	123.3	58.0	82.5	81.5	—	—
n-Hexane	131.6	68.3	96.5	97.2	96.8	95.0
2,2-Dimethylbutane	133.7	68.3	—	98.5	—	—
2,3-Dimethylbutane	131.2	68·2	95.3[h]	96.5	—	—
n-Heptane	147.5	78.5	110	111	111	—
2,3-Dimethylpentane	145.0	78.5	—	109	—	—
2,4-Dimethylpentane	150.0	78.5	—	113	—	—
n-Octane	163.5	88.7	123	126	125	125

a) Densities (25°C) from Refs. 9 and 10   b) Ref. 3   c) Eq. (2), a, b from Ref. 11 and B from Ref. 12   d) Eq. (6), critical properties from Ref. 13   e) Eq. (5)   f) Ref. 8, by $d_1-d_v=C''(T_c-T)^{1/3}$ g) At saturation pressure   h) a, b calculated from the critical properties[13]

Table 2   Volume properties of olefinic and naphthenic hydrocarbons   (ml/mole)

Compound	V_T[a]	V_W[b]	V_0	
			c)	d)
Propene	83.3[e]	34.1	50.9[f]	49.9[g]
1-Butene	95.3[e]	44.3	64.4[f]	66.4[g]
2-Methylpropene	95.5[e]	44.3	64.5[f]	65.8[g]
1-Pentene	110.4	54.5	79.0[f]	78.0[h]
1-Hexene	125.9	64.8	92.8[f]	91.2[h]
1-Heptene	141.7	75.0	107[f]	104[h]
1-Octene	157.9	85.2	120[f]	116[h]
1-Dodecene	223.0	126.2	173[f]	158[g]
Cyclopentane	94.7	50.0	69.9[i]	71.6[j]
Cyclohexane	108.7	60.2	82.3[i]	83.8[j]
Cycloheptane	121.2	70.5	94.9[i]	94.8[k]

a) Densities (25°C) from Ref. 10   b) Ref. 3   c) Eq. (2)   d) Eq. (6)   e) At saturation pressure   f) a, b from Ref. 14 or calculated by the method in Ref. 14, B from Ref. 15   g) Critical properties from Ref. 13   h) Critical properties calculated as described in Ref. 14   i) a, b from Ref. 16, B from Ref. 17   j) Critical properties from Ref. 16 (observed value)   k) Critical properties from Ref. 16 (calculated value)

Table 3   Volume properties of hydrocarbons   (ml/mole)

Compound	V_T[a]	V_W	V_V[b]	V_E[b]
n-Pentane	116.1	58.0	24.9	33.2
2,2-Dimethylpropane	123.3	58.0	24.5	40.8
n-Hexane	131.6	68.3	28.2	35.1
2,3-Dimethylbutane	131.2	68.2	27.1	35.9
n-Heptane	147.5	78.5	31.5	37.5
n-Octane	163.5	88.7	34.5	40.3
1-Pentene	110.4	54.5	24.5	31.4
1-Hexene	125.9	64.8	28.0	33.1
1-Heptene	141.7	75.0	31.7	35.0

a) At 25°C   b) From V_0 by Eq. (2)

the agreements between the V_0 values derived by different methods are not excellent in higher hydro-carbons. However, they still provide very useful information for our purposes.   Table 3 shows V_V and V_E values for several compounds calculated from the values in Tables 1 and 2[18].   It can be seen clearly that the van der Waals volume is only about 50–60% of the macroscopic volume at 25°C in those compounds, and about 20–30% is the expansion volume showing the vigorous thermal motions and continuous collisions of molecules[19].   It is also important to point out the role of the void volume. It consists of about 20–22% of the macroscopic volume.

The dependence of the void and the expansion volumes on pressure must become important when we deal with the systems under high pressure.   It is a difficult task to estimate the compressi-bility of the hypothetical liquid at 0°K.   Probably the most reasonable approach to this problem is the one proposed by Haward[21].   He tried to apply the van der Waals equation to the liquid under high pressure and found the necessity to assign a finite pressure independent isothermal compressibility to the parameter, b_0, which is equal to our V_0.   From the viscosity measurements at high pressures a

9) J. A. Riddick and W. B. Bunger, "Organic Solvents", Wiley-Interscience, New York (1970)
10) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", Carnegie Press, Pittsburg (1953)
11) G. Thodos, A. I. Ch. E. J., **1**, 168 (1955)
12) N. E. Sondak and G. Thodos, ibid., **2**, 347 (1956)
13) K. A. Kobe and R. E. Lynn, Chem. Rev., **52**, 117 (1953)
14) G. Thodos, A. I. Ch. E. J., **1**, 165 (1955)
15) C. H. Smith and G. Thodos, ibid., **6**, 569 (1960)
16) G. Thodos, ibid., **2**, 508 (1956)
17) G. J. Pasek and G. Thodos, J. Chem. Eng. Data, **7**, 21 (1962)
18) Although the values of V_V and V_E are given down to the fractions of one millilitre in the following tables, it does not necessarily mean that the authors claim the accuracy of the estimation better than ±0.5 ml/mole.
19) The van der Waals volume change with the temperature[20] is neglected in our discussion.
20) Ref. 2, p. 38
21) R. N. Haward, Trans. Faraday Soc., **62**, 828 (1966)

similar conclusion was reached[22, 23]. The value of 4.5×10^{-6} atm^{-1} was obtained for n-octane by Haward[21]. Later the same author gets 8.1×10^{-6} atm^{-1} from the internal pressure change with temperature[24]. In considering the accuracy of our zero-point volumes it may be good enough to assume that the zero-point volumes of n-hexane, heptane and octane have the compressibility of 5×10^{-6} atm^{-1}. The volume properties of these hydrocarbons at 25°C under pressure are given in Table 4.

Table 4   Volume properties of hydrocarbons under pressure[a]   (ml/mole)

P, atm	n-Hexane $V_W = 68.3$			n-Heptane $V_W = 78.5$			n-Octane $V_W = 88.7$		
	V_T[b]	V_V[c]	V_E[b]	V_T[b]	V_V[c]	V_E[b]	V_T[b]	V_V[c]	V_E[b]
1	131.6	28.2	35.1	147.5	31.5	37.5	163.5	34.5	40.3
1,000	119.2	27.7	23.2	134.6	30.9	25.2	150.8	33.9	28.2
2,000	113.1	27.2	17.6	128.0	30.4	19.1	143.9	33.3	21.9
3,000	109.0	26.8	13.9	123.6	29.8	15.3	139.1	32.7	17.7
4,000	105.9	26.3	11.3	120.2	29.3	12.4	135.5	32.0	14.8
5,000	103.5	25.8	9.4	117.5	28.7	10.3	132.6	31.4	12.5

a) Densities from Ref. 25   b) At 25°C   c) See text

All of the compression of the zero-point volume is attributed to the void volume. In spite of these rough approximations Table 4 reveals an important and fundamental fact. The expansion volume decreases very rapidly during the initial compression. At 2,000 atm it is already 1/2 of the value at 1 atm and in that pressure range the zero-point volume compression is practically negligible compared with the expansion volume decrease. However, the former contribution will become substantial above 5,000 atm. By extrapolating the plot of log V_E against pressure it seems that the zero-point volume compression will be as large as the expansion volume compression at about 8,000 atm. Bondi[26] has pointed out that about 65,000 atm is required to "squeeze out of all of the empty space in n-heptane".

