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SOME EVALUATED THERMOPHYSICAL PROPERTIES OF GASEOUS ETHYNE

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The evaluations of compressibility factor, specific heat, viscosity, and thermal conductivity of gaseous ethyne (acetylene) under pressures have been carried out on the experimental data reported in the literatures.

The available data are too short to be well evaluated and processed, yet the correlation equation or the numerical figures given here would be regarded as the most probable in the present circumstance.

Introduction

As one of the subjects in the data evalution project sponsored by the Agency of Science and Technology, processings to determine the most reliable data on *PVT*, specific heat, viscosity and thermal conductivity of gaseous C_2H_2 under high pressure have been carried out based on the experimental data in the literature by the member*1) of the Committee for that project.

Available observed data on these properties, however, are quite scanty, and much difficulties have been experienced in the works, and the results are by no means as sufficiently correct as those reported hitherto*2); nevertheless in view of the lack of evaluated complilation, the presented here will be of utility, especially for indutrial use.

PVT Relation of Gaseous Ethyne

Source of experimental data: We could find only 5 papers dealing with the experimental determination of volume or density under pressure.

Sameshima (1926)[1] At 0 and 25°C; respectively, several measuring points between 1~11.4 atm.

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*2) For lower hydrocarbons see the relevant papers in *This Journal*, **41** (1971)~**48** (1978)

[1] J. Sameshima, *Bull. Chem. Soc. Japan*, **1**, 41 (1926)

Remarski *et al.* (1933)[2] At 20°C only, 7 points between 11.4~20.6 atm.

Kiyama *et al.* (1951)[3] Only graphical representation is given by smoothing the observed values for −8~250°C and 1~135 atm.

Hölemann *et al.* (1954)[4] Five points between 5.5~24.0 atm, along every 5 isotherms between 0 and 50°C.

Bottomley (1959)[5] Five isotherms between 0~40°C, 4 measrured points between 0.5~2 atm along respective isotherm.

Also, more than 5 papers report the density at 0°C, 1 atm, *viz.*, Leduc (1898)[6], Stahrfoss (1918)[7], Maass (1918)[8], Howarth (1924)[9] and Bando (1967)[10].

Furthermore there are 4 reports, the authors of which, though they did not produce any data, have compiled or calculated according to some equations and have given the results in the form of the table: Teranishi[11] obtained the raw data of Kiyama and calculated residual volume $\varDelta\equiv v\left(\frac{Pv}{RT}-1\right)$ or $\alpha\equiv\frac{RT}{P}-v$ and got Z values $\left(\equiv\frac{Pv}{RT}\right)$ by smoothing out $\varDelta$ or α graphically. Weber[12], adopting Hölemann's data for lower pressures and Teranishi's for higher pressures, calculated α and gave the smoothed values. Din's table[13] was prepared by calculation using the Clasuius equation, $\{P+\mathrm{a}/T(v+\mathrm{c})^2\}(v-\mathrm{b})=RT$, the constant being determined from the critical constants. Canjar[14] gave no description on the derivation of numerical figures, but the results are in good agreement with Din's.

In Fig. 1 is given the range in which the above data are presented; for lower temperatures measurements are made down to the closest to the saturation line. However, as can be easily supposed, it is almost impossible to compare them intact at common P and T conditions.

Units and general constans: *PVT* relation is represented by Z at each temperature and pressure, and the reported numerical values have been recalculated and transferred to Z using the following constants: $R=8.31441\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}(\equiv\mathrm{m^3\cdot Pa\cdot K^{-1}\cdot mol^{-1}})=82.0568\,\mathrm{cm^3\cdot atm\cdot K^{-1}\cdot mol^{-1}}$ given by CODATA, 1973[15]; therefore $(Pv)_{0^\circ\mathrm{Ideal}}=22.41383\times10^{-3}\,\mathrm{m^3\cdot atm\cdot mol^{-1}}$; molecular weight C=12.011 and H=1.0079 by IUPAC, 1975[16]. As the temperature scale T_{68}/K (International Practical

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2) W. Rimarski and M. Konschak, *Autogene Metallbearbeitung*, **26**, 129 (1933)

3) R. Kiyama, T. Ikegami and K. Inoue, *This Journal*, **21**, 58 (1951)

4) P. Hölemann and R. Hasselmann, *Forschungsberichte des Wirtschafts-u. Verkersministriums Nordhein Westfalen*, **78**, 1 (1954)

5) G. A. Bottomley, C. G. Reeves and G. H. F. Seiflow, *J. Appl. Chem.*, **9**, 517 (1959)

6) A. Leduc, *Annalen der Physik*, **15**, 36 (1898)

7) K. Stahrfoss, *J. Chimie Physique*, **16**, 175 (1918)

8) O. Maass and J. Russell, *J. Am. Chem. Soc.*, **40**, 1847 (1918)

9) J. Howarth and F. P. Burt, *Trans. Faraday Soc.*, **20**, 544 (1924)

10) K. Bando, *Kogyokagaku Zasshi* (J. Ind. Chem., Japan), **70**, 2201 (1967)

11) H. Teranishi, *This Journal*, **25**, 25 (1955).

12) J. H. Weber, *A. I. Ch. E. Journal*, **5** (1), 17 (1959)

13) F. Din, "Thermodynamic Functions of Gases" vol. 2 Buttroworths (1962) p. 75

14) L. N. Canjar and F. S. Manning, "Thermodynamic Properties & Reduced Correlations for Gases" Gulf (1967), p. 105

15) *CODATA Bulletin*, 11 (1973)

16) *Kagaku To Kogyo* (Chem. and Ind., Japan), 29 (4), (1976)

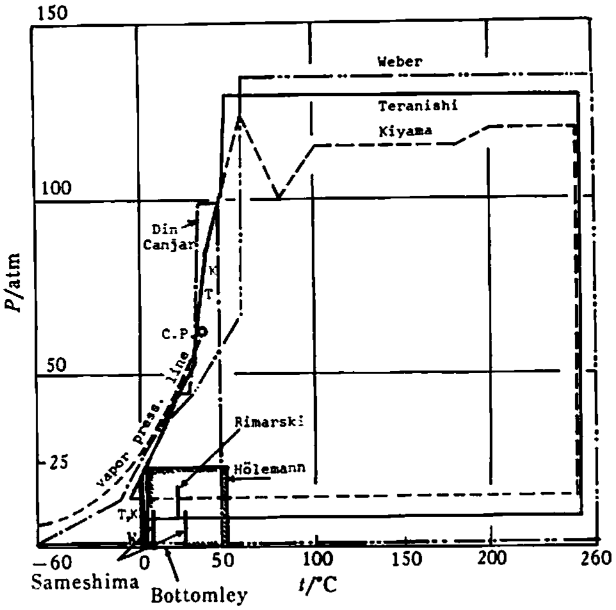

Fig. 1 Range of Reported Z Value

Temperature Scale, 1968 17)) was used; the reported temperatures given in t_{27} and t_{48} were recalculated into t_{68} and then transfered to T_{68}; $T_{\mathrm{ice}}=273.1500\,\mathrm{K}$ 17).

