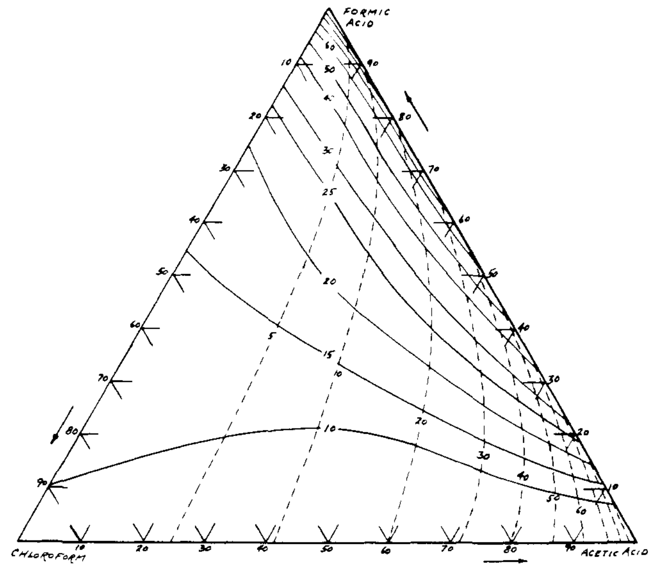

Figure 18. Vapor-liquid equilibria of acetic acid–formic acid–chloroform
——— Weight % formic acid in vapor
— — — Weight % acetic acid in vapor

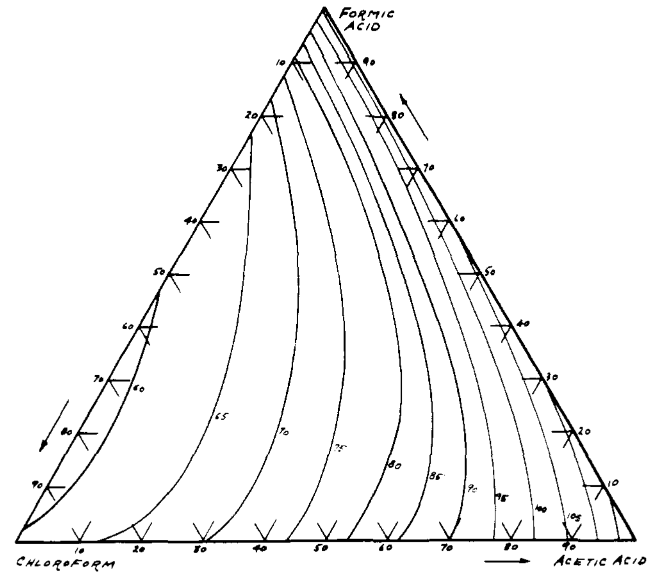

Figure 19. Liquid boiling temperatures of acetic acid–formic acid–chloroform, °C.

this manner are shown in Figure 6 and indicate good linear relationships for each of the systems.

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Collision Integrals for the Viscosity of Polar Gases

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MANY CALCULATIONS have been made of the thermodynamic properties of both nonpolar and polar gases, and of the transport properties of nonpolar gases for several intermolecular potential functions. The only calculation of transport properties for polar gases reported to date was that for viscosity by Krieger (*3*).

Calculations for polar gases usually have been made with the Stockmayer potential function (*7*)

$$E(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}] - \mu^2 r^{-3} f(\Theta_1 \times \Theta_2 \times \phi) \qquad (1)$$

which expresses the energy variation as a function of molecular separation, r, and certain parameters ϵ, σ, and μ. Parameters ϵ and σ represent the maximum depth in the potential "well," and the molecular separation for zero intermolecular energy, respectively; μ is the dipole moment.

The Krieger Model. The function f includes the effect of relative orientation of the two polar molecules specified in terms of certain angles Θ_1, Θ_2, ϕ. Krieger found Equation 1 was too difficult to employ in the calculation of viscosity and set $f(\Theta_1, \Theta_2, \phi) = 2$, an assumption implying that molecules only collide in the end-on position. Making this assumption, Krieger computed the viscosity to be given by

$$10^7 \eta = 266.93\,(MT)^{1/2}/W[T/\Theta, \delta] \qquad (2)$$

where η is the viscosity in poises, T is absolute temperature, Θ is reduced temperature, ϵ/k, M is molecular weight, and $W[T/\Theta,\ \delta]$ is a collision intregal dependent upon the reduced temperature, T/Θ, and the reduced dipole moment, δ, defined by

