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# THE VISCOSITY OF FREONS UNDER PRESSURE

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In the previous papers, a rolling-ball viscometer for compressed gases was described in detail, and the viscosity of carbon dioxide, ammonia, acethylene, argon and oxygen was measured under pressures up to 100 kg/cm$^2$ at 50° intervals from 50° to 300°C[1,2]. Although the viscosity of freons at the atmospheric pressure has been known[3,4], there is no report on the effect of pressure upon the viscosity of freons. Therefore, the viscosity of three freons is measured at the following conditions in which the available data of the density exist[4]:

| | | | |
|---|---|---|---|
| dichlorodifluoro-methane | (freon-12), | 25°~200°C, | 1.03~16 kg/cm$^2$; |
| chlorodifluoro-methane | (freon-22), | 25°~200°C, | 1.03~19 kg/cm$^2$; |
| dichlorofluoro-methane | (freon-21), | 25°~150°C, | 1.03~ 7 kg/cm$^2$. |

## Experimentals

The apparatus used in this measurement is, as previously described in detail, the rolling-ball viscometer which was calibrated by carbon dioxide.

Freons used in the present investigation are the commercials**, purified by redistillation and checked on their vapour pressures.

## Results and Considerations

The results of the present measurement are shown in Table 1, where the known values[3,4] at the atmospheric pressure are also tabulated and found to coincide with the present values within 1%. The viscosity isotherms against pressure are plotted in Fig. 1, where it is found that the pressure coefficient of viscosity at constant temperature, $(\partial\eta/\partial P)_T$, has the positive sign over all the region of temperature and pressure, and becomes smaller with increasing temperature. Therefore, the temperature coefficient of viscosity at constant pressure, $(\partial\eta/\partial T)_P$, is positive in sign at low

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** Freons (their purity is above 99.0%) were supplied by the Osaka Kinzoku Kogyo Co. Ltd.

1) R. Kiyama and T. Makita, *This Journal*, 21, 63 (1951)

2) R. Kiyama and T. Makita, *ibid.*, 22, 49 (1952)

3) A. F. Benning and W. H. Markwood, Jr., *Ref. Eng.*, 37, 243 (1939); *The NBS-NACA Table of Thermal Properties of Gases*, U. S. Department of Commerce, National Bureau of Standards (1950)

4) *The Refrigerating Data Book*, Basic Vol., The American Society of Refrigerating Engineers, New York (1951)

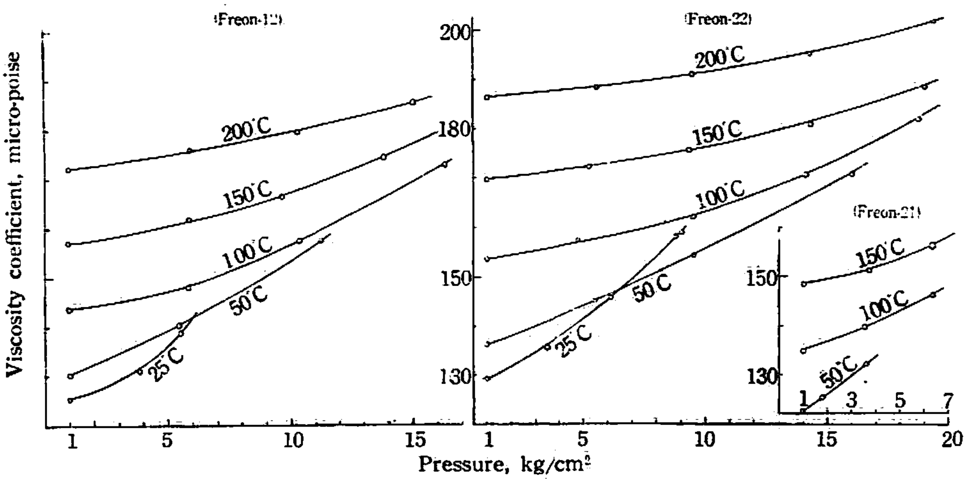

Fig. 1 Viscosity isotherms against pressure.

pressure and becomes smaller with increasing pressure, and its sign converts from positive to negative near the liquefying point, as observed in the case of freon-22 in Fig. 1, where the isotherm of 25°C crosses over the isotherm of 50°C at the pressure near 6 kg/cm². Although such crossing is not observed in the case of freon-12 or -21, it seems that the crossing between isotherms will occur at a higher pressure than that in this measurement.