The effect of error accompanying these constans can be neglected for the accuracy of Z in the present case. As to the unit of pressure, 10^5 Pa (=1 bar=0.986923 atm) is used in the final expression.

Accessment: Procedure of accessment is as follows:

First the Committee examines each of the reports which give "observed values" referring to the next items 18).

1. Carreer of the investigator in that research.
2. Contribution of the institute in that field.
3. Character of the journal in which that work was published.
4. Principal aim of the report.
5. Purity or method of preparation and purification of the sample.
6. Experimental method adopted and the theory on which the measurement was based.
7. Construction of equipments, and calibration method or the standard used.
8. Precaution paid in measuring techniques.
9. Precision of experimental conditions.
10. Fundamental constants used in calculation.
11. Experimental errors reported and corrections made therein.

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17) *Keiryo Kenkyusho Hokoku* (Report Natl. Res. Lab. Metrology, Japan), **48** (3), 43 (1969)

18) Y. Takezaki, "The Evaluation of Physical Properties of Fluids Under Pressures" (The Physico-Chemical Soc. Japan) (1975), p. 11; J. Osugi, Y. Takezaki, H. Iwasaki, T. Makita and K. Watanabe, "Proc. 5th Biennial Int. CODATA Conf." (1976), p. 451

12. Extent of scattering of observed values.
13. Comparison with other values in literature.

Then, usually, the Committee endows each group of data with a relative weight as the result of overall judgement.

Before we proceed further, however, some comment on Kiyama's paper will be presented. Although Kiyama did not give numerical figures, his paper is the sole report in which measurements were conducted in higher pressures and temperatures, so it is strongly hoped to retrace his original data; fortunatelly the lognote could become avaibable by favor of the reporters and the raw data could be processed. The following points were noted:

1. Volume or density was not measured and only the ratio of volumes before and after compression was observed together with pressure. The amount of the sample taken in the piezometer of known volume near NTP was calculated as an ideal gas. Therefore correction was made by us, as the first approximation, using the average values of Z or thermal expansion coefficient in the vicinity of NTP given by Sameshima, Bottomley and Hölemann.
2. The measuring points usually do not lie exactly on isothermal lines, scattering within ±1°C (see later).

Now, on examination of the description of the reports listed above it was inferred that Bottomley's experiment appears to be the most precise and the values the most reliable, next to this comes Hölemann's, and next Sameshima's; Rimarki's and Kiyama's seem to be appreciably less accurate. On the density at 0°C and 1 atm the experiments of Maass, Sameshima, Howarth and Bando are considered equally reliable, but Bando's measurement is more elaborate.

As to the Item 12, we have tested the scattering of the observed Z's of each paper by comparing them with experimental equations, $Z=1+AP+BP^2+CP^3$, prepared by least squares fitting, in several sections on one isotherm of respective paper if necessary; on the other hand, for Kiyama's raw data the coefficients of the polynomial involving P terms up to the third power and $1/T$ terms up to the second were determined by two dimensional least quares with the observed Z's at different P and T within 10∼20 atm and 0∼50°C.

The result is:		mean scattering	max.
Sameshima		∼0.05%	0.1%
Rimarki		∼0.3%	0.7%
Kiyama	0∼30°C	∼0.14%	0.28%
	40°C	∼0.42%	1.22%
	52°C	∼0.30%	0.54%
Hölemann		∼0.05%	0.1%
Bottomley		∼0.0001%	0.0002%

These trends of scattering seem in line with the above inference on the elaboration and precision of experimental procedures.

Processing: As the first step, in order to get accurate values as far as possible, we have limited the range of processing to 1～20 atm and 0～50°C, and adopting the original data of Hölemann, Bottomley, and four ρ vaules at 0°C, 1 atm each from Maass, Sameshima, Howarth and Bando, have prepared the experimental equation $Z=1+\mathrm{A}P+\mathrm{B}P^2+\mathrm{C}P^3+\frac{\mathrm{D}P+\mathrm{E}P^2+\mathrm{F}P^3}{T}+\frac{\mathrm{G}P+\mathrm{H}P^2+\mathrm{I}P^3}{T^2}$ by P, T two dimentional equal weight least squares. It was found that the scattering of the observed values (in total 39 points) is: mean 0.07% (maximum deviation 0.26%, 7 points giving 0.25～0.1% deviation, 25 points for 0.1～0.01%, 3 points for <0.01%) and the standard deviation σ of the most probable values ($\equiv\sqrt{\frac{\sum(\mathrm{residue})^2}{39(39-9)}}$; 9 is the number of coefficients.) is 0.00017. Addition of Sameshima's data doubles the mean scattering.

Second step: As mentioned before, Kiyama's data show much larger scattering, suggesting that they will not be included in the processing unless with much lessened weight. However, this paper is the sole source of measured values at higher temperatures and pressures, so if it was able to extend the P-T range by connecting smoothly Kiyama's data of higher P, T range with the above and make the whole uncertainty not to increase too much, it would be quite beneficial especially on practical standpoint.

Thus, this time two dimentional equal weight least quares have been performed on the Benedict-Webb-Rubin equation,

$$Z=1+(\mathrm{A}+\mathrm{B}/T+\mathrm{C}/T^3)\rho+(\mathrm{D}+\mathrm{E}/T)\rho^2+\frac{\mathrm{F}}{T}\rho^5+\frac{\mathrm{G}\rho^2}{T^3}(1+\gamma\rho^2)\cdot\exp(-\gamma\rho^2), \qquad (1)$$

utilizing all the date adopted in the first step for pressure less than 20 atm and Kiyama's for pressure above 10 atm.

The obtained result is given in Table 1 together with the coefficient of eq. (1), where the number of data is 129, mean deviation 0.51%, maximum deviation 3.3%, deviation of 3.2～1% 61 points, deviation of 1～0.51% 28 points, deviation of 0.50～0.1% 61 points and those with less than 0.1% deviation are 23 points, and the standard deviation σ of calculated Z (see before) is 0.00046.

From the comparison of the results between the first step and the second one in the region of 1～50 atm and 0～50°C, we can find that the discrepancies between corresponding Z's at common P and T are usually less than 0.002, seldom reach 0.008, being located within the sum of 3σ's in both steps, *viz.*, 0.0005+0.0014.