From the examples given so far it is predictable that the void and the expansion volumes play important roles in the determination of reaction and activation volumes under usual conditions.

Reaction volume

In his review, Hamann[27] points out the following for the reactions between nearly nonpolar molecules. "(a) The reactions which involve the formation of new carbon-carbon covalent bonds·········are all accompanied by substantial contractions. ········· (c) Reactions in which no new carbon-carbon bonds are formed ········· occur with relatively small volume changes." Several examples for hypothetical reactions are given in Table 5. It is quite obvious from Table 5 that the van der Waals

22) A. J. Matheson, *J. Chem. Phys.*, **44**, 695 (1966)

23) D. L. Hogenboom, W. Webb and J. A. Dixon, *ibid.*, **46**, 2586 (1967)

24) R. N. Haward and B. M. Parker, *J. Phys. Chem.*, **72**, 1842 (1968)

25) H. E. Eduljee, D. M. Newitt and K. E. Weale, *J. Chem. Soc.*, 3086 (1951)

26) A. Bondi, *J. Phys. Chem.*, **58**, 929 (1954)

27) S. D. Hamann, "High Pressure Physics and Chemistry", Vol. 2, Chapt. 7, ed. by R. S. Bradley, Academic Press, New York (1963)

Table 5   Volume changes for pure liquid reactions at 25°C and 1 atm   (ml/mole)

Reaction	ΔV_{T}	ΔV_{W}	ΔV_{V}[a]	ΔV_{E}[a]
2 (Propene) $\longrightarrow$ 1-Hexene	-40.7	-3.4	-5.6	-31.7
2(1-Butene) $\longrightarrow$ 1-Octene	-32.7	-3.4	-5.2	-24.1
2 (1-Hexene) $\longrightarrow$ 1-Dodecene	-28.8	-3.4	-8.9	-16.5
1-Pentene $\longrightarrow$ Cyclopentane	-15.7	-4.5	-4.6	-6.6
1-Hexene $\longrightarrow$ Cyclohexane	-17.2	-4.5	-5.9	-6.7
1-Heptene $\longrightarrow$ Cycloheptane	-20.5	-4.5	-7.3	-8.7
n-Pentane $\longrightarrow$ 2,2-Dimethylpropane	$+7.2$	-0.0	-0.4	$+7.6$
n-Hexane $\longrightarrow$ 2,3-Dimethylbutane	-0.4	-0.0	-1.1	$+0.8$

a) From V_0 by Eq. (2)

volume change constitutes only a small portion ($<15\%$) of the total volume change in the dimerization of olefins.   Even in the cyclization which is accompanied by no molecular weight change, ΔV_{W} is a minor factor.   These results clearly demonstrate the importance of the void volume and the expansion volume.   Hamann[27] tried to estimate ΔV_{T} on the molecular basis by means of the cylindrical model and obtained -16 ml/mole for the dimerizations.   He concludes, in the review, "On a molecular scale these effects arise from the large differences between the van der Waals radii and their covalent radii."[28]   However in the light of the present results it seems to be reasonable to conclude that the major part of ΔV_{T} arises from the void and/or the expansion volume changes at least for the nonpolar reactants in pure state[31].   Considering the uncertainties in the estimation of V_0, it might be unreasonable to elaborate the discussion further on the basis of the data listed in Table 5.   However it may be allowed to point out that ΔV_{E} must be a function of the external degrees of freedom and, in pure liquid reactions, of the internal pressure of the reactant and the product from the definition of V_{E}[21].

Before we proceed to the discussion about solution, it seems to be worthwhile to take a look at an interesting model provided by Hamann[29].

"Consider the dimerization of a simple molecule A to A_2.   And suppose that both A and A_2 have the shape of sausages ········· and have the same cross-sectional radii r.   Also suppose that the van der Waals volume of A_2 is exactly twice that of A, so that $\Delta V_{\mathrm{W}}=0$.   Finally, suppose that the molecules are at zero temperature and in a close-packed arrangement in which 'strings' of sausages are aligned parallel and in contact in the x,z plane ········· and are stacked vertically in a hexagonal close-packed array in the y direction" as depicted in Figs. 1 a and b.   The van der Waals volumes and the total volumes are given by Eqs. (7), (8) and (9).

28) He has pointed out later[29] that the value obtained by the cylindrical model includes ΔV_{V} inherently.   It must be also mentioned here that the late Gonikberg[30] pointed out the importance of "free volume" change in activation volumes. However he has never tried to estimate its magnitude.

29) Private communication

30) M. G. Gonikberg, "Chemical Equilibria and Reaction Rates at High Pressures", Moscow (1969), Japanese translation by Y. Ogo, Nikkan Kogyo Shinbunsha, Tokyo (1972)

31) In the following reactions, ΔV_{W} seems to be a major contribution to ΔV_{T}. 1-Hexyne→Cyclohexene, 1-Pentyne→Cyclopentene.
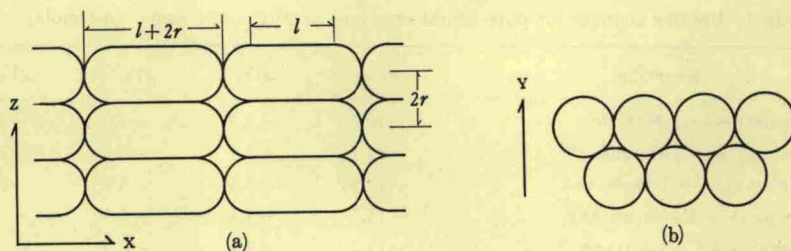
Fig. 1   A hypothetical liquid, A, at 0°K[29]

$$V_W(A) = \frac{1}{2}V_W(A_2) = \pi\left(l + \frac{4r}{3}\right)r^2 N_0, \tag{7}$$

$$V_T(A) = V_0(A) = 2\sqrt{3}\,(l + 2r)r^2 N_0, \tag{8}$$

$$V_T(A_2) = V_0(A_2) = 2\sqrt{3}\left(2l + \frac{10r}{3}\right)r^2 N_0. \tag{9}$$

N_0 : Avogadro's number

Suppose $l = 6\text{Å}$ and $r = 2\text{Å}$, then we obtain,

$$V_W(A) = \frac{1}{2}V_W(A_2) = 65.59 \text{ m}l/\text{mole}, \tag{10}$$

$$V_T(A) = 83.45 \text{ m}l/\text{mole}, \tag{11}$$

$$V_T(A_2) = 155.77 \text{ m}l/\text{mole}, \tag{12}$$

$$\Delta V_T = \Delta V_0 = \Delta V_V = -11.13 \text{ m}l/\text{mole (for } 2A \rightarrow A_2). \tag{13}$$

This model demonstrates the importance of the void volume elegantly.