Table 1 The viscosity of the vapour of freons

| Temp. (°C) | Freon-12 | | | | Freon-22 | | | | Freon-21 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $P$ | $\rho$ | $\eta$ | $\nu$ | $P$ | $\rho$ | $\eta$ | $\nu$ | $P$ | $\eta$ | $\rho$ | $\nu$ |
| 25° | 1.03 | 5.240 | 125.1 3) | | 1.03 | 3.600 | 129.4 4) | | 1.03 | 3.811 | 114.4 4) | |
| | | | 125.6 4) | | | | 129.3 | 35.92 | | | 114.3 | 29.99 |
| | | | 125.2 | 23.89 | 3.5 | 12.75 | 135.5 | 10.63 | | | | |
| | 3.8 | 19.40 | 131.1 | 6.758 | 6.1 | 23.00 | 146.1 | 6.352 | | | | |
| | 5.5 | 29.09 | 139.0 | 4.778 | 9.0 | 36.14 | 159.3 | 4.408 | | | | |
| 50° | 1.03 | 4.820 | 131.8 3) | | 1.03 | 3.312 | 137.4 4) | | 1.03 | 3.509 | 121.3 4) | |
| | | | 132.2 4) | | | | 136.3 | 41.15 | | | 122.7 | 34.97 |
| | | | 130.1 | 26.99 | 5.5 | 18.71 | 145.0 | 7.750 | 1.79 | 6.95 | 125.3 | 18.03 |
| | 5.5 | 26.20 | 140.4 | 5.359 | 9.5 | 34.12 | 154.5 | 4.528 | 3.6 | 14.48 | 132.2 | 9.130 |
| | 11.3 | 60.80 | 157.1 | 2.584 | 16.0 | 64.54 | 171.0 | 2.650 | | | | |
| 100° | 1.03 | 4.145 | 144.6 3) | | 1.03 | 2.857 | 154.4 4) | | 1.03 | 3.025 | 134.9 4) | |
| | | | 144.7 4) | | | | 153.8 | 53.85 | | | 135.0 | 44.63 |
| | | | 143.8 | 34.69 | 4.8 | 13.77 | 157.6 | 11.45 | 3.5 | 11.90 | 139.9 | 11.76 |
| | 5.8 | 23.20 | 148.0 | 6.380 | 9.5 | 28.19 | 162.3 | 5.757 | 6.4 | 22.62 | 146.3 | 6.468 |
| | 10.4 | 43.30 | 157.6 | 3.640 | 14.1 | 43.57 | 170.8 | 3.922 | | | | |
| | 16.4 | 73.80 | 172.8 | 2.341 | 18.7 | 60.07 | 181.8 | 3.026 | | | | |
| 150° | 1.03 | 3.635 | 157.2 | 43.25 | 1.03 | 2.519 | 169.7 | 67.37 | 1.03 | 2.658 | 148.6 | 55.91 |
| | 5.9 | 20.15 | 163.5 | 8.114 | 5.2 | 13.02 | 172.3 | 13.23 | 3.8 | 11.13 | 151.2 | 13.58 |
| | 9.7 | 33.90 | 166.1 | 4.900 | 9.3 | 23.73 | 176.0 | 7.417 | 6.4 | 19.31 | 156.4 | 8.099 |
| | 13.8 | 49.90 | 174.4 | 3.495 | 14.3 | 37.40 | 180.8 | 4.834 | | | | |
| | | | | | 19.0 | 50.35 | 188.0 | 3.734 | | | | |
| 200° | 1.03 | 3.260 | 172.3 | 52.85 | 1.03 | 2.275 | 186.1 | 81.80 | | | | |
| | 5.9 | 17.80 | 176.2 | 9.899 | 5.5 | 12.20 | 188.3 | 15.43 | | | | |
| | 10.3 | 31.50 | 179.4 | 5.695 | 9.5 | 21.34 | 191.0 | 8.955 | | | | |
| | 15.0 | 47.00 | 185.3 | 3.943 | 14.3 | 32.62 | 195.0 | 5.978 | | | | |
| | | | | | 19.4 | 44.62 | 201.5 | 4.516 | | | | |