Thus, in spite of rather larger standard deviation ($3\sigma=0.0014$) and the lack in sufficient security of correctness of the observed data, which is primarily due to the absence of comparable data, we are to propose the result of the second step as the most probable as a whole judgement (Table 1). One of the reasons to prefer the second step is that, as seen in the succeeding section the calculated values of c_p derived from the second derivative of Z show normal change with pressure, whereas improper use of data (*e.g.*, too narrow range or incorrect data) is apt to lead to quite an irregular, even negative in some cases, tendency.

Departures of the literature values from the present correlation, % deviation$=\frac{Z-Z_m}{Z_m}\times 100$ (Z_m

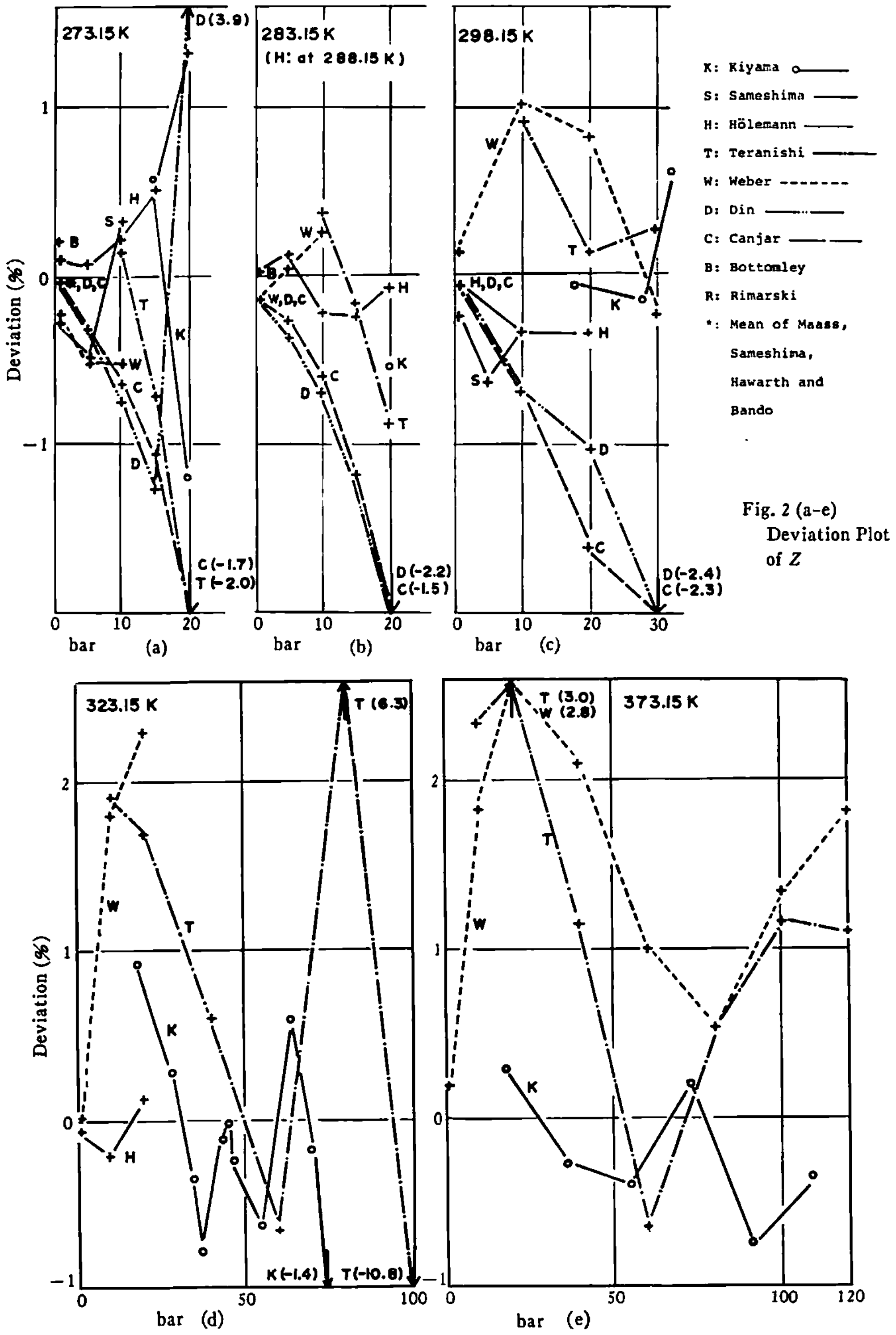

Fig. 2 (a-e) Deviation Plot of Z

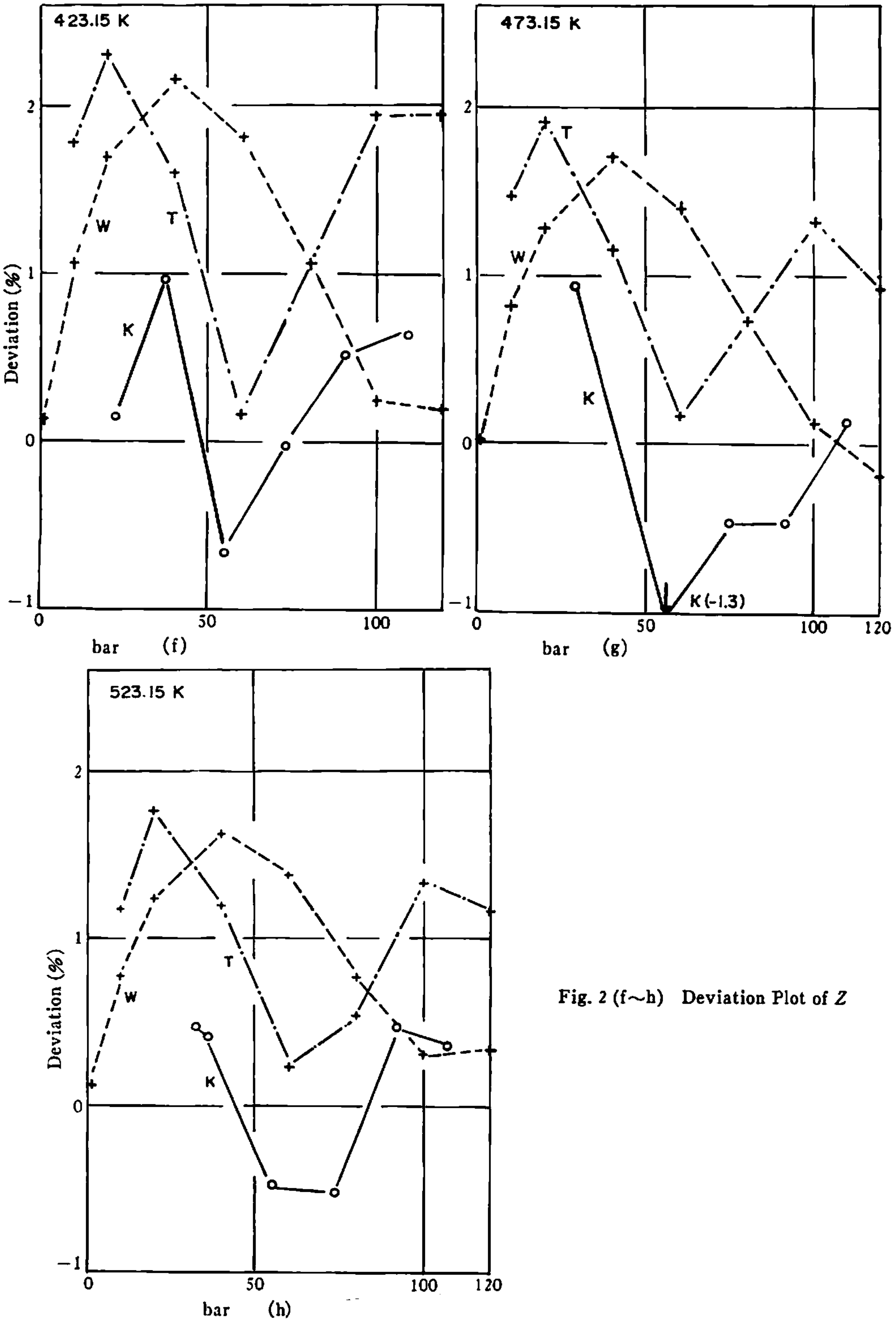

Fig. 2 (f~h) Deviation Plot of Z

Table 1 The most probable values of Z (uncertainty $3\sigma=0.0014$)

t/℃	T/K	P/bar																	
		1	5	10	15	20	25	30	35	40	45	50	60	70	80	90	100	120	140
0	273.15	0.991	0.956	0.908	0.856	0.798													
5	278.15	0.992	0.959	0.914	0.866	0.813													
10	283.15	0.992	0.961	0.920	0.875	0.827													
15	288.15	0.993	0.963	0.925	0.883	0.839													
20	293.15	0.993	0.966	0.929	0.891	0.849	0.805	0.755											
25	298.15	0.994	0.968	0.933	0.897	0.859	0.818	0.773											
30	303.15	0.994	0.969	0.937	0.903	0.868	0.829	0.788	0.743	0.691									
35	308.15	0.994	0.971	0.941	0.909	0.875	0.840	0.802	0.761	0.715	0.663	0.601							
40	313.15	0.995	0.972	0.944	0.914	0.883	0.849	0.814	0.777	0.735	0.690	0.637	0.482	0.246					
45	318.15	0.995	0.974	0.947	0.919	0.889	0.858	0.825	0.791	0.753	0.712	0.667	0.550	0.298	0.264	0.267	0.276		
50	323.15	0.995	0.975	0.949	0.923	0.895	0.866	0.835	0.803	0.769	0.732	0.692	0.595	0.444	0.296	0.284	0.287	0.303	
60	333.15	0.996	0.977	0.954	0.930	0.905	0.880	0.853	0.825	0.796	0.765	0.732	0.658	0.568	0.449	0.354	0.330	0.329	
70	343.15	0.996	0.979	0.958	0.937	0.914	0.891	0.868	0.843	0.817	0.791	0.763	0.703	0.635	0.557	0.473	0.409	0.372	0.375