Partial molal volume and solution reactions

So far we have limited our discussion to pure liquid reactions. In order to proceed to solution reactions it is necessary to understand the physical meaning of partial molal volume. For this purpose it might be beneficial to use a cycle shown below, where A and S stand for one mole of solute and

$$
\begin{array}{ccc}
T°K & nS(l) \xrightarrow[\varnothing(A)]{+A} & [A+nS](l) \\
& \downarrow{\scriptstyle -nV_E(S)} & \uparrow{\scriptstyle +V_E(A+nS)} \\
0°K & nS(l) \xrightarrow[\delta V_W + \delta V_V]{+A} & [A+nS](l)
\end{array}
$$
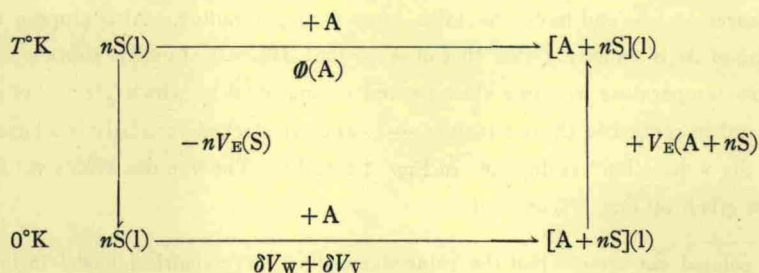
solvent respectively and n is a number of mole of the solvent which is large enough to satisfy the condition of infinite dilution. The molal volume of A, $\varnothing(A)$, is given by Eq. (14) and it is converted to Eq. (15),

$$\varPhi(A) = -nV_E(S) + V_W(A) + V_V(A+nS) - nV_V(S) + V_E(A+nS) \tag{14}$$

$V_V(A+nS)$: total void volume of the solution

$V_E(A+nS)$: total expansion volume of the solution

$$= \delta V_W + \delta V_V + \delta V_E, \tag{15}$$

where the operator, δ, means to take the difference before and after the operation to add one mole of A. The role of δV_V is easily realized if we think a small spherical solute with a radius which is no greater than 0.414 times that of the solvent sphere. Such a solute can occupy the octahedral hole without disturbing the closest-packed lattice of the solvent at 0°K. Therefore, $\delta V_V = -\delta V_W$ and $\varPhi(A) = \delta V_E$. Assarsson and Eirick[32] have shown the possibility to explain the volume of transfer of dimethylacetamide into water as the void volume change during the mixing. However, it is impossible to calculate δV_V in actual solutions at this stage. The role of δV_E is demonstrated by the examples given in Table 6.

Table 6   Partial molal volume of methane and ethane in several
solvents at 25°C[a]   (ml/mole)

Solvent	Methane $V_W = 17.1$		Ethane $V_W = 27.3$	
	$\varPhi$	$\varPhi - V_W$	$\varPhi$	$\varPhi - V_W$
Perfluoroheptane	68.4	51.3	82.9	55.6
n-Hexane	60.0	42.9	69.3	42.0
Carbontetrachloride	52.4	35.3	65.9	38.6
Benzene	52.0	34.9	66.0	38.7
Water	37.3[b]	20.2	51.2[b]	23.9

a) Partial molal volumes from Ref. 33 for organic solvents and from Ref. 34 for water
b) 37.4 (methane), 53.3 (ethane), Ref. 35

The large positive molal volumes of these rather small solutes clearly indicate large positive δV_E in both solutes. It is this δV_E term that is responsible for the temperature and pressure effects on partial molal volumes. The ratio, $V_W/\varPhi = \delta V_W/\varPhi$, is the so-called packing density. Recently, King[36] has demonstrated that the ratio becomes nearly constant in alkylammonium salts with increasing molecular weight and successfully applied the fact to estimate the ionic molal volume of H^+[37].

From Eq. (14) the following relations are derived.

$\Delta V = \Sigma \varPhi$ (products) $- \Sigma \varPhi$ (reactants)

$= V_W(P) + V_V(P+nS) - nV_V(S) + V_E(P+nS) - nV_E(S) - V_W(R)$

$- V_V(R+nS) + nV_V(S) - V_E(R+nS) + nV_E(S)$

$= \{V_W(P) - V_W(R)\} + \{V_V(P+nS) - V_V(R+nS)\} + \{V_E(P+nS)$

$- V_E(R+nS)\} \tag{16}$

32) P. Assarsson and F. R. Eirick, *J. Phys. Chem.*, **72**, 2710 (1968)

33) J. C. Gjaldbaek and J. H. Hildebrand, *J. Am. Chem. Soc.*, **72**, 1077 (1950)

34) W. L. Masterton, *J. Chem. Phys.*, **22**, 1830 (1954)

35) E. W. Tiepel and K .E. Gubbins, *J. Phys. Chem.*, **76**, 3044 (1972)

36) E. J. King, *ibid.*, **73**, 1220 (1969)

37) E. J. King, *ibid.*, **74**, 4590 (1970)

$$= \Delta V_W + \Delta V_V + \Delta V_E. \tag{17}$$

Likewise,

$$\Delta V^{\neq} = \Delta V_W^{\neq} + \Delta V_V^{\neq} + \Delta V_E^{\neq}. \tag{18}$$

As δV_V and δV_E constitute significant parts of $\varnothing$, it is reasonable to expect ΔV_V ($\Delta V_V^{\neq}$) and ΔV_E ($\Delta V_E^{\neq}$) to be also important in ΔV ($\Delta V^{\neq}$). Probably the Diels-Alder reactions will provide the best examples to have an insight into the real situation, because they are believed to be nonionic in many cases[38] and several accurate experimental results[39-41] are available. Unfortunately we are not able to get ΔV_V and ΔV_E separately. In addition because of the lack of the information about the structure of the activated complex, even $\Delta V_W^{\neq}$ is not available. However the observed ΔV, $\Delta V^{\neq}$ and the estimated ΔV_W show that ΔV_W is less than one half of ΔV. Several examples are given in Table 7.

Table 7   Changes in the volume properties for several Diels-Alder reactions   (ml/mole)

Reaction	Solvent	$T°C$	$\Delta V^{\neq a)}$	$\Delta V^{a)}$	ΔV_W	$\Delta V - \Delta V_W$
Maleic anhydride— 1, 3-cyclohexadiene	CH_2Cl_2	35	-39.6	-30.3	-9	-21
Maleic anhydride— isoprene	CH_3COCH_3	35	-39.0	-35.9	-9	-27
Maleic anhydride— isoprene	$CH_3CO_2C_2H_5$	35	-37.4	-36.8	-9	-28
Maleic anhydride— isoprene	CH_3NO_2	35	-32.5	-30.7	-9	-22
Dimethyl acetylene- dicarboxylate— cyclopentadiene	$CH_3CO_2C_2H_5$	10	-30.2	-33.8	-12	-22

a) Refs. 39, 40 and 41

The difference, $\Delta V^{\neq} - \Delta V_W$, may serve as a fairly good measure for $\Delta V_V^{\neq} + \Delta V_E^{\neq}$ because the transition state is believed to be close to the final product geometrically[41]. Furthermore, since the transition state is similar to the initial state electronically[42], $\Delta V_E^{\neq}$ may be determined mainly by the loss of the degrees of freedom of the reactants during the activation step.