$P$ : Absolute pressure, kg/cm², $\rho$ : Density, g/l,
$\eta$ : Viscosity coefficient, micro-poise, $\nu$ : Kinematic viscosity, $10^{-3}$cm²/sec.

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The kinematic viscosity against pressure, which is tabulated in the last columns of Table 1, decreases rapidly at low pressure and moderately at high pressure. The present measurement shows an intermediate state, in which the kinematic viscosity becomes smaller with increasing pressure and converges to the liquid state⁵⁾.

## Discussion

**At the atmospheric pressure** On the effect of temperature upon the viscosity at low pressure, Hirschfelder, Bird and Spotz⁶⁾ have published the tables of collision integrals based on the refined kinetic theory of Chapman and Cowling⁷⁾, which permits accurate calculation of viscosity for nonpolar smooth spherical molecules, and Bromley and Wilke⁸⁾ have presented a convenient form for practical use. When the present values of freons are compared with the theory, the considerable difference is found as follows: 3.8~16.1% higher for freon-12, 3.9~7.5% higher for freon-22 and 4.2~14.1% higher for freon-21. Such discrepancy seems to be obtained in the cause that freons do not fulfil the basic assumptions of the theory completely, as carbon tetrachloride or methylchloride⁶⁾.

The present results of freons are examined by Reinganum's equation⁹⁾:

$$\eta = AT^{\frac{1}{2}} e^{-\frac{D}{T}}, \tag{1}$$

where $\eta$ is viscosity coefficient in micro-poise, $T$ is absolute temperature and $A$ and $D$ are characteristic constants. It is found that Eq. 1 fulfils the viscosity of freons over all the temperature range. $A$ and $D$ are determined by the experimental results and the following equations are obtained:

$$\begin{aligned} &\text{Freon-12,} \quad \eta = 9.423T^{\frac{1}{2}} e^{-\frac{16.04}{T}}; \\ &\text{Freon-22,} \quad \eta = 11.16T^{\frac{1}{2}} e^{-\frac{23.80}{T}}; \\ &\text{Freon-21,} \quad \eta = 8.892T^{\frac{1}{2}} e^{-\frac{16.61}{T}}. \end{aligned} \tag{2}$$

These equations are reproducible over all the temperature range within the error of 2%.

**Under pressure** General correlations for the effect of pressure and temperature on the viscosity of gases based on the principle of corresponding state have been published as follows:

Comings and Egly¹⁰⁾, $\eta_p/\eta_1 = f(P_r, T_r)$;

Uyehara and Watson¹¹⁾, $\eta_p/\eta_c = f(P_r, T_r)$;

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5) E. Schröer and G. Becker, *Z. Phys. Chem.*, A 173, 178 (1935)

6) J. O. Hirschfelder, R. B. Bird and E. L. Spotz, *J. Chem. Phys.*, **16**, 968 (1948)

7) S. Chapman and T. G. Cowling, *Mathematical Theory of Non-uniform Gases*, London (1939)

8) L. A. Bromley and C. R. Wilke, *Ind. Eng. Chem.*, **43**, 1641 (1951)

