Viscosity and Thermal Conductivity of Sulfur Dioxide in the Gaseous and Liquid States

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VISCOSITY and thermal conductivity of the inert and diatomic gases (*5, 25, 27, 28*) have been studied extensively in both the liquid and gaseous states. The majority of these substances were nonpolar, and therefore could readily be treated from a theoretical viewpoint. An attempt to extend the study of viscosity and thermal conductivity to polar substances has been presented by Groenier and Thodos (*16*), who developed reduced state correlations for ammonia in the liquid and gaseous regions. In this study, a similar approach has been utilized to develop reduced state viscosity and thermal conductivity correlations for another polar substance, sulfur dioxide.

VISCOSITY AT ATMOSPHERIC PRESSURE

A critical survey of the literature for viscosities at atmospheric pressure revealed the experimental data of six investigators (*30–34, 36*). The resulting values of the viscosity at atmospheric pressure, μ^*, are plotted against reduced temperature on log-log coordinates in Figure 1.

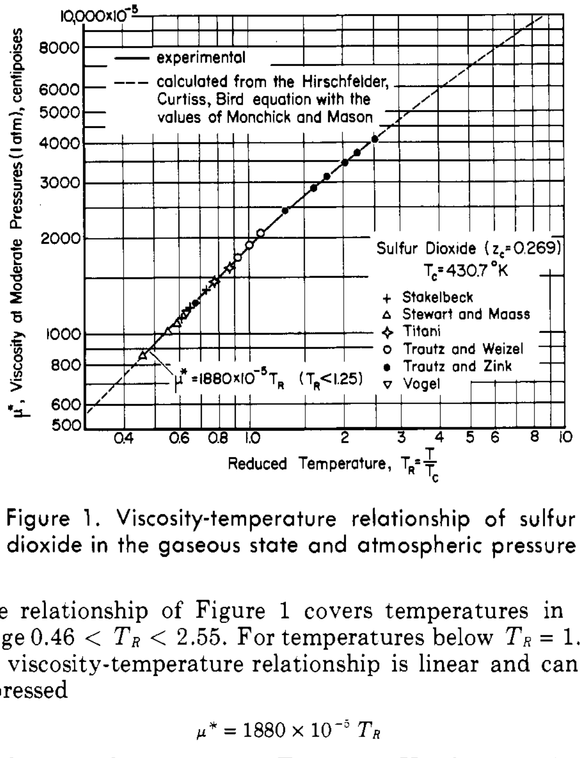

Figure 1. Viscosity-temperature relationship of sulfur dioxide in the gaseous state and atmospheric pressure

The relationship of Figure 1 covers temperatures in the range $0.46 < T_R < 2.55$. For temperatures below $T_R = 1.25$, the viscosity-temperature relationship is linear and can be expressed

$$\mu^* = 1880 \times 10^{-5}\, T_R \tag{1}$$

At the critical temperature, $T_c = 430.7°$ K., the viscosity of gaseous sulfur dioxide at atmospheric pressure becomes $\mu^*_{T_c} = 1880 \times 10^{-5}$ cp.

In order to extend the relationship of Figure 1 to reduced temperatures of $T_R > 2.55$, the theoretical relationship developed by Hirschfelder, Curtiss, and Bird (*18*),

$$[\mu^*]_3 = 266.93 \times 10^{-5} f_\mu^{(3)} \frac{(MT)^{1/2}}{\sigma^2 \Omega^{(2,2)*}[T_N, \delta_{\max}]} \tag{2}$$

has been used along with values of the collision integrals for polar molecules, $\Omega^{(2,2)*}[T_N, \delta_{\max}]$, reported by Monchik and Mason (*23*). These collision integrals are functions of the normalized temperature, $T/(\epsilon/\kappa)$, and of $d_{\max} = \mu^2/2\epsilon\sigma^3$, where ϵ/κ and σ are the Lennard-Jones force constants and μ the dipole moment of the polar molecule. The dimensionless polarity parameter, $\delta_{\max}$, characterizes the polar nature of the molecule.