Although the examples given here are rather limited, there seems to be little cause to doubt that the void and the expansion volume changes constitute a major part of ΔV and $\Delta V^{\neq}$ in solution.

38) For example, see J. Hine, "Physical Organic Chemistry", Chapt. 25, 2nd ed., McGraw-Hill, New York (1962).

39) R. A. Grieger and C. A. Eckert, *Trans. Faraday Soc.*, **66**, 2579 (1970)

40) R. A. Grieger and C. A. Eckert, *J. Am. Chem. Soc.*, **92**, 2918 (1970)

41) R. A. Grieger and C. A. Eckert, *ibid.*, **92**, 7149 (1970)

42) K. F. Wong and C. A. Eckert, *Trans. Fraday Soc.*, **66**, 2313 (1970)

Conclusion

The volume change and the activation volume for nonplolar reactions are used to be attributed to the difference between the van der Waals and covalent radii with possible minor geometrical contributions from the solvent packing. However as demonstrated here, the van der Waals volume change is not a dominant factor in many cases. Quite often the change in the void and/or the expansion volume is much larger than the van der Waals volume change. The hypothetical division of volumes proposed here seems to be beneficial when we deal with the effects of pressure, temperature and steric hindrance on ΔV and $\Delta V^{\pm}$. The last case will be discussed in near future.

Acknowledgment

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11790
U. S. A.

EVALUATION OF P-V-T PROPERTIES DATA

The Most Probable Values of Compressibility Factor of

Gaseous Ethane and Ethene

BY KAORU DATE*, KOICHI WATANABE** AND MASAHIKO UEMATSU**

The critical evaluations of the P-V-T data of gaseous ethane and ethene have been carried out based upon the experimental data available in literatures. All of the experimental measurements under high pressure were evaluated in view of their reliability and the data were correlated with temperature and pressure. The most probable values and the reference values of the compressibility factor of gaseous ethane and ethene are presented in the form of numerical tables covering the range of temperature from 273.15 to 498.15 K and that of pressure up to 303.98×10^5 Pa for ethane, and from 273.15 to 423.15 K and up to 810.60×10^5 Pa for ethene. The estimated uncertainty of the tabulated values is also presented in the tables.

Introduction

The evaluation of P-V-T properties of gases at high presure has been made as a part of program of "High Pressure Data Center of Japen" organized in the Society of Material Science, Japan, with the sponsorship of the Agency of Science and Technology. In the program, the work for the evaluation of P-V-T properties of gaseous methane had already been made and reported previously in this journal[1]. Next to it, this work for gaseous ethane and ethene has also been performed in a similar manner to the case of methane. The following members of the Committee and researchers attended for the discussion on the present work :

    J. Osugi, Y. Takezaki   (Kyoto Univ.) ;

    I. Tanishita   (Nippon Univ.) ;

    H. Iwasaki, S. Takahashi (Tohaku Univ.) ;

    T. Makita, Y. Tanaka   (Kobe Univ.) ;

    A. Nagashima   (Keio Univ.),

to whom the authors wish to express sincere gratitude for their valuable suggestions and disscussions.

1) J. Osugi, Y. Takezaki and T. Makita, This Journal, **41**, 60 (1971)

Survey and evaluation of *P-V-T* data

There exist seven and eleven different measurements an the *P-V-T* relations of gaseous ethane and ethene, respectively, under high pressures as listed below :

Ethane

A. Michels, W. Van Straaten and J. Dawson	(1954) [2]
A. Michels, snd G. W. Nederbragt	(1939) [3]
J. A. Beattie, G. J. Su and G. L. Simard	(1939) [4]
J. A. Beattie, C. Hadlock and N. Poffenberger	(1935) [5]
H. H. Reamer, R. H. Olds, B. H. Sage and W. N. Lacey	(1944) [6]
B. H. Sage, D. C. Webster and W. N. Lacey	(1937) [7]
V. M. Miniovich and G. A. Sorina	(1971) [8]

Ethene

A. Michels and M. Geldermans	(1942) [9]
A. Michels, J. De Gruyter and F. Niesen	(1936) [10]
A. Sass, B. F. Dodge and R. H. Bretton	(1967) [11]
W. Thomas and M. Zander	(1966) [12]
P. S. Ku and B. F. Dodge	(1967) [13]
R. J. Walters, J. H. Tracht, E. B. Weinberger and	
J. K. Rodgers	(1954) [14]
R. C. Lee and W. C. Edmister	(1970) [15]
H. G. McMath and W. C. Edmister	(1969) [16]
V. H. Danneel and H. Stoltzenberg	(1929) [17]
C. A. Crommelin and H. G. Watts	(1927) [18]

2) A. Michels, W. Van Straaten and J. Dawson, *Physica*, **20**, 17 (1954)

3) A. Michels and G. W. Nederbragt, *ibid.*, **6**, 656 (1939)

4) J. A. Beattie, G. J. Su and G. L. Simard, *J. Am. Chem. Soc.*, **61**, 926 (1939)

5) J. A. Beattie, C. Hadlock and N. Poffenberger, *J. Chem. Phys.*, **3**, 93 (1935)

6) H. H. Reamer, R. H. Olds, B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **36**, 956 (1944)

7) B. H. Sage, D. C. Webster and W. N. Lacey, *ibid.*, **29**, 658 (1937)

8) V. M. Miniovich and G. A. Sorina, *Zh. Fiz. Khim.*, **1971**, 45 (3) 552 (1971)

9) A. Michels and M. Geldermans, *Physica*, **9**, 967 (1942)

10) A. Michels, J. De Gruyter and F. Niesen, *ibid.*, **3**, 346 (1936)

11) A. Sass, B. F. Dodge and R. H. Bretton, *J. Chem. Eng. Data*, **12**, 168 (1967)

12) W. Thomas and M. Zander, *Z. angew. Phys.*, **20**, 417 (1966)

13) P. S. Ku and B. F. Dodge, *J. Chem. Eng. Data*, **12**, 158 (1967)

14) R. J. Walters, J. H. Tracht, E. B. Weinberger and J. K. Rodgers, *Chem. Eng. Progess*, **50**, 511 (1954)

15) R. C. Lee and W. C. Edmister, *A. I. Ch. E. Journal*, **16**, 1047 (1970)

16) H. G. McMath and W. C. Edmister, *ibid.*, **15**, 370 (1969)

17) V. H. Danneel and H. Stoltzenberg, *Z. angew. Chem.*, **42**, 1121 (1929)

18) C. A. Crommelin and H. G. Watts, *Comm. Phys. Lab. Leiden*, No. 189–C (1927)

I. Masson and L. G. F. Dolley   (1923)[19]

The original papers were carefully read through and examined from viewpoint of the reliability of the reported data by the same operations as in the previous work for gaseous methane[1].