$$\delta = 1/2\ \frac{\mu^2}{\epsilon\sigma^3} \qquad (3)$$

Table I. The Collision Integral $W(T/\Theta, t^*)$

T/Θ	t^* 0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4
0.70	1.908	2.057	...	...	...	...	...	...	...	...	...	...	...	...	...
0.80	1.780	1.907	2.032	...	...	...	...	...	...	...	...	...	...	...	...
0.90	1.675	1.781	1.887	1.994	2.102	...	...	...	...	...	...	...	...	...	...
1.00	1.587	1.679	1.769	1.864	1.953	2.041	2.127	2.210	2.293	2.375	2.450	2.521	2.577	2.608	2.620
1.10	1.514	1.600	1.686	1.772	1.859	1.944	2.027	2.104	2.181	2.263	2.338	2.406	2.468	2.503	2.519
1.20	1.450	1.529	1.605	1.681	1.761	1.840	1.921	2.000	2.077	2.155	2.229	2.302	2.362	2.402	2.424
1.30	1.400	1.468	1.539	1.611	1.685	1.757	1.830	1.903	1.976	2.055	2.134	2.207	2.267	2.314	2.340
1.40	1.353	1.414	1.478	1.545	1.614	1.681	1.751	1.821	1.891	1.968	2.045	2.122	2.185	2.234	2.268
1.50	1.314	1.367	1.424	1.485	1.548	1.623	1.680	1.745	1.814	1.890	1.969	2.045	2.133	2.164	2.201
1.60	1.280	1.327	1.380	1.437	1.497	1.558	1.621	1.688	1.749	1.820	1.892	1.975	2.038	2.095	2.137
1.70	1.248	1.291	1.340	1.392	1.448	1.505	1.565	1.623	1.683	1.750	1.825	1.913	1.968	2.030	2.076
1.80	1.222	1.263	1.308	1.356	1.406	1.458	1.516	1.576	1.631	1.699	1.769	1.842	1.910	1.972	2.020
1.90	1.197	1.234	1.276	1.321	1.368	1.414	1.472	1.527	1.581	1.643	1.713	1.782	1.850	1.915	1.966
2.00	1.175	1.210	1.248	1.288	1.333	1.377	1.428	1.479	1.536	1.595	1.659	1.728	1.797	1.864	1.915
2.10	1.138	1.168	1.201	1.235	1.271	1.310	1.355	1.401	1.450	1.507	1.566	1.629	1.699	1.762	1.817
2.40	1.106	1.132	1.160	1.190	1.222	1.255	1.294	1.335	1.379	1.429	1.482	1.542	1.610	1.673	1.729
2.60	1.082	1.104	1.128	1.152	1.179	1.207	1.240	1.274	1.315	1.360	1.410	1.465	1.523	1.584	1.646
2.80	1.058	1.076	1.098	1.119	1.141	1.165	1.195	1.223	1.260	1.302	1.347	1.393	1.445	1.503	1.572
3.00	1.038	1.057	1.077	1.094	1.111	1.131	1.154	1.183	1.215	1.251	1.292	1.340	1.393	1.445	1.501
3.20	1.022	1.040	1.055	1.069	1.084	1.100	1.120	1.144	1.172	1.205	1.245	1.291	1.340	1.392	1.436
3.40	1.007	1.022	1.036	1.048	1.061	1.075	1.092	1.112	1.126	1.164	1.199	1.241	1.288	1.338	1.379
3.60	0.993	1.007	1.019	1.030	1.040	1.052	1.066	1.082	1.103	1.129	1.162	1.200	1.243	1.289	1.328
3.80	0.981	0.993	1.003	1.012	1.021	1.030	1.042	1.057	1.075	1.097	1.124	1.158	1.200	1.245	1.282
4.00	0.970	0.980	0.989	0.997	1.004	1.012	1.022	1.034	1.051	1.070	1.095	1.125	1.163	1.204	1.238
4.20	0.960	0.969	0.977	0.984	0.989	0.995	1.003	1.014	1.027	1.043	1.066	1.094	1.127	1.163	1.196
4.40	0.951	0.959	0.966	0.972	0.976	0.979	0.986	0.994	1.005	1.019	1.039	1.063	1.094	1.129	1.160
4.60	0.942	0.949	0.955	0.960	0.963	0.965	0.971	0.978	0.988	1.001	1.019	1.041	1.067	1.097	1.126
4.80	0.934	0.941	0.946	0.950	0.952	0.954	0.958	0.963	0.971	0.981	0.997	1.018	1.043	1.070	1.096
5.00	0.927	0.933	0.938	0.941	0.943	0.944	0.947	0.952	0.958	0.968	0.980	0.998	1.020	1.046	1.073

The tabulation of $W[T/\Theta, \delta]$ given by Krieger has been re-examined by the author in connection with certain calculations of transport properties. This paper presents a retabulation of W as a function of T/Θ and t^* where t^* is the commonly accepted parameter for polar molecules first introduced by Rowlinson (*6*) and given by

$$t^* = \frac{1}{2(2)^{1/2}} \times \frac{\mu^2}{\epsilon\sigma^3} \tag{4}$$

This retabulation covers only the range $0.7 \leqq T/\Theta \leqq 5.0$. As noted elsewhere (*4*), the Krieger tabulation for higher temperatures contains several anomalies which occur to a minor extent in the present temperature range. As the original punched cards were inadvertently destroyed (*2*), no reasons for these occurrences can be suggested. Furthermore, a complete recalculation of the collision integral is under consideration at this time and hence the present tabulation has been made only in the temperature region normally encountered in common calculations.

R.A.Svehla and associates at the Nat. Aeronant. Space Admin., A. Lewis Research Center, Cleveland, have recently made a complete recalculation of collision integrals. This recalculation agrees with the Krieger values for small t^* but not at low T/Θ and large t^*.

The retabulation, presented in Table I, was made to assure that the $W(T/\Theta, t^*)$ agreed with the values of Hirschfelder, Curtiss, and Bird (*1*) for $t^* = 0.0$ and that no irregularities existed in the variation of W with t^* at constant T/Θ. The original tabulation for $T/\Theta = 1(0.2)4,5$ and $\delta = 0.00(0.25)2.00$ was smoothed, and additional values for $T/\Theta = 0.7(0.1)0.9(0.2)1.9,\ 4.2(0.2)4.8,\ t^* = 0.1(0.1)1.4$ were added so that 400 values are now available for this region.

No estimate can be given of the absolute accuracy of this tabulation. However, the data should be accurate to about 0.5% for zero t^*, decreasing in accuracy to some 1.5% for high t^* values. Values of the parameters ϵ/k, σ, and δ obtained by Krieger from fitting *P-V-T* data, can be arrived at (