The dipole moment for sulfur dioxide, $\mu = 1.63$ debyes, and the Lennard-Jones force constants, $\epsilon/\kappa = 347°$ K. and $\sigma = 4.04$ A., reported by Monchick and Mason (*23*) produced a polarity parameter value for sulfur dioxide of $\delta_{\max} = 0.421$. Viscosity values calculated from Equation 2 with these parameters and the collision integrals reported by Monchick and Mason for the region $0.46 < T_R < 2.55$ were found to be in excellent agreement with the corresponding experimental values. Therefore, viscosities calculated in this manner enabled the extension of the relationship of Figure 1 to reduced temperatures up to approximately $T_R = 10$.

THERMAL CONDUCTIVITY AT ATMOSPHERIC PRESSURE

The only experimental thermal conductivities for sulfur dioxide at atmospheric pressure are the values by Dickins (*1*), Andrussow (*3*), and Foz Gazulla and Perez (*13*) for the temperature range 0 to 22° C. Because the single value of Andrussow was not consistent with the others, it was not included in the analysis. The single value reported by Dickins (*10*) at 18.9° C. ($T_R = 0.678$), $k^* = 2.216 \times 10^{-5}$ cal./sec. cm. ° K., was used to produce a value of $k^*/c_v\mu^* = 1.48$ from the corresponding viscosity value obtained from Figure 1, $\mu^* = 12.7 \times 10^{-5}$ poises, and the value of the heat capacity at constant volume, $C_v = 9.57 - 1.99 = 7.58$ cal./g.-mole ° K., reported by Wagman (*37*). Both Eucken (*12*) and Bromley (*6*) report an identical value of $k^*/c_v\mu^*$ for sulfur dioxide. This quantity was suggested to be temperature independent by Maxwell (*22*). With this assumption, thermal conductivities were calculated from this value of $k^*/c_v\mu^*$, the viscosity relationship of Figure 1, and the heat capacity data reported by Wagman for sulfur dioxide at 1 atm. The heat capacity data of Kelley (*20*) enabled Wagman's data to be extended from $T_R = 3.5$ to $T_R = 10$. Thermal conductivities calculated in this manner were plotted against reduced temperature, as shown in Figure 2 for the temperature range $0.6 < T_R < 10$.

For a polar molecule, the translational contribution to thermal conductivity can be obtained from the following equation presented by Hirschfelder, Curtiss, and Bird (*18*):

$$[k^*]_3 = 19.891 \times 10^{-5} f_k^{(3)} \frac{(T/M)^{1/2}}{\sigma^2 \Omega^{(2,2)*}[T_N, \delta_{\max}]} \tag{3}$$

Thermal conductivities were also calculated for sulfur dioxide from Equation 3 with the Eucken correction factor for polyatomic molecules, $(4/15)(C_v/R) + 3/5$. Similar calculations were also made by the use of Equation 3 and the correction factor, $0.115 + 0.345\,(C_p/R)$, which has been recently proposed by Hirschefelder (*17*). The collision integrals, force constants, and the polarity parameter reported by Monchick and Mason (*23*) were used in these calculations. The resulting thermal conductivity values were plotted against temperature, as shown on Figure 2. Since the relationship resulting from the use of $k^*/c_v\mu^* = 1.48$ coincided at low reduced temperatures with the relationship obtained from the Eucken correction factor and was essentially parallel to that obtained from the Hirschfelder correction factor, it was accepted as the basis for further phases of this investigation.

DENSITY OF SULFUR DIOXIDE

No experimental density data are reported in the literature for sulfur dioxide in the superheated region, with the exception of a limited number of values for low pressures (*26*). However, sufficient density data have been reported to enable the construction of the saturated liquid line of the substance from $T_R = 0.517$ to the critical point (*2, 8, 9, 21*). The saturated vapor densities of Cailletet and Mathias (*8*) and those reported by Fiske (*26*) were found to be internally inconsistent; consequently, it became necessary to utilize vapor pressures to terminate the isobars developed in this work at the saturated vapor curve. With this approach, the saturated vapor curve was extrapolated beyond the values reported by Cardoso and Sorrentino (*9*) to establish its behavior in the region below $T_R = 0.82$.

Since only meager data have been reported for regions other than the saturated state of the substance, it became necessary to utilize the theorem of corresponding states to establish density values for the superheated region and compressed liquid state of sulfur dioxide. Reduced density values available in the literature for nitrogen (*7*) and ammonia (*15*) were used with the saturated liquid densities for sulfur dioxide at the same reduced temperatures to establish the reduced density of sulfur dioxide through the following relationship:

$$\frac{\rho_R}{\rho'_R} = \frac{\rho_{R_S}}{\rho'_{R_S}} \tag{4}$$

where ρ' and ρ'_{R_S} are the densities of the reference substance. The densities calculated in this manner for sulfur dioxide were accepted if the values resulting from the use of each reference substance differed by less than 0.5%. This approach enabled the establishment of isobars up to $P_R = 40$ for temperatures in the range $0.65 < T_R < 0.80$.