The final evaluation was performed by the Committee members and several researchers in this field as described above. As the results for ethane, the set of data by Michels *et al.*[2] was considered to be the most reliable and given the highest weight. The weight second to the above were given to other four sets of data[3~6]. The weight third to the above was given to the set of data[7] and no weight was given to the remainder[8] in which the data were reported only in the limited range around the critical point. For ethene, the set of data by Michels *et al.*[9] was considered to be the most reliable and given the highest weight. The weight second to the above were given to other two sets of data[11,12]. The weight third to the above was given to the set of data[13]. The weights fourth to the above were given to three sets of data[14~16]. No weight was given to three earlier data[17~19]. It was also given to the early data by Michels *et al.*[10]because they were represented in the set of their new data[9] with some corrections.

Methods and results of correlation

The *P-V-T* properties of gases in original papers were expressed in various forms such as compressibility factor *Z*, specific volume *V*, *PV* in Amagat unit and so on, with various units of pressure, temperature, volume and mass. At first, they were reduced to the common expression *Z* with the SI units of pressure and temperature :

compressibility factor, $Z = PV/RT$,

pressure, *P*, in 10^5 Pa ($=1$ bar$=0.986923$ atm) and in atm,

temperature, *T*, in K,

specific volume, *V*, in cm^3/mole.

In these processes, the atomic weights recommended by IUPAC (1969)[20] were adopted as follows ; $C = 12.011 \pm 0.001$ and $H = 1.0080 \pm 0.0003$. For the universal gas constant, the numerical value recommended by IUPAC (the 23rd Conference)[21~23] was adopted :

$R = 8.31433 \pm 0.00044$ (J/K·mole)

$= 82.056 \pm 0.004$ (cm^3·atm/K·mole).

The maximum relative uncertainties of *Z* due to the uncertainties of atomic weights, which amount to 1.2×10^{-4} for ethane and ethene, are not significantly lower than the experimental errors in the precisest measurements. The relative uncertainty of *Z* due to the uncertainties of *R* amounts to

19) I. Masson and L. G. F. Dolley, *Proc. Roy. Soc.*, **A103**, 524 (1923)

20) Commission on Atomic Weights, *Pure and Appl. Chem.*, **21**, 95 (1970)

21) M. L. McGlashan, *ibid.*, **21**, 37 (1970)

22) F. R. Rossini, *ibid.*, **9**, 453 (1964)

23) Thermodynamics Research Center Project, "Selected Values of Properties of Chemical Compounds", Texas A and M Univ., pp. 11~20 (1966)

5.3×10^{-5}, which can be neglected even for the precisest measurements.

It is difficult to estimate the relative uncertainty of Z due to the impurities in the sample gases. However the majority of the samples were pure above 99.9%, and it was regarded that the most abundant impurities were similar hydrocarbons having the like values of Z to the value of ethane or ethene. No correction was made in the calculation of Z and the considerations on purity were taken into the evaluation together with other factors.

In the present correlations of the compressiblitity factors of ethane and of ethene at high pressure, the so-called grid-point method was employed predominantly as follows.

It is the same method as used in the early correlation of the *P-V-T* properties of methane. That is, the values of Z at common grid-points of temperatures and pressures were obtained from the original data reported in respective works. When the data reported are not at one of the common grid-points specified, the interpolation procedures were carried out along an isotherm or an isobar on a digital computer using the least squares method. The precaution was paied for this procedure in order to keep on the experimental accuracy in each original data. Then the mean values at each grid-point were calculated with the weights determined by the critical evaluation in the preceding section. The standard deviations σ were also calculated by the following expression :

$$\sigma = \sqrt{\frac{\Sigma[\omega_i(Z_i - \overline{Z})^2]}{\Sigma\omega_i(n-1)}} \ ,$$

where $\omega_i =$ the weight given,

   $Z_i =$ the compressibility factor in the original work,

   $\overline{Z} =$ the tabulated compressibility factor value,

   $n =$ the number of data sources.

The weighted mean compressibility factor values obtained for ethane are shown in Table 1. The values surrounded by the broken line in the table are "the most probable values of Z" recommended in the Committee because they were obtained by treating the original data in the region containing the most reliable one. The standard deviations to them are also given in the parentheses. The values outside of the broken line in the table are relatively less reliable than the above, because they were obtained only from the data given by low weights. However, they are useful as the reference values, because there is no data more reliable in the present than the data used.

Similarly, as the most probable Z values recommended in the Committee, the weighted mean values obtained for ethene are shown together with the standard deviations in the range surrounded by the broken line in Table 2.

For the evaluation of the compressibility factor of ethane and that of ethene, another method was also tried as follows. At first, sets of the original values of Z with the weights given by the Committee were developed to the power series of density along respective experimental isotherms up to 0.3 g/cm^3 for ethane and up to 0.45 g/cm^3 for ethene. Then the values of Z at round densities calculated by the above procedures were developed to the power series of temperature along each isochore with the reasonable weights given to the values of Z on each isotherm, and the values of Z were calculated at round densities and at the tabulated temperatures. Using these values, the correlations for the isotherms were obtained in the power series of density. Finally, the correlated values of Z at the grid-

K. Date, K. Watanabe and M. Uematsu

Table 1 Most probable values and additional recommended values for the
compressibility factor of ethane

Pressure		Temperature K (°C)									
10^5 Pa	(atm)	273.15 (0)	298.15 (25)	323.15 (50)	348.15 (75)	373.15 (100)	398.15 (125)	423.15 (150)	448.15 (175)	473.15 (200)	498.15 (225)
1.01325	(1)	0.99003 (0.00030)	0.99233 (0.00030)	0.99406 (0.00030)	0.99534 (0.00030)	0.99628 (0.00030)	0.99699 (0.00030)	0.99755 (0.00030)	0.99799 (0.00030)	0.99837 (0.00030)	0.99870 (0.00030)
10.132	(10)	0.8921	0.9199 (0.0012)	0.9386 (0.0009)	0.9523	0.9623	0.9697	0.9755	0.9800	0.9835	0.9864
20.265	(20)	0.7522 (0.00008)	0.8268 (0.0009)	0.8718 (0.0006)	0.9025 (0.0016)	0.9237 (0.0018)	0.9387 (0.0014)	0.9502 (0.0017)	0.9593	0.9662	0.9726
30.398	(30)		0.7125 (0.0015)	0.7976 (0.0008)	0.8491 (0.0010)	0.8836 (0.0011)	0.9084 (0.0007)	0.9269 (0.0010)	0.9400	0.9510	0.9603
40.530	(40)		0.5301 (0.0005)	0.7116 (0.0007)	0.7921 (0.0010)	0.8426 (0.0011)	0.8776 (0.0009)	0.9031 (0.0011)	0.9212	0.9363	0.9486
50.662	(50)			0.6069 (0.0005)	0.7312 (0.0009)	0.8006 (0.0012)	0.8463 (0.0007)	0.8793 (0.0011)	0.9033	0.9235	0.9382
60.795	(60)			0.4664 (0.00001)	0.6664 (0.0013)	0.7576 (0.0010)	0.8157 (0.0008)	0.8566 (0.0011)	0.8865	0.9097	0.9274
70.928	(70)				0.5976 (0.0006)	0.7146 (0.0008)	0.7859 (0.0011)	0.8347 (0.0014)	0.8697	0.8969	0.9178
81.060	(80)				0.5327 (0.0009)	0.6735 (0.0008)	0.7571 (0.0008)	0.8135 (0.0011)	0.8541	0.8853	0.9092
91.192	(90)				0.4849 (0.0004)	0.6365 (0.0008)	0.7306 (0.0008)	0.7942 (0.0012)	0.8396	0.8744	0.9003
101.32	(00)				0.4618 (0.0003)	0.6059 (0.0007)	0.7072 (0.0009)	0.7767 (0.0013)	0.8264	0.8643	0.8933
111.46	(110)					0.5839 (0.0007)	0.6873 (0.0009)	0.7614 (0.0013)	0.8151	0.8557	0.8866
121.59	(120)					0.5713 (0.0011)	0.6720 (0.0005)	0.7484 (0.0010)	0.8056	0.8485	0.8812
131.72	(130)					0.5668 (0.0008)	0.6612 (0.0004)	0.7391 (0.0008)	0.7972	0.8423	0.8766
141.86	(140)					0.5678 (0.0008)	0.6555 (0.0005)	0.7320 (0.0010)	0.7912	0.8377	0.8732
151.99	(150)					0.5738	0.6540 (0.0004)	0.7275 (0.0007)	0.7886	0.8342	0.8707
162.12	(160)					0.5835	0.6568 (0.0004)	0.7259 (0.0007)	0.7862	0.8322	0.8694
172.25	(170)					0.5957	0.6618 (0.0004)	0.7270 (0.0007)	0.7859	0.8335	0.8689
182.38	(180)					0.6104	0.6694	0.7302 (0.0004)	0.7869	0.8348	0.8729
192.52	(190)					0.6250	0.6789	0.7358 (0.0004)	0.7900	0.8366	0.8744
202.65	(200)						0.6900	0.7426 (0.0005)	0.7943	0.8396	0.8768
253.31	(250)							0.7954	0.8330	0.8693	0.9021
303.98									0.8895	0.9163	0.9425