80	353.15	0.996	0.981	0.962	0.942	0.922	0.901	0.880	0.858	0.835	0.812	0.788	0.737	0.682	0.623	0.560	0.501	0.432	0.418
90	363.15	0.997	0.983	0.965	0.947	0.928	0.910	0.890	0.871	0.851	0.830	0.809	0.765	0.719	0.671	0.621	0.573	0.499	0.469
100	373.15	0.997	0.984	0.968	0.951	0.934	0.917	0.900	0.882	0.864	0.845	0.826	0.788	0.748	0.708	0.667	0.627	0.560	0.522
125	398.15	0.997	0.987	0.973	0.959	0.945	0.931	0.917	0.903	0.889	0.874	0.860	0.831	0.802	0.773	0.744	0.717	0.670	0.636
150	423.15	0.998	0.989	0.977	0.965	0.954	0.942	0.930	0.919	0.907	0.895	0.883	0.860	0.838	0.816	0.794	0.775	0.740	0.714
175	448.15	0.998	0.990	0.980	0.970	0.960	0.950	0.940	0.930	0.920	0.910	0.901	0.882	0.863	0.846	0.829	0.814	0.788	0.768
200	473.15	0.998	0.991	0.982	0.973	0.965	0.956	0.947	0.939	0.930	0.922	0.914	0.898	0.883	0.868	0.855	0.843	0.822	0.807
225	498.15	0.998	0.992	0.984	0.976	0.968	0.961	0.953	0.945	0.938	0.931	0.924	0.910	0.897	0.885	0.874	0.864	0.847	0.836
250	523.15	0.999	0.993	0.985	0.978	0.971	0.964	0.957	0.951	0.944	0.938	0.932	0.920	0.908	0.898	0.889	0.880	0.867	0.858

$A=-0.620437515682\times10^{2}$, $B=0.120787859720\times10^{5}$, $C=-0.360699381752\times10^{10}$
$D=0.247241663937\times10^{5}$, $E=-0.113258291377\times10^{8}$, $F=-0.596257686191\times10^{11}$
$G=0.561257757555\times10^{12}$, $\gamma=5.00$

denote the compressibility factor, Z obtained in this work), are represented in Figs. 2a~2h, where the tie lines are merely for easiness of comparison.

Again, it should be kept in mind that, though named "the most probable", the part of higher pressures and temperatures in the table presented here is based on only single paper of Kiyama, into which sufficient examination on the correctness of data is impossible.

One of the author (Y. T.) is much obliged to Drs. K. Inoue and T. Ikegami, co-workers of Kiyama, for the kindness in offering the lognote to him.

(Y. Takezaki)

Isobaric Specific Heat Capacity of Ethyne

Calculation procedure: When a reliabe equation of state is available, it becomes possible to calculate the isobaric specific heat capacity of a pure substance by means of an analytical procedure in thermodynamics.