To establish density values for sulfur dioxide for temperatures of $T_R > 0.80$, the following relationship applicable at constant reduced density was used with saturated liquid data for ammonia:

$$\frac{T_R}{T'_R} = \frac{T_{R_S}}{T'_{R_S}} \tag{5}$$

This approach enabled the establishment of all the isobars up to $P_R = 40$ for reduced temperatures up to $T_R = 1.5$. Density values calculated in this manner for the isobars in the temperature range $0.65 < T_R < 0.80$ compared favorably with those established by the previous procedure for this region.

Densities for the isobar $P_R = 20$ were also determined from Equation 5 by the use of saturated liquid data for nitrogen, and compared favorably with those calculated from the ammonia data. Density values were calculated for the other isobars from the corresponding values for the isobar $P_R = 20$ at the same reduced temperature, by the use of the data for ammonia and the relationship:

$$\frac{\rho_R}{\rho'_R} = \frac{(\rho_R)_{P_R=20}}{(\rho'_R)_{P_R=20}} \tag{6}$$

Densities calculated in this manner were found to be in close agreement with the values established previously for these isobars from Equation 5.

In Figure 3, the resulting reduced state density correlation is presented for reduced temperatures up to $T_R = 1.5$ and reduced pressures up to $P_R = 40$. Density values for reduced temperatures of $T_R > 1.5$ were obtained from the isobars of Figure 3 and the Nelson-Obert compressibility factor charts (*24*).

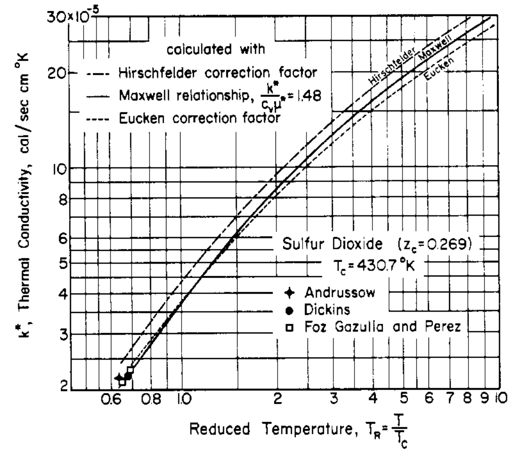

Figure 2. Thermal conductivity–temperature relationships for sulfur dioxide in the gaseous state and atmospheric pressure