(   ) : Value of standard deviation

[......] : The most probable values

points were calculated from these expressions by the Newton-Raphson method.

These correlated values were compared with those obtained by the grid-point method. Both the values were in good agreement within their standard deviations, but there are slight differences at 298.15 K and 40 atm for ethane, and at 298.15 K and 60 atm for ethene.

Compared with the grid-point method, the above method of correlation is useful for the ranges

Table 2 Most probable values and additional recommended values for the compressibility factor of ethene

Pressure 10⁵ Pa	(atm)	Temperature K (℃)						
		273.15 (0)	298.15 (25)	323.15 (50)	348.15 (75)	373.15 (100)	398.15 (125)	423.15 (150)
1.01325	(1)	0.99242 (0.00030)	0.99443 (0.00030)	0.99571 (0.00030)	0.99661 (0.00030)	0.99727 (0.00030)	0.99779 (0.00030)	0.99822 (0.00030)
10.132	(10)	0.9215 (0.0015)	0.9406 (0.0011)	0.9546	0.9647	0.9720 (0.0001)	0.9778	0.9821
20.265	(20)	0.8284 (0.0005)	0.8749 (0.0006)	0.9066	0.9283	0.9438 (0.0002)	0.9555	0.9645
30.398	(30)		0.8030 (0.0010)	0.8552 (0.0009)	0.8904 (0.0004)	0.9153 (0.0002)	0.9334	0.9471
40.530	(40)		0.7195 (0.0018)	0.8013 (0.0013)	0.8518 (0.0005)	0.8866 (0.0002)	0.9114	0.9302
50.662	(50)		0.6190 (0.0003)	0.7436 (0.0014)	0.8124 (0.0006)	0.8579 (0.0003)	0.8898	0.9136
60.795	(60)		0.4844 (0.0003)	0.6818 (0.0016)	0.7723 (0.0009)	0.8295 (0.0004)	0.8688	0.8977
70.928	(70)		0.3409 (0.0003)	0.6171 (0.0019)	0.7323 (0.0011)	0.8017 (0.0006)	0.8484	0.8825
81.060	(80)		0.3170	0.5541 (0.0022)	0.6934 (0.0013)	0.7749 (0.0007)	0.8290	0.8682
91.192	(90)		0.3273	0.5017 (0.0023)	0.6572 (0.0015)	0.7497 (0.0007)	0.8108	0.8548
101.32	(100)		0.3451	0.4706 (0.0026)	0.6255 (0.0016)	0.7268 (0.0006)	0.7942	0.8425
111.46	(110)		0.3656	0.4605	0.6012 (0.0020)	0.7074 (0.0005)	0.7793	0.8314
121.59	(120)		0.3872	0.4622	0.5847 (0.0022)	0.6913 (0.0005)	0.7665	0.8218
131.72	(130)		0.4096	0.4711	0.5756 (0.0022)	0.6793 (0.0008)	0.7559	0.8136
141.86	(140)		0.4321	0.4841	0.5731 (0.0021)	0.6712 (0.0009)	0.7478	0.8070
151.99	(150)		0.4549	0.4996	0.5770	0.6668 (0.0010)	0.7421	0.8020
162.12	(160)		0.4777	0.5166	0.5839	0.6657 (0.0009)	0.7388	0.7987
172.25	(170)		0.5005	0.5346	0.5937	0.6679 (0.0009)	0.7379	0.7969
182.38	(180)		0.5233	0.5533	0.6055	0.6728 (0.0008)	0.7391	0.7969
192.52	(190)		0.5460	0.5724	0.6188	**0.6801** (0.0010)	0.7422	0.7980
202.65	(200)		0.5687	0.5906 (0.0036)	0.6333	**0.6889** (0.0008)	0.7470	0.8007
253.31	(250)		0.6798 (0.0033)	0.6898 (0.0039)	0.7149 (0.0013)	0.7494 (0.0008)	0.7896	0.8309
303.98	(300)		0.7889 (0.0040)	0.7888 (0.0044)	0.8027 (0.0018)	0.8233 (0.0008)	0.8503	0.8800
354.64	(350)		0.8962 (0.0049)	0.8880 (0.0055)	0.8916 (0.0025)	0.9027 (0.0009)	0.9189	0.9390
405.30	(400)		1.0015 (0.0058)	0.9851 (0.0063)	0.9802 (0.0029)	0.9839 (0.0009)	0.9913	1.0033
455.96	(450)		1.1046 (0.0064)	1.0813 (0.0071)	1.0684 (0.0032)	1.0653 (0.0006)	1.0652	1.0702
506.62	(500)		1.2063 (0.0070)	1.1758 (0.0077)	1.1560 (0.0034)			
607.95	(600)		1.4058 (0.0082)	1.3615 (0.0089)	1.3293 (0.0035)			
709.28	(700)		1.6008 (0.0088)	1.5430 (0.0099)	1.4995 (0.0037)			
810.60	(800)		1.7920 (0.0086)	1.7208 (0.0107)				