9) M. Reinganum, *Ann. Physik*, **10**, 334 (1903)

10) E. W. Comings and R. S. Egly, *Ind. Eng. Chem.*, **32**, 714 (1940)

11) O. A. Uyehara and K. M. Watson, *Natl. Petroleum News, Tech. Sec.*, **36**, R714 (1944)

Grundberg and Nissan[12], $\eta_p/\eta_1 = f(\rho_r, T_r)$;

where $\eta_1$, $\eta_p$ and $\eta_c$ are the viscosities at the atmospheric pressure, at high. pressure and at the critical point, and $P_r$, $T_r$ and $\rho_r$ are the reduced pressure, temperature and density, respectively. When the correlation of Comings and Egly is compared with the present results of freons, good coincidence is not found and the maximum deviation reaches to 40% at the regions of low reduced temperature. Other correlations cannot be examined because of the lack of $\eta_c$ for Uyehara and Watson's equation, and of the narrow range of $\rho_r$ for Grundberg and Nissan's.

Based on the additive property for the physical constants of organic compounds, Smith and Brown[13] have published the following correlation for a homologous series:

$$\eta/\sqrt{M} = f(P_r, T_r),$$

where $M$ is molecular weight. But, in the case of three freons, the isotherms of $T_r$ in the diagram of $\eta/\sqrt{M}$ versus $P_r$ deviate considerably each other, that is, the isotherm of freon-22 deviates +16.8~25.0% from the isotherm of freom-12 at the same reduced temperature, and that of freon-21 deviates +14.4~18.4% from that of freon-12.

Othmer and Josefowitz[14] have found a straight relation which is shown by the following equation:

$$\log\eta = K\log p + C, \tag{3}$$

where $\eta$ is the viscosity of gas or vapour in micro-poise, $p$ is the vapour pressure of a liquid in kg/cm², and $K$ and $C$ are constants. Then, the viscosity of freons is plotted as isobars on the log-log diagrams against the vapour pressure of their liquids at the measured temperatures, and the slope $K$ and the section $C$ of the straight lines obtained are determined as shown in Fig. 2, where the slope $K$ (full line) is a characteristic function of the measured pressure and the section $C$ (dotted line) is the general function of reduced pressure. As to three freons, if one reads $K$ and $C$ at the desired pressure from Fig. 2 and knows the vapour pressure of its liquid at the desired temperature, the viscosity of the vapour can be calculated by Eq. (3)

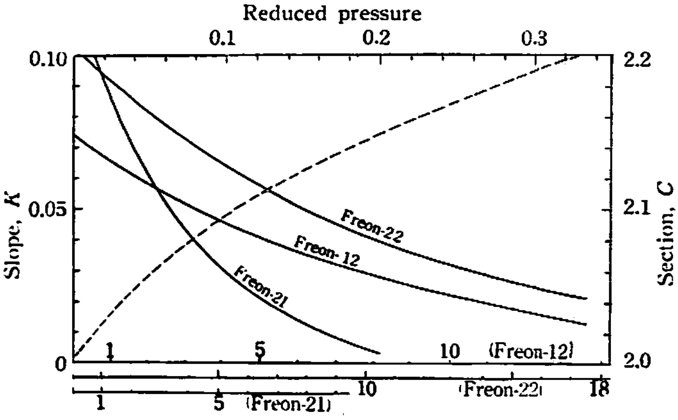

Fig. 2 Slope and section of Eq. (3) as function of pressure. The full lines show the slope on the left axis and the dotted line shows the section on the right axis.

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12) L. Grundberg and A. H. Nissan, *Ind. Eng. Chem.*, 42, 885 (1950)

13) A. S. Smith and G. G.Brown, *ibid.*, 35, 705 (1943)

14) D. F. Othmer and S. Josefowitz, *ibid.*, 38, 111 (1946)

within the deviation of 5%.