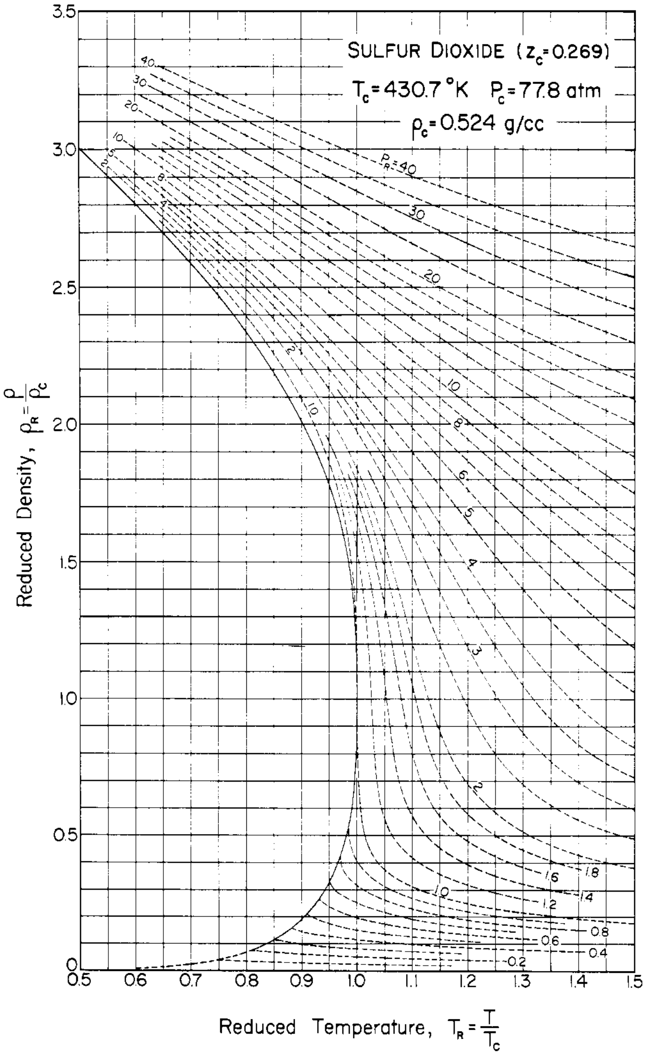

Figure 3. Reduced density behavior of sulfur dioxide

Since no experimental densities have been reported for the superheated and the compressed liquid regions, the reliability of the reduced state correlation presented in Figure 3 cannot be verified except for the saturated envelope. However, until direct density data are available, it is felt that this correlation is a good representation of the density behavior of sulfur dioxide in the gaseous and liquid states.

VISCOSITY

Awbery and Griffiths (*4*) and Stakelbeck (*30*) have reported viscosity values for the liquid state of sulfur dioxide; while Shimotake and Thodos (*29*) have determined viscosities for this substance for the dense gaseous region. From these limited experimental values, the residual viscosity, $\mu - \mu^*$, was calculated by the use of the atmospheric viscosity value obtained at the same temperature from Figure 1 for each point. These residual viscosities were plotted against the corresponding reduced density values obtained from the reduced state density correlation of Figure 3 to produce a continuous relationship for the dense gaseous and liquid regions. Relationships of this type were proposed to exist for the viscosity and thermal conductivity of a pure substance by Abas-zade (*1*). The low pressure values of Stakelbeck (*30*) were found to scatter considerably from the smooth curve of Figure 4. However, this relationship permits high pressure viscosity values to be accurately established for sulfur dioxide. The relationship of Figure 4 also permits the establishment of the viscosity of sulfur dioxide at the critical point as $\mu_c = 3590 \times 10^{-5}$ cp. from the residual viscosity at the critical point, $(\mu - \mu^*)_c = 1710 \times 10^{-5}$ cp., and the atmospheric viscosity at the critical temperature, $\mu^*_{T_c} = 1880 \times 10^{-5}$ cp.

The residual viscosity plot of Figure 4 was used in conjunction with the atmospheric viscosity plot of Figure 1 and the reduced density correlation presented in Figure 3 to establish viscosity values for various isobars for reduced temperatures up to $T_R = 10$. These viscosity values were reduced with the established value of the viscosity at the critical point and plotted against the corresponding reduced temperatures and pressures to produce the reduced state viscosity correlation for sulfur dioxide for temperatures up to $T_R = 10$ and pressures up to $P_R = 40$ presented in Figure 5. This correlation is presented on reduced coordinates to permit comparisons with similar correlations which have been developed for other substances. Viscosity values for sulfur dioxide calculated from the generalized viscosity correlation presented by Uyehara and Watson (*35*) produced an average deviation of 11.7% from the 71 corresponding experimental viscosities.