(   ) : Value of standard deviation

⌐ ¬ : The most probable values

Table 3   The estimated uncertainties of compressibility factor of ethane

Pressure 10^5Pa	(atm)	Temperature K (℃)									
		273.15 (0)	298.15 (25)	323.15 (50)	348.15 (75)	373.15 (100)	398.15 (125)	423.15 (150)	448.15 (175)	473.15 (200)	498.15 (225)
1.01325	(1)	0.030%	0.030%	0.030%	0.030%	0.030%	0.030%	0.030%	0.030%	0.030%	0.030%
10.132	(10)	0.10	0.12	0.09	0.17	0.20	0.15	0.17	0.20	0.30	0.30
20.265	(20)	0.10	0.12	0.10	0.17	0.20	0.14	0.16	0.20	0.30	0.30
30.398	(30)		0.12	0.10	0.17	0.17	0.12	0.16	0.25	0.35	0.40
40.530	(40)		0.12	0.10	0.16	0.15	0.12	0.15	0.30	0.40	0.45
50.662	(50)			0.10	0.15	0.15	0.11	0.15	0.30	0.40	0.55
60.795	(60)			0.11	0.14	0.14	0.11	0.15	0.35	0.40	0.55
70.928	(70)				0.13	0.13	0.11	0.15	0.35	0.40	0.55
81.060	(80)				0.12	0.12	0.11	0.15	0.35	0.40	0.55
91.192	(90)				0.11	0.12	0.11	0.15	0.35	0.40	0.50
101.32	(100)				0.10	0.13	0.11	0.15	0.35	0.40	0.50
111.46	(110)					0.15	0.11	0.15	0.35	0.40	0.50
121.59	(120)					0.17	0.11	0.14	0.40	0.40	0.50
131.72	(130)					0.19	0.11	0.14	0.35	0.40	0.45
141.86	(140)					0.23	0.12	0.14	0.25	0.40	0.45
151.99	(150)					0.27	0.13	0.13	0.20	0.40	0.45
162.12	(160)					0.32	0.16	0.13	0.20	0.40	0.45
172.25	(170)					0.35	0.18	0.13	0.20	0.30	0.40
182.38	(180)					0.39	0.20	0.13	0.20	0.25	0.25
192.52	(190)					0.44	0.20	0.13	0.20	0.25	0.25
202.65	(200)						0.20	0.13	0.20	0.25	0.25
253.31	(250)							0.20	0.20	0.25	0.25
303.98	(300)								0.20	0.25	0.25
354.64	(350)								0.20		

in which the number of sources available is very restricted.   In the case of ethene, there was only one source by Michels *et al.*[9] for the grid-points outside of the broken line in the table, and the mean values could not be obtained by the grid-point method.   Thus, for these ranges, the values obtained by the correlation method are presented as the additional recommended values in Table 2.   They are reconciled well with the adjacent values obtained by the grid-point method.

For ethane and ethene, the reliable values of Z at low pressure cannot be obtained by extrapolating the experimental values of Z at high pressures to the low pressures.   The authors collected the reliable data of the experimental second and third virial coefficients, B_T and C_T, at low pressure for ethane[2, 24~30] and ethene[10~13, 18, 24, 25, 31~36].   Then using the expression : $Z = 1 + B_T P + C_T P^2$, each value of Z at 1 atm and at each experimental temperature was calculated.   Their equally weighted mean values at the grid-points on 1 atm were calculated developing to the power series of temperature using the least square method.   In Tables 1 and 2, those values are given as the recommended values of Z at the normal pressure, 1.01325×10^5 Pa $(=1$ atm), together with the standard deviations shown in the parentheses.

The original data sources are few at most of the grid-points for ethane and ethene.   Thus the standard deviations calculated have little significance in regard to the statistical meaning and they showed some unreasonable irregularities at some local grid-points practically.   From these viewpoints,

Table 4   The estimated uncertainties of compressibility factor of ethene

Pressure		Temperature K　(℃)						
10^5 Pa	(atm)	273.15 (0)	298.15 (25)	323.15 (50)	348.15 (75)	373.15 (100)	398.15 (125)	423.15 (150)
1.01325	(1)	0.030%	0.030%	0.030%	0.030%	0.030%	0.030%	0.030%
10.132	(10)	0.10	0.11	0.05	0.04	0.03	0.10	0.10
20.265	(20)	0.10	0.12	0.07	0.05	0.03	0.10	0.10
30.398	(30)		0.13	0.10	0.06	0.03	0.10	0.10
40.530	(40)		0.15	0.15	0.07	0.04	0.10	0.10
50.662	(50)		0.16	0.19	0.08	0.05	0.10	0.10
60.795	(60)		0.17	0.24	0.11	0.06	0.10	0.10
70.928	(70)		0.18	0.28	0.14	0.07	0.10	0.10
81.060	(80)		0.20	0.32	0.15	0.09	0.10	0.10
91.192	(90)		0.22	0.35	0.17	0.11	0.10	0.10
101.32	(100)		0.23	0.38	0.18	0.12	0.10	0.10
111.46	(110)		0.25	0.41	0.20	0.13	0.10	0.10
121.59	(120)		0.27	0.43	0.22	0.14	0.10	0.10
131.72	(130)		0.28	0.46	0.23	0.15	0.10	0.10
141.86	(140)		0.30	0.48	0.24	0.15	0.10	0.10
151.99	(150)		0.32	0.50	0.25	0.16	0.10	0.10
162.12	(160)		0.34	0.52	0.25	0.16	0.10	0.10
172.25	(170)		0.36	0.54	0.26	0.16	0.10	0.10
182.38	(180)		0.38	0.55	0.28	0.16	0.10	0.10
192.52	(190)		0.40	0.56	0.28	0.16	0.10	0.10
202.65	(200)		0.43	0.57	0.29	0.15	0.10	0.10
253.31	(250)		0.48	0.69	0.30	0.14	0.10	0.10
303.98	(300)		0.51	0.61	0.30	0.13	0.10	0.10
354.64	(350)		0.55	0.63	0.30	0.11	0.10	0.10
405.30	(400)		0.57	0.64	0.30	0.09	0.10	0.10
455.96	(450)		0.58	0.65	0.30	0.07	0.10	0.10
506.62	(500)		0.58	0.66	0.30			
607.95	(600)		0.58	0.65	0.28			
709.28	(700)		0.55	0.64	0.25			
810.60	(800)		0.48	0.62				

it is appropriate that the values determined as below are adopted for the uncertainty or the tolerance instead of the standard deviations.   The standard deviations were plotted in graph against pressures

24) A. E. Eucken and A. Parts, *Z. Phys. Chem.*, **B20**, 184 (1933)

25) J. D. Lambert, G. A. Roberts, J. S. Rowlinson and V. J. Wilkinson, *Proc. Roy. Soc.*, **A196**, 113 (1949)

26) J. O. Hirschfelder, *et al.*, *J. Chem. Phys.*, **10**, 201 (1942)

27) S. D. Hamann and W. J. McManamey, *Trans. Faraday Soc.*, **49**, 149 (1953)

28) H. G. David, S. D. Hamann and R. G. H. Prince, *J. Chem. Phys.*, **20**, 1973 (1952)

29) J. A. Huff, *et al.*, *J. Chem. Eng. Data*, **8**, 306 (1963)

30) A. E. Hoover, I. Nagata, T. W. Leland and R. Kobayashi, *J. Chem. Phys.*, **48**, 2633 (1968)