**A correlation of viscosity under pressure** The viscosity of gases increases with increasing pressure at a constant temperature and the ratio $\eta_p/\eta_1$ at low temperature is larger than at high temperature, that is, $[\partial(\eta_p/\eta_1)/\partial T]_p<0$. Also the density of gases increases with increasing pressure at a constant temperature and the ratio of the density at high pressure, $\rho_p$, to the density at atmospheric pressure, $\rho_1$, is larger at low temperature than at high temperature, that is, $[\partial(\rho_p/\rho_1)/\partial T]_p<0$. When $\eta_p/\eta_1$ and $\rho_p/\rho_1$ are plotted as isobars against temperature, it is found that the $\eta_p/\eta_1$ curve is parallel to the $\rho_p/\rho_1$ curve for many gases described below, and that $(\eta_p/\eta_1)/(\rho_p/\rho_1)$ is independent on the temperature over a wide region of the temperature and pressure. When $\nu_1$ and $\nu_p$ are kinematic viscosities at the ordinary pressure and at high pressure, respectively, the ratio is as follows:

$$\frac{(\eta_p/\eta_1)}{(\rho_p/\rho_1)}=\frac{(\eta_p/\rho_p)}{(\eta_1/\rho_1)}=\frac{\nu_p}{\nu_1}. \tag{4}$$

That is, the kinematic viscosity ratio, $\nu_p/\nu_1$ does not depend on the temperature.

Table 2 Gases used for the correlation

| A | | | B | | |
|---|---|---|---|---|---|
| Gas | Temperature range | Literature | Gas | Temperature range | Literature |
| He | 21°C | (15) | $CO_2$ | −20∼+40°C<br>20°<br>40°<br>50∼300° | (22)<br>( 5)<br>(23)<br>( 2) |
| A | 50∼300°<br>20° | ( 2)<br>(15) | $NH_3$ | 50∼300° | ( 2) |
| $H_2$ | −100∼+400°<br>21° | (16)<br>(15) | $C_2H_2$ | 20∼250° | ( 2) |
| $N_2$ | 25∼75°<br>21° | (17)<br>(15) | $C_2H_4$ | 40°<br>24° | (23)<br>(24) |
| $O_2$ | 25∼200° | ( 2) | $C_2H_6$ | 15∼200° | (13) |
| Air | 50∼150°<br>21° | (18)<br>(15) | $C_3H_8$ | 15∼200°<br>25∼225° | (13)<br>(21) |
| $N_2+H_2$ | 50∼100° | (19) | Freon-12 | 25∼200° | This paper |
| $CH_4$ | 73∼160°<br>25∼225° | (20)<br>(21) | Freon-22 | 25∼200° | This paper |
| | | | Freon-21 | 50∼150° | This paper |

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17) A. Michels and R. O. Gibson, *Proc. Roy. Soc., London*, **134 A**, 288 (1932)
18) H. Iwasaki, *Bull. Chem. Research Institute of Non-aqueous Solutions*, **1**, 27 (1951)
19) H. Iwasaki, *ibid.*, **3**, 117 (1953)
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21) L. B. Bicher and D. L. Katz, *Ind. Eng. Chem.*, **35**, 754 (1943)
22) H. Stakelbeck, *Z. gas. Kälte-Ind.*, **40**, 33 (1933)
23) E. W. Comings and R. S. Egly, *Ind. Eng. Chem.*, **33**, 1224 (1941)
24) M. G. Gonikberg and L. F. Vereshchagin, *Compt. Rend. Acad. Sci. (USSR)*, **55**, 801 (1947)

The kinematic viscosity ratios of 17 gases listed in Table 2 are plotted against pressure up to 120 atm., as shown partly in Fig. 3, in which the ordinate of $\nu_p/\nu_1$ is the logarithmic scale to indicate the small values of $\nu_p/\nu_1$ in detail. In this figure, the full line represents the curves of eight gases listed in " A " column of Table 2 over all the temperature ranges within the deviation of 5%, and, on the other hand, in the case of nine gases listed in "B" column, the isotherms at low temperature ranges decrease more rapidly with increasing pressure, as shown by the dotted lines in Fig. 3. The deviation of the latter gases from the full line described above is examined and the result is given in reduced form on Fig. 4, in which the region where the deviation is within 10% is designated as "available" and the region where it exceeds 10% is designated as "unavailable".