For example, the compressibility factor Z of the pure substance is expressed as a function of density ρ and temperature T. Such an equation of state may be written as

$$Z=Z(\rho,T) \qquad (2)$$

It is well known that the isobaric specific heat capacity c_p, then, is able to be given as follows due to the general thermodynamic relations:

$$c_p = -RT\int_0^{\rho}\left[\frac{T}{\rho}\left(\frac{\partial^2 Z}{\partial T^2}\right)_{\rho}+\frac{2}{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\right]d\rho+\frac{RT^2}{\rho}\frac{\left[\left(\frac{\partial Z}{\partial T}\right)_{\rho}+\frac{Z}{T}\right]^2}{\left(\frac{\partial Z}{\partial \rho}\right)_T+\frac{Z}{\rho}}+c_p^0(T)-R \tag{3}$$

where R denotes the gas constant of the substance and $c_p^0(T)$ is the isobaric specific heat capacity at the ideal gas state given as a single function of temperature T.

Therefore, it becomes feasible to calculate c_p values from Eqs. (2) and (3) with an aid of the established correlation for $c_p^0(T)$.

Calculated results: The present equation of state, Eq. (1), has exactly the same functional form as Eq. (1). Hence, the first and second derivatives of the compressibility factor Z with respect to temperature T, as well as the first derivative of Z with respect to ρ were derived from Eq. (1). Those derived expressions were then substituted into Eq. (3) and the required calculus has been performed.

On the other hand, a proposed correlation for the isobaric specific heat capacity at the ideal state by Makita[19] was used in the present calculatiations. This correlation was proposed recently for temperatures 200~600 K by his careful study of the available theoretically determined values for

Table 2 Isobaric specific heat capacity of gaseous C_2H_2 in KJ/(kg·K)

		P/bar																	
t/℃	T/K	1	5	10	15	20	25	30	35	40	45	50	60	70	80	90	100	120	140
0	273.15	1.65	1.77	1.96	2.19	2.51													
5	278.15	1.66	1.77	1.94	2.15	2.42													
10	283.15	1.67	1.78	1.93	2.12	2.35													
15	288.15	1.68	1.78	1.92	2.09	2.29													
20	293.15	1.69	1.79	1.92	2.07	2.25	2.48	2.78											
25	298.15	1.71	1.79	1.91	2.05	2.21	2.41	2.66											
30	303.15	1.72	1.80	1.91	2.03	2.18	2.35	2.57	2.85	3.27									
35	308.15	1.73	1.81	1.91	2.02	2.15	2.31	2.49	2.73	3.05	3.54	4.41							
40	313.15	1.74	1.81	1.91	2.01	2.13	2.27	2.43	2.63	2.89	3.26	3.82	8.64	5.48					
45	318.15	1.75	1.82	1.91	2.00	2.11	2.24	2.38	2.56	2.77	3.06	3.46	5.41	14.0	4.79	3.30	2.53		
50	323.15	1.77	1.83	1.91	2.00	2.10	2.21	2.34	2.49	2.68	2.91	3.22	4.39	10.2	7.60	4.58	3.47	2.31	
60	333.15	1.79	1.84	1.91	1.99	2.07	2.17	2.27	2.39	2.53	2.70	2.90	3.51	4.79	8.30	8.07	5.73	3.92	
70	343.15	1.81	1.86	1.92	1.99	2.06	2.14	2.22	2.32	2.43	2.56	2.71	3.10	3.73	4.87	6.66	7.05	5.28	4.32
80	353.15	1.83	1.88	1.93	1.99	2.05	2.12	2.19	2.27	2.36	2.46	2.57	2.85	3.25	3.83	4.69	5.64	5.77	5.04
90	363.15	1.86	1.89	1.94	1.99	2.05	2.10	2.17	2.23	2.31	2.39	2.48	2.69	2.97	3.34	3.83	4.42	5.25	5.14
100	373.15	1.88	1.91	1.95	2.00	2.04	2.09	2.15	2.21	2.27	2.34	2.41	2.58	2.79	3.05	3.37	3.76	4.50	4.80
125	398.15	1.93	1.95	1.98	2.02	2.05	2.09	2.13	2.17	2.21	2.26	2.30	2.41	2.53	2.67	2.83	3.01	3.39	3.73
150	423.15	1.97	1.99	2.01	2.04	2.07	2.09	2.12	2.15	2.18	2.22	2.25	2.33	2.41	2.50	2.59	2.70	2.92	3.14
175	448.15	2.01	2.03	2.05	2.07	2.09	2.11	2.13	2.15	2.18	2.20	2.23	2.28	2.34	2.40	2.47	2.54	2.68	2.83
200	473.15	2.05	2.06	2.08	2.09	2.11	2.13	2.14	2.16	2.18	2.20	2.22	2.26	2.30	2.35	2.40	2.46	2.55	2.66
225	498.15	2.08	2.09	2.11	2.12	2.13	2.14	2.16	2.17	2.19	2.20	2.22	2.25	2.28	2.32	2.35	2.39	2.47	2.55
250	523.15	2.12	2.12	2.13	2.14	2.15	2.17	2.18	2.19	2.20	2.21	2.22	2.25	2.27	2.30	2.33	2.36	2.42	2.48

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19) T. Makita, Private communication to the present authors (1978)

ethyne and it has a functional form shown below;

$$c_p^0(T)=\frac{152.0353}{T}-1.180445+0.01224117\,T$$
$$-1.734395\times10^{-5}T^2+9.410105\times10^{-9}T^3 \qquad (4)$$

where $c_p^0(T)$ is given in kJ/(kg·K) and T in K.

The numerical calculations have been conducted for the gaseous phase covering the same temperatures and pressures given ih Table 1. Some of the typical calculated results along several isotherms are given in Table 2 and also shown diagrammatically in Fig. 3. From Fig. 3 it may be understood that the rational behaviour of the isobaric specific heat capacity is reproduced by the present equation of state, Eq. (1).

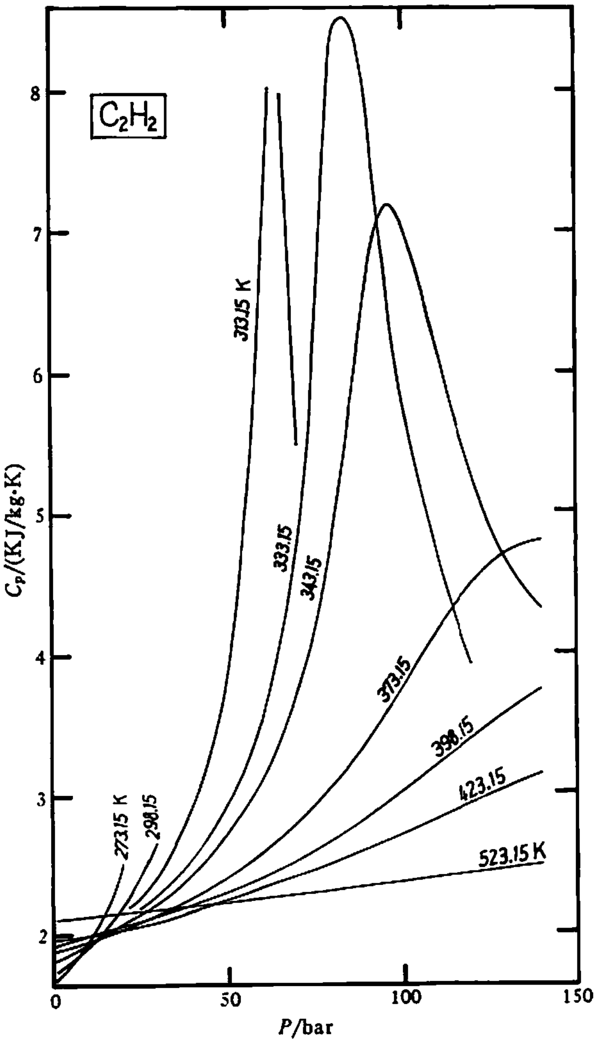

Fig. 3 Typical calculated results of the isobaric specific heat capacity of C_2H_2