31) W. Cawood and H. S. Patterson, *J. Chem. Soc.*, **1933**, 619

32) E. E. Roper, *et al.*, *J. Phys. Chem.*, **44**, 835 (1940)

33) R. B. Bird, *et al.*, *J. Chem. Phys.*, **18**, 1395 (1950)

34) G. A. Bottomley, D. S. Massie and R. Whytlaw-Gray, *Proc. Roy. Soc.*, **A200**, 210 (1950)

35) H. M. Ashton and E. S. Halberstadt, *ibid.*, **A245**, 373 (1958)

36) E. G. Butcher and R. S. Dadson, *ibid.*, **A277**, 448 (1964)

on each isotherm. The smoothed curves were drawn for each set of the standard deviations, with the
precautions to keep in harmony with those of the adjacent isotherms and to exceed reasonably most
of points of the standard deviations.   The values read from the curves were recommended as the
uncertainties of the tabulated values of Z.   They are shown in Tables 3 and 4, in the form of the
percentage deviation calculated by the following definition :

$$\text{uncertainty} = \frac{100 \times \bar{\sigma}}{\bar{Z}},$$

where $\bar{\sigma}$ is the smoothed standard deviation obtained by the method mentioned above and $\bar{Z}$ is the
tabulated most reliable compressibility factor value.

The percentage deviations of the original data from the tabulated values were also calculated by :
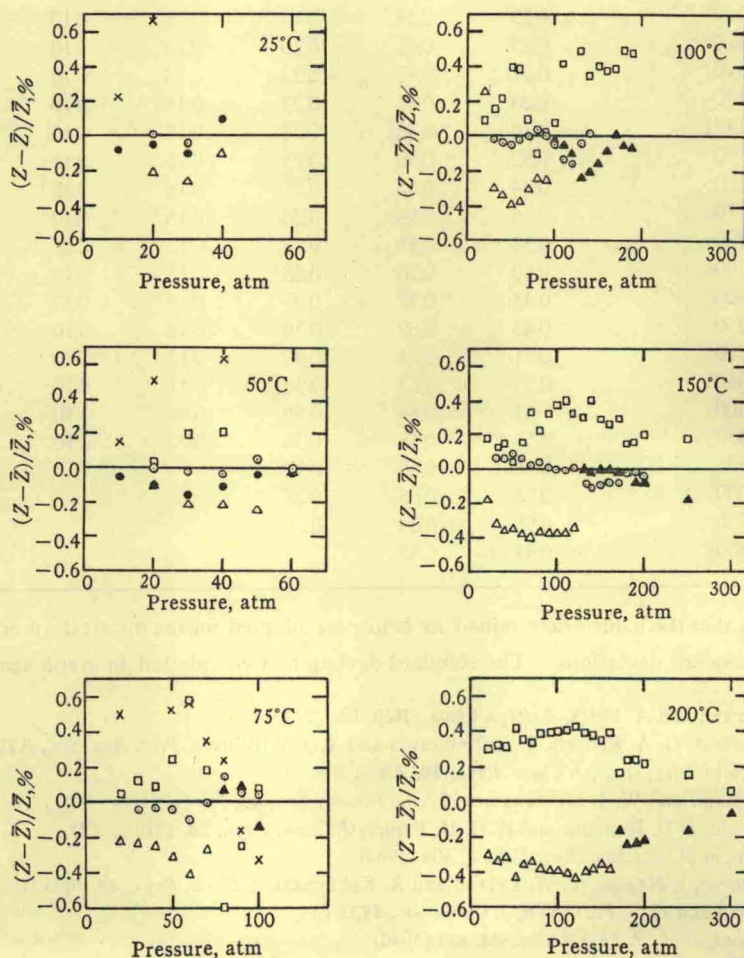
Fig. 1   Percentage deviation diagrams for ethane

⊙: Ref 2),   ●: Ref 3),   ▲: Ref 4)
△: Ref 5),   □: Ref 6),   ×: Ref 7)

percentage deviation $= \dfrac{100(Z - \overline{Z})}{\overline{Z}}$,

where Z is the compressibility factor interpolated from the original measurements and $\overline{Z}$ is the tabulated most reliable compressibility factor value.   Some of them are given graphically in Figs. 1 and 2.
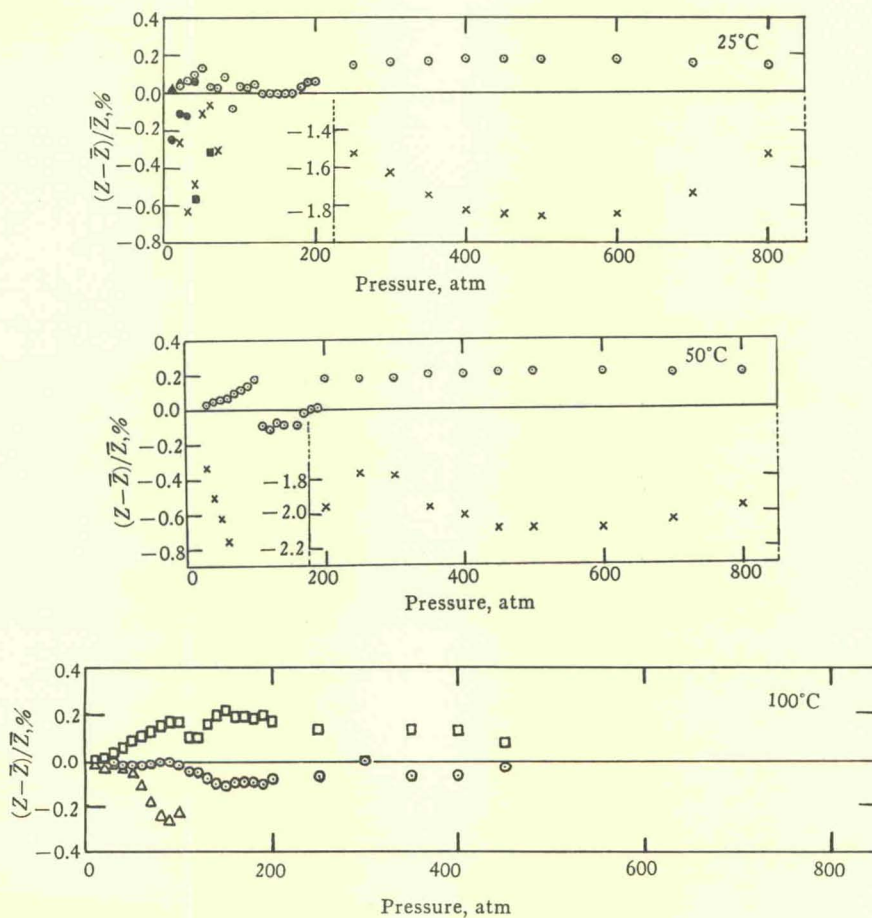
Fig. 2   Percentage deviation diagrams for ethene

⊙: Ref 9),   □: Ref 11),   ▲: Ref 12)
△: Ref 13),   ●: Ref 14),   ×: Ref 15)
■: Ref 16)

Acknowledgment