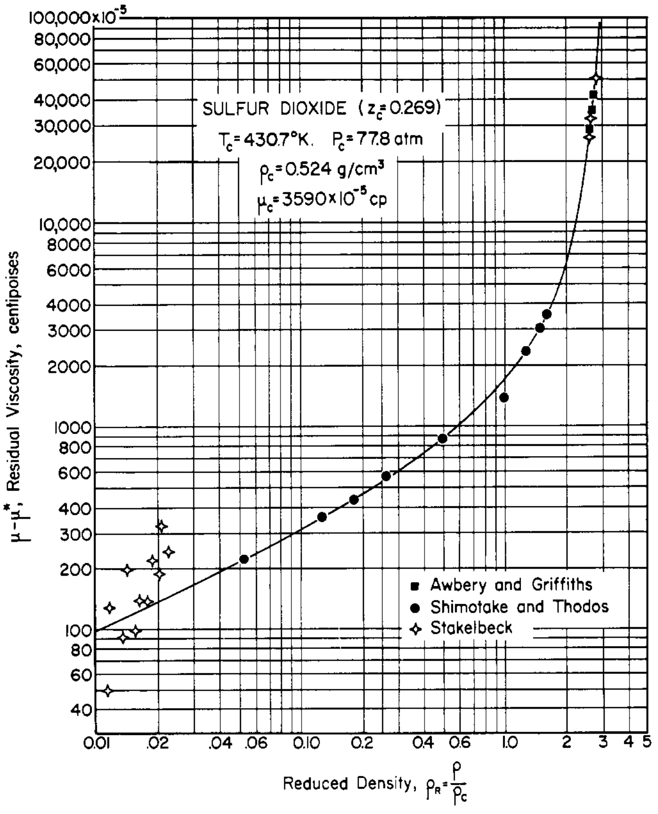

Figure 4. Residual viscosity–reduced density relationship for sulfur dioxide in the dense phase region

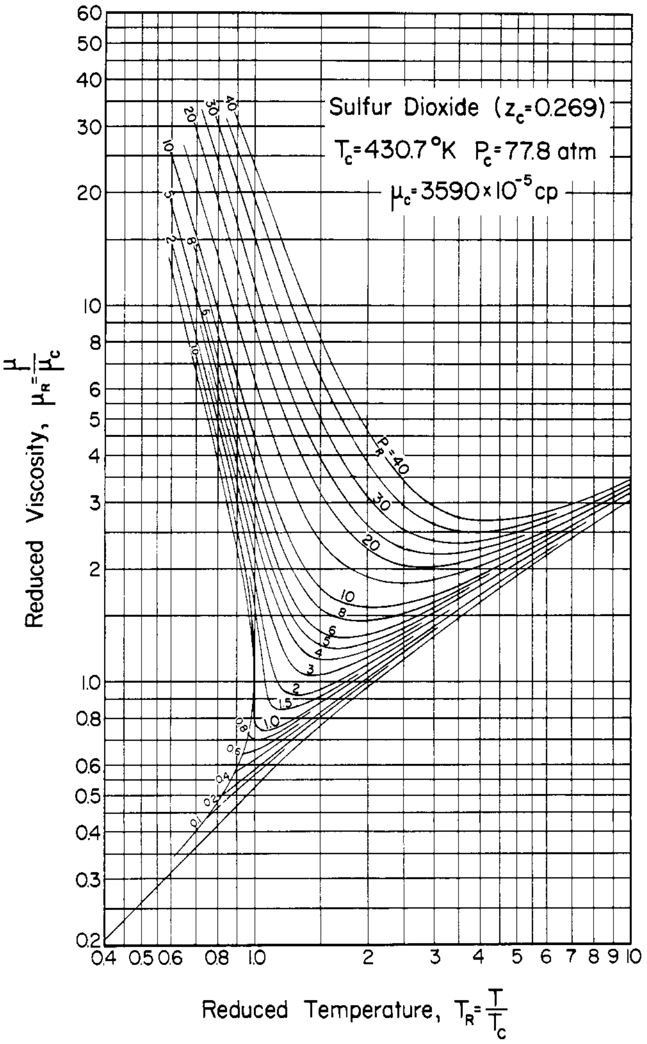

Figure 5. Reduced viscosity correlation for sulfur dioxide

THERMAL CONDUCTIVITY

The only experimental thermal conductivity values which have been reported for sulfur dioxide at high densities are those of Kardos (*19*) for the liquid state. Therefore, it became necessary to use the information for the viscosity behavior of sulfur dioxide to calculate thermal conductivity values for the dense gaseous and liquid regions from the ratio of the Enskog relationships for viscosity and thermal conductivity (*11*),

$$\frac{\mu}{\mu^*} = b\rho\left[\frac{1}{b\rho\chi} + \frac{4}{5} + 0.7614\, b\rho\chi\right] \qquad (7)$$

$$\frac{k}{k^*} = b\rho\left[\frac{1}{b\rho\chi} + \frac{6}{5} + 0.7574\ b\rho\chi\right] \qquad (8)$$

where

$$b\rho\chi = \frac{z_c}{\rho_R}\left(\frac{\partial P_R}{\partial T_R}\right)_{\rho_R} - 1$$

Values of the quantity $b\rho\chi$ were determined from the reduced density correlation of Figure 3 for $T_R = 1.099$, for which viscosity values are reported for the dense gaseous region of sulfur dioxide (*29*). The resulting $b\rho\chi$ values are as follows:

P_R	$b\rho\chi$	P_R	$b\rho\chi$
0.2	0.140	1.5	1.010
0.4	0.290	2.0	1.325
0.6	0.410	3.0	1.895
0.8	0.570	4.0	2.300
1.0	0.695	5.0	2.560

By the use of these $b\rho\chi$ values and the ratio of Equations 7 and 8, thermal conductivities were calculated for which the corresponding residual values were determined from Figure 2 and plotted against the reduced density to produce the single relationship presented in Figure 6. This relationship also passes through the residual thermal conductivities for the liquid region resulting from the investigation of Kardos (*19*). Figure 6 enabled the determination of the thermal conductivity at the critical point for sulfur dioxide to be $k_c = 8.35 \times 10^{-5}$ cal./sec. cm. ° K. from $(k - k^*)_c = 4.62 \times 10^{-5}$ cal./sec. cm. ° K. and $k^*_{T_c} = 3.73 \times 10^{-5}$ cal./sec. cm. ° K.

This value was used to reduce thermal conductivities for sulfur dioxide which were obtained as functions of reduced temperature for various isobars from Figures 2, 3, and 6. These reduced values were plotted against the corresponding reduced temperatures and pressures to produce the reduced state thermal conductivity correlation presented in Figure 7 for reduced temperatures up to $T_R = 10$ and reduced pressures up to $P_R = 40$. Thermal conductivity values calculated for sulfur dioxide from the generalized correlation presented by Gamson (*14*) produced an average deviation of 14.8% for the four thermal conductivity values reported for atmospheric pressure. Since Gamson's correlation cannot be used for the liquid region, the experimental values reported by Kardos (*19*) could not be compared.

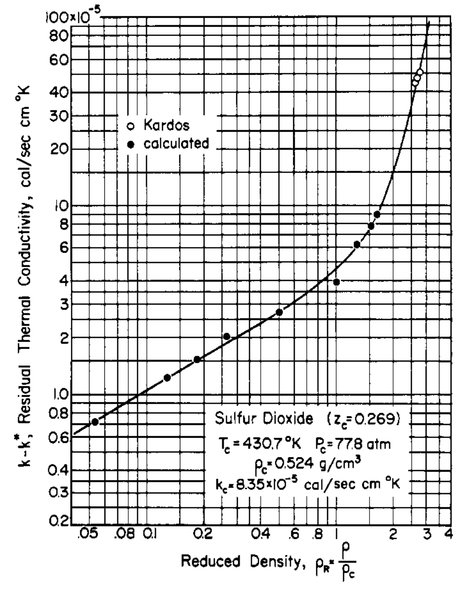

Figure 6. Residual thermal conductivity–reduced density relationship for sulfur dioxide in the dense phase region