Since there exists no experimental c_p values for ethyne, the calculated c_p values are compared with those compiled by Din[20] for the range of temperatures 170~320 K and of pressures 0.1~40 atm. The results show a satisfactory coincidence between them, except for a narrow region in the very vicinity of the coexistence curve where the maximum deviation was found around 10%. However, taking into consideration a fairly poor availability of the reliable *PVT* property data for this substance, the present calculated results for c_p may be considered satisfactorily reasonable.

One of the authors (K. W.) would like to express his thanks to Mr. S. Saegusa, graduate student of Mechanical Engineering, Keio University, for his assistance in the present calculation.

(K. Watanabe)

Viscosity of Gaseous Ethyne

Source of experimental data: Seven sets of original measurements[21~27] are available in literature for the viscosity of ethyne, covering an overall temperature range from 273 to 609 K. In Table 3 the first author, the experimental method, temperature and pressure ranges and number of data points are listed in the order of publication. Among these sets, the measurement of Kiyama and Makita[25] by a rolling-ball viscometer solely covers a high pressure range up to 100 bar. No experimental viscosity data is found for the saturated liquid and vapor of ethyne. In view of this situation

Table 3 Experimental studies on the viscosity of ethyne

First Author	Year	Method	Temp. Range (K)	Press. Range (10^5 Pa. s)	No. of Data	Ref. No.
Vogel	1914	Osci. Disk	273	n	1	1
Titani	1930	Transp.	293-393	n	7	2
Adzumi	1937	Transp.	293-373	n	9	3
Wobser	1941	Roll. Ball	293-373	n	7	4
Kiyama	1952	Roll. Ball	293-523	1-98	44	5
Pal	1968	Osci. Disk	303-473	n	5	6
Bailey	1970	Transp.	344-609	n	6	7

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20) F. Din, "Thermodynamic Fuctions of Gases", Vol. 2, 56, Butterworths Scientific Publications, London (1956)

21) H. Vogel, *Ann. Physik*, **43** (4), 1235 (1914)

22) T. Thitani, *Bull. Chem. Soc. Japan*, **5**, 98 (1930)

23) H. Adzumi, *ibid.*, **12**, 199 (1937)

24) R. Wobser, and F. Muller, *Kolloid-Beihefte*, **52**, 165 (1941)

25) R. Kiyama and T. Makita, *This Journal*, **22**, 49 (1952)

26) A. K. Pal and A. K. Barua, *J. Chem. Phys.*, **48**, 872 (1968)

27) B. J. Bailey, *J. Phys. D.* (*App. Phys.*), 3 (4), 550 (1970)

of available data as well as a serious discrepancy among the data at high temperatures above 500 K, further accumulation of new and reliable experimental data is desired for ethyne, especially at high pressures. Thus, the present data analysis and correlation are performed for gaseous ethyne at the atmospheric pressure and high pressure.

Viscosity at the atmospheric pressure: Although there exist several sources of information for the viscosity of gaseous ethyne at the atmospheric pressure, the values obtained from statistical mechanical calculations and empirical correlations are excluded from the present analysis. Seven experimental works[21~27] were carefully read through and examined from the viewpoint of the reliability of data in the similar manner to our previous works[28~30].

The discrepancy of collected data is within 2% throughout the temperature range from 273 to 609 K except the values of Bailey[27] above 500 K by a capillary viscometer and the results of Pal and Barua[26] below 328 K obtained by the the oscillating-disk method. Bailey's results[27], covering temperatures from 344 to 609 K, are systematically higher than any others above 540 K and the difference reaches about 5% at 600 K. Although his measurement is the newest and reliable, and he insists that the ealier data before 1940 are generally too low at high temperatures for every substance as compared with the values of recent precise measurements, there is no indisputable reason for the viscosity of gaseous ethyne at the present time to adopt his data alone. Thus, the present correlation is limited below 523 K partly because gaseous ethyne might commence to react above this temperature, low polymers being formed as mentioned later. The viscosity data adopted were given an equal weight and adjusted to a quartic equation as a function of temperature. The correlation formula thus obtained for temperatures from 273 to 523 K is as follows;

$$\eta_0 = 1.407\times10^{2} - 1.20476T + 6.4272\times10^{-3}T^{2} - 1.17697\times10^{-5}T^{3} + 7.8440\times10^{-9}T^{4} \qquad (5)$$

where η_0 is the viscosity at the normal pressure in 10^{-7} Pa.s ($=10^{-6}$ P) and T the the temperature in K. Eq. (5) is found to fit the original 39 data with the mean deviation of 0.78% and the maximum of 2.4%. The most probable viscosity values of gaseous ethyne at 1 atm were generated from the above equation and given in Table 4. The deviations of the original data from the equation are plotted in Fig. 4.

Viscosity under high pressure: So far as we know, the measurement of Kiyama and Makita[25] by a rolling-ball viscometer is the only experimental study for the viscosity of gaseous ethyne that covers an extensive range of temperature and pressure. The rolling-ball method tends to give a higher pressure effect on the viscosity of gases as compared with other viscometers, which might be due to the occurrense of turbulent flow at high pressure. In view of this situation as well as the lack of

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28) T. Makita, Y. Tanaka and A. Nagashima, *This Journal*, **43** (1), 54 (1973)
29) T. Makita, Y. Tanaka and A. Nagashima, *ibid.*, **44** (2), 98 (1975)
30) Y. Tanaka and T. Makita, *ibid.*, **45** (2), 93 (1976)