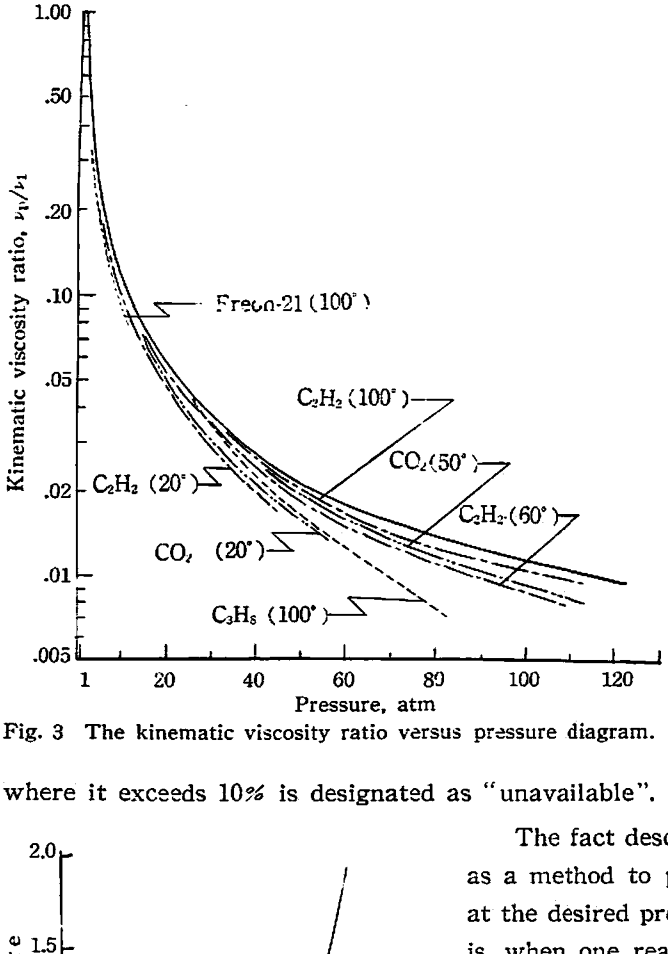

Fig. 3 The kinematic viscosity ratio versus pressure diagram.

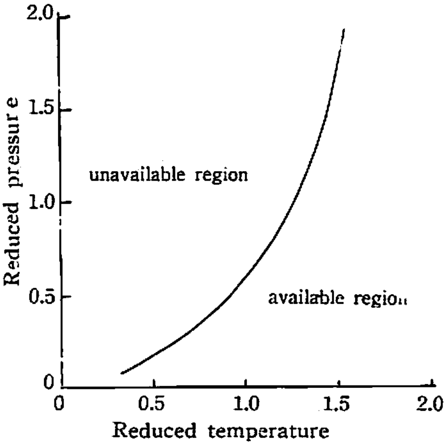

Fig. 4 The available region of the full line in Fig. 3 for the gases listed in "B" column of Table 2.

The fact described above will be applicable as a method to predict the viscosity of gases at the desired pressure and temperature. That is, when one reads the value of $\nu_p/\nu_1$ at a desired pressure from the full line in Fig. 3 and knows the values of $\rho_p/\rho_1$ and $\eta_1$ at the desired temperature, the viscosity, $\eta_p$, can be calculated by means of Eq. (4).

This method is convenient for practical use with a view that the correlation is given by only one curve without the knowledge of the critical values, differing from other methods[10–13].

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