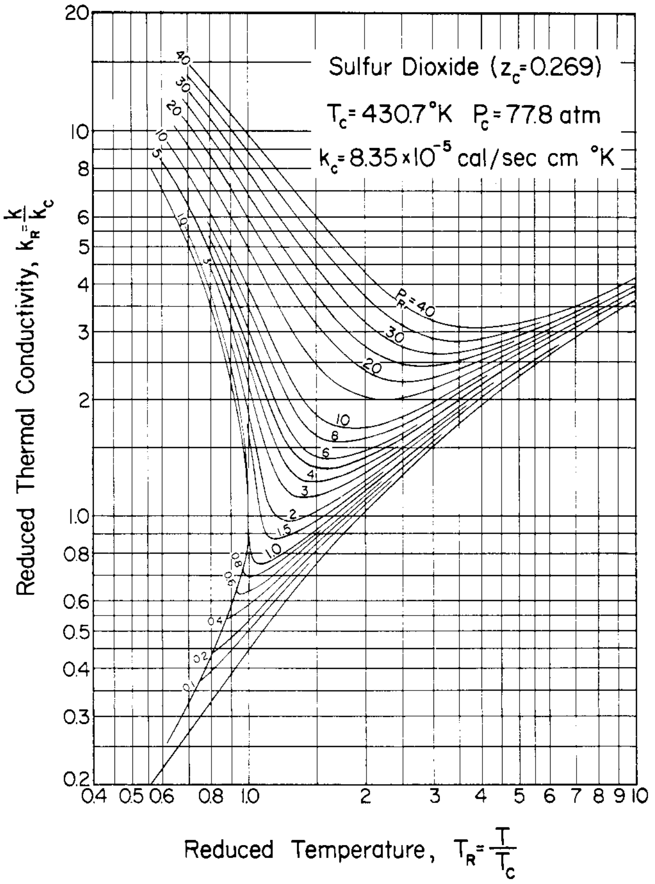

Figure 7. Reduced thermal conductivity correlation for sulfur dioxide

NOMENCLATURE

b = constant for Enskog equations, Equations 7 and 8
C_p = molar heat capacity at constant pressure, cal./g-mole ° K.
c_v = heat capacity at constant volume, cal./g. ° K.
C_v = molar heat capacity at constant volume, cal./g.-mole ° K.
f_k^{3} = third approximation thermal conductivity correction factor
f_μ^{3} = third approximation viscosity correction factor
k = thermal conductivity, cal./sec. cm. ° K.
k^* = thermal conductivity of gases at normal pressures, cal./sec. cm. ° K.
k_c = thermal conductivity at the critical point, cal./sec. cm. ° K.
k_R = reduced thermal conductivity, k/k_c
M = molecular weight
R = gas constant
P = pressure, atmospheres
P_c = critical pressure, atmospheres
P_R = reduced pressure, P/P_c
T = absolute temperature, ° K.
T_c = critical temperature, ° K.
T_N = normalized temperature, $T/(\epsilon/\kappa)$
T_R = reduced temperature, T/T_c
T_{R_s} = reduced temperature at saturated conditions
v_c = critical volume, cc./g.-mole
z_c = critical compressibility factor, $P_c v_c/RT_c$

Greek

$\delta_{\max}$ = dimensionless polarity parameter, $\mu^2/2\epsilon\sigma^3$
ϵ = maximum energy of attraction for Lennard-Jones potential, ergs
κ = Boltzmann constant, 1.38047×10^{-16} ergs/° K.
μ = dipole moment, debye units
μ = viscosity, cp.
μ^* = viscosity of gases at normal pressures, cp.
$\mu^*_{T_c}$ = viscosity of gases at normal pressures and the critical temperature, cp.
μ_c = viscosity at the critical point, cp.

μ_R = reduced viscosity μ/μ_c
ρ = density, g./cc.
ρ_c = density at the critical point, g./cc.
ρ_R = reduced density, ρ/ρ_c
ρ_{R_s} = reduced density at saturated conditions
σ = collision diameter for Lennard-Jones potential, A.
χ = factor for probability of collisions
$\Omega^{(2,2)*}[T_{N_1}\sigma_{\max}]$ = collision integral function for polar molecules