Table 4 Viscosity of gaseous ethyne at the atmospheric pressure

t/℃	T/K	$\eta/10^{-7}$Pa. s	t/℃	T/K	$\eta/10^{-7}$Pa. s
0	273.15	95.0	150	423.15	141.5
10	283.15	98.1	160	433.15	144.3
20	293.15	101.3	170	443.15	147.2
30	303.15	104.5	180	453.15	150.1
40	313.15	107.7	190	463.15	153.0
50	323.15	110.9	200	473.15	155.9
60	333.15	114.1	210	483.15	158.9
70	343.15	117.3	220	493.15	162.0
80	353.15	120.4	230	503.15	165.2
90	363.15	123.5	240	513.15	168.4
100	373.15	126.6	250	523.15	171.8
110	383.15	129.7			
120	393.15	132.7			
130	403.15	135.6			
140	413.15	138.5			

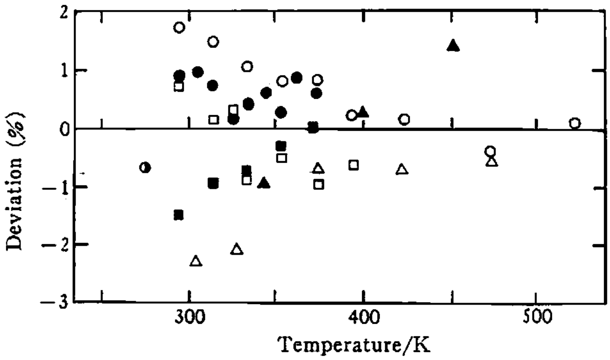

Fig. 4 Deviation of original data from Eq. (5).
◐ Vogel (1) □ Titani (2)
● Adzumi (3) ■ Wobser (4)
○ Kiyama (5) △ Pal (6)
▲ Bailey (7)

experimental deta, it is impossible at the present time to determine the most probable values of viscosity with the same reliability as those of our previous works[28~30]. Therefore only the smoothed values are generated on the basis of the results of Kiyama and Makita[25] for industrial use.

The original data of Kiyama and Makita[25] consist of 44 data points along six viscosity-pressure isotherms covering temperatures from 293 to 523 K and pressures up to 100 bar. However they observed an abnormal enhancement of viscosity above 98 bar at 200°C and above 43.5 bar at 250°C, which resulted from the deposition of a polymer of ethyne on the surface of the viscometer-tube. Therefore six data are discarded in preparation of the correlation formula. Each isotherm was slightly shifted along the viscosity coordinate in order to keep an internal consistence between the values at the atmospheric pressure and those under high presure. The modified viscosity data thus obtained are adjusted by the following equation as a function of temperature and pressure:

$$\eta=\sum_{j=0}^{4}\left(\sum_{i=0}^{3}A_{ij}T^{i-2}\right)P^{j} \qquad (6)$$

where η is the viscosity in 10^{-7} Pa. s, T the temperature in K and P the pressure in 10^5Pa (=bar). Eq. (6) fits the adopted data with a mean deviation of 0.34% and the maximum of 1.76%. The empirical coefficients are listed in Table 5. The smoothed values given in Table 6 and Fig. 5 are generated from the above equation. This equation seems to be a reliable interpolaion formula within the range of temperature and pressure in the Table 5.

Table 5 Numercal constants in Eq. (6)

$A_{00} = 9.331986 \times 10^{4}$
$A_{01} = -6.262785 \times 10^{6}$
$A_{02} = 4.439914 \times 10^{5}$
$A_{03} = -9.545344 \times 10^{3}$
$A_{04} = 6.994934 \times 10$

$A_{10} = -1.236351 \times 10^{3}$
$A_{11} = 4.79841 \times 10^{4}$
$A_{12} = -3.354166 \times 10^{3}$
$A_{13} = 7.229607 \times 10$
$A_{14} = -5.270769 \times 10^{-1}$

$A_{20} = 1.820988 \times 10$
$A_{21} = -1.206993 \times 10^{2}$
$A_{22} = 8.391162$
$A_{23} = -1.815755 \times 10^{-1}$
$A_{24} = 1.319446 \times 10^{-3}$

$A_{30} = 2.963132 \times 10^{-1}$
$A_{31} = 9.994272 \times 10^{-2}$
$A_{32} = -6.916353 \times 10^{-3}$
$A_{33} = 1.506029 \times 10^{-4}$
$A_{34} = -1.092965 \times 10^{-6}$

Table 6 Viscosity of gaseous ethyne under high pressure (10^{-7} Pa.s = 10^{-6} P)

		P/bar									
t/℃	T/K	1	10	20	30	40	50	60	70	80	90
20	293.15	101	103	113	125						
30	303.15	105	107	115	126						
40	313.15	108	111	118	127						
50	323.15	111	114	121	128	136	145	157	175	204	
60	333.15	114	118	123	130	136	144	155	169	192	
70	343.15	117	121	126	131	137	144	153	166	183	209
80	353.15	120	124	128	133	139	145	153	163	178	199
90	363.15	123	126	131	135	141	146	153	162	174	192
100	373.15	126	129	133	138	143	148	154	162	173	188
125	398.15	134	136	140	144	149	153	159	165	175	188
150	423.15	141	143	146	151	155	160	165	171	180	193
175	448.15	149	150	153	158	162	167	172	179	187	
200	473.15	156	158	161	165	170	175	181	186	193	
225	498.15	164	166	169	173	177	183	189			
250	523.15	172	174	177	180						

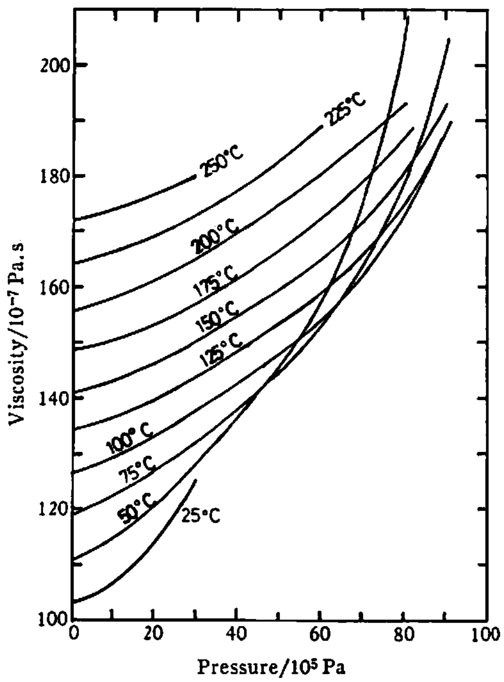

Fig. 5 Viscosity of gaseous ethyne under high pressure

(Y. Tanaka)

Thermal Conductivity of Gaseous Ethyne

Sources of experimental data: On the thermal conductivity of gaseous ethyne, only seven out of about thirty literatures detected from Chemical Abstract and the Retrieval Guide were found to contain original experimental data. These references are listed in Table 7. The range of temperature of these measurements extends from 189 K to 673 K. All of them are under atmospheric or lower pressure. Three sets of data, namely those by Senftleben³¹⁾, Mukhopadhyay *et al.*³²⁾ and

Table 7 Measurements of the thermal conductivity of gaseous ethyne

First Author	Year	Method	Temp. Range (K)	Press.(10^5Pa)	No. of Data
Eucken	1913	Hot-wire	273.1	1	1
Delaplace	1937	—	—	Low pressure	Graphical
Lenoir	1953	—	189-422	1	19
Gardiner	1956	Hot-wire	273-573	1	5
Senftleben	1964	Hot-wire (horizontal)	273-673	1	8
Mukhopadhyay	1967	Hot-wire	273-473	1	5
Green	1968	Hot-wire	313.6-393.6	1	Graphical

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31) H. Senftleben, *Z. Angew. Phys.*, 17, 86 (1964)

32) P. Mukhogadhyay, A. K. Barua, *Trans. Faraday*, 65, 2379 (1967)

Green *et al.*[33], were published after 1960. In the case of the thermal conductivity of various fluids, experience shows that data published prior to 1960 are often less reliable. Since reports by Delaplace[34] and Green *et al.*[33] contain no numerical data but express measured results in graphical form only, they are not suitable for critical analysis. Reports by Lenoir[35] lists 19 values from unknown source. Survey by Liley[36] treated these data as experimental. But in the present report, they are not considered explicitly as experimental data.

All of available data were obtained with the aid of a steady-state hot-wire method or a slightly modified form of the hot-wire method. Eucken[37] measured only at 273.1 K and his main aim was to test applicability of the Eucken factor. Delaplace's measurement[34] was performed to study behavior of the thermal conductivity of gases at very low pressure. Both of these data were much older than other sets of data. Measurements by Gardiner and Schaefer[38] were done using an absolute hot-wire apparatus. They measured also other gases and comparisons of their data for other substances support reliability of the data for ethyne. Senftleben[31] used the hot-wire cell in the horizontal position. It is known that the thin wire in horizontal position can more easily be affected by convection than in vertical position. Also possibility of polymerization is more serious above 300°C (573 K). Data by Mukhopadhyay *et al.*[32] are estimated as less reliable because they used the thicker hot wire and calibrated the apparatus with theoretically estimated data. Green *et al.*[33] used a hot-wire apparatus with larger gap and measured with large temperature drop (about 10°C) through the liquid layer.

Correlation: The selected data, in which data by Gardiner and Schaefer were most highly credited, were correlated into the following equation:

$$\lambda = -1.312\times10^{-2} + 1.121\times10^{4}\,T + 1.0\times10^{-8}\,T^{2} \qquad (7)$$

where T is in K and λ in W/mK.

This equation is valid in the range of temperature 273.15~573.16 K, where at least two sets of experimental data are available. Figure 6 shows comparison of experimental data with equation (7). Deviation plot of experimental data from the equation is shown in Figure 7. Although the limit of temperature for equation (7) is assumed to be 300°C, comparisons of up to 400°C are shown in Figure 7. As an example of previous correlations, the equation by Liley is shown as a broken line in Figure 7. Standard deviation of available experimental data from equation (7) in the range 0~300°C (273.15 ~573.15 K) is 3.9%, while that of Gardiner's data is 0.9%. Thermal conductivity of gaseous ethyne calculated with the aid of equation (7) is given at every 10 degrees in Table 8.

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33) R. L. Green, D. F. Swinehart, *Proc. 4th Syma. Thermophys. Prop.*, 405 (1968)

34) R. Delaplace, *Compt. Rend.*, **204**, 263 (1937)

35) J. M. Lenoir, *Univ. Arkaneas Eng. Exp. Sta.-Bull.*, **18**, 1 (1953)

36) P. E. Liley, *Proc. 4th Symp. Thermophys. Proc.*, 323 (1968)

37) A. Eucken, Z. Physik., **14**, 324 (1913)

38) W. C. Gardiner, K. Schfer, *Z. Elekrochem.*, **60**, 588 (1965)

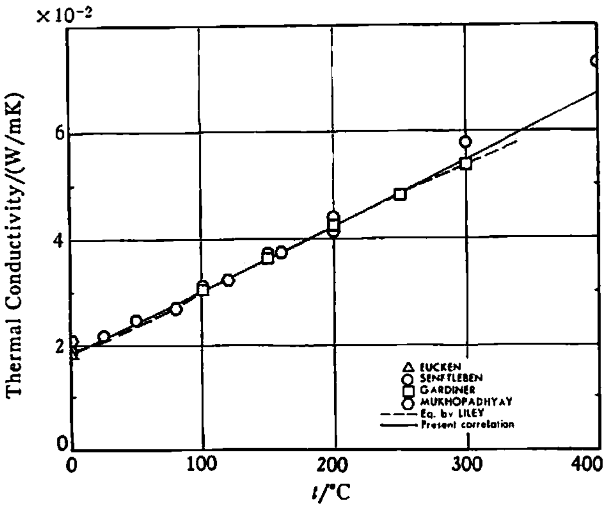

Fig. 6 Thermal conductivity of gaseous ethyne at 0.1 M Pa

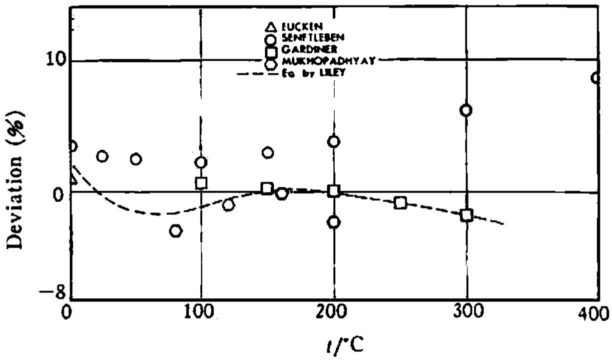

Fig. 7 Deviations of experimental data from Eq. (7).

Table 8 Thermal conductivity of gaseous ethyne

t/℃	λ/Wm^{-1}K^{-1}	t/℃	λ/Wm^{-1}K^{-1}	t/℃	λ/Wm^{-1}K^{-1}
	×10^{-2}		×10^{-2}		×10^{-2}
0	1.852	110	3.130	210	4.338
10	1.942	120	3.250	220	4.459
20	2.060	130	3.370	230	4.581
30	2.178	140	3.490	240	4.704
40	2.296	150	3.611	250	4.826
50	2.415	160	3.731	260	4.949
60	2.534	170	3.852	270	5.072
70	2.652	180	3.973	280	5.195
80	2.772	190	4.094	290	5.318
90	2.891	200	4.216	300	5.442
100	3.010				

(A. Nagashima)