LITERATURE CITED

(1) Abas-zade, A.K., *Zh. Eksperim. i Teor. Fiz.* **23**, 60 (1952).
(2) Andréeff, E., *Ann. Chem.* **110**, 1 (1859).
(3) Andrussow, Leonid, *Z. Elektrochem.* **57**, 374 (1953).
(4) Awbery, J.H., Griffiths, E., *Proc. Phys. Soc. (London)* **48**, 372 (1936).
(5) Brebach, Wm. J., Thodos, George, *Ind. Eng. Chem.* **50**, 1095 (1958).
(6) Bromley, L.A., *U. S. At. Energy Comm., Tech. Inform. Service* **UCRL-1852**, 1952.
(7) Byrne, Robert, Thodos, George, *A.I.Ch.E. Journal* **7**, 185 (1961).
(8) Cailletet, L., Mathias, E., *Compt. Rend.* **104**, 1563 (1887).
(9) Cardoso, Ettore, Sorrentino, E., *J. Chim. Phys.* **24**, 77 (1927).
(10) Dickins, B.G., *Proc. Roy. Soc. (London)* **A143**, 517 (1934).
(11) Enskog, David, *Kgl. Svenska Vetenskapsakad. Handl.* **63**, No. 4 (1921).
(12) Eucken, A., *Forschung.* **11**, 6 (1940).
(13) Foz Gazulla, O.R., Perez, S.S., *Z. Physik. Chem.* **193**, 162 (1944).
(14) Gamson, B.W., *Chem. Eng. Progr.* **45**, 154 (1949).
(15) Groenier, W.S., Thodos, George, J. CHEM. ENG. DATA **5**, 285 (1960).
(16) *Ibid.*, **6**, 240 (1961).
(17) Hirschfelder, J.O., *J. Chem. Phys.* **26**, 282 (1957).
(18) Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
(19) Kardos, A., *Z. Ges. Kälte-Ind.* **41**, 1-35 (1934).
(20) Kelley, K.K., *U. S. Bur. Mines, Bull.* **406**, pp. 1-154, 1937.
(21) Lange, A., *Z. Angew Chem.* **12**, 275 (1899).
(22) Maxwell, J.C., "Collected Works," Vol. 2, p. 1, Cambridge, London, 1890.
(23) Monchick, L., Mason, E.A., *J. Chem. Phys.* **35**, 1676 (1961).
(24) Nelson, L.C., Obert, E.F., *Trans. Am. Soc. Mech. Engrs.* **76**, 1057 (1954).
(25) Owens, E.J., Thodos, George, *A.I.Ch.E. Journal* **3**, 454 (1957).
(26) Perry, J.H., "Chemical Engineers' Handbook," p. 2564, 2nd ed., McGraw-Hill, New York, 1941.
(27) Schaefer, C.A., Thodos, George, *A.I.Ch.E. Journal* **5**, 367 (1959).
(28) Shimotake, Hiroshi, Thodos, George, *Ibid.*, **4**, 257 (1958).
(29) Shimotake, Hiroshi, Thodos, George, "Viscosity of Sulfur Dioxide at 200° C. for Pressures up to 3500 P.S.I.," unpublished data, 1960.
(30) Stakelbeck, H., *Z. Ges. Kälte-Ind.* **40**, 33 (1933).
(31) Stewart, W.W., Maass, Otto, *Can. J. Research* **6**, 453 (1932).
(32) Titani, Toshizo, *Bull. Chem. Soc. Japan* **5**, 98 (1930).
(33) Trautz, Max, Weizel, Walter, *Ann. Physik* **78**, 305 (1925).
(34) Trautz, Max, Zink, Robert, *Ibid.*, [5] **7**, 427 (1930).
(35) Uyehara, O.A., Watson, K.M., Natl. Petrol. News, **36**, R764 (October 4, 1944).
(36) Vogel, Hans, *Ann. Physik* **43**, 1235 (1914).
(37) Wagman, D.D., "Selected Values of Chemical Thermodynamic Properties," U. S. Natl. Bur. Std., July 1, 1953.

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Thermochemistry of Sulfamic Acid and Aqueous Sulfamate Ion

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THERMOCHEMICAL investigations of sulfamic acid have yielded the following heats of solution and reaction:

$$HSO_3NH_2(c) = H^+(aq) + SO_3NH_2^-(aq) \qquad \Delta H_1$$

$$NaNO_2(c) = Na^+(aq) + NO_2^-(aq) \qquad \Delta H_2$$

$$NaNO_2(c) + SO_3NH_2^-(aq) = SO_4^{-2}(aq) + Na^+(aq) + N_2(g) + H_2O \qquad \Delta H_3$$

$$NO_2^-(aq) + SO_3NH_2^-(aq) = SO_4^{-2}(aq) + N_2(g) + H_2O \qquad \Delta H_4$$

EXPERIMENTAL

The high precision solution calorimeter employed has been described in detail elsewhere (*4*). Temperature changes were followed by means of a Maier transposed bridge circuit with thermistors in two opposite arms. An electric heater made of manganin wire was used for calibration. All heats of solution and reaction were determined at 25.0° ± 0.2° C. in 950 ml. of solution.

Sulfamic acid was purified according to the method described by Sisler, Butler, and Audrieth (*1*). The crystals were dried in a vacuum desiccator, broken up with a glass rod, then dried in an oven at 40° C. for 4 hours, and again placed in a desiccator. Heats of solution of samples from several preparations were identical within the limits of our calorimetric accuracy.

Sodium nitrite was recrystallized from water and then dried in a desiccator for two months.

The extent of reaction of sulfamate ions with nitrite ions in alkaline solution has been determined by measuring in a gas buret the volume of nitrogen evolved. The reaction of sulfamic acid with nitrous acid in slightly acidic solution is known to be quantitative, but it was necessary to check the completeness of this reaction in base because the calorimetric reaction was carried out in basic solution to prevent disproportionation of HNO_2. We found, by collecting and measuring the evolved N_2, that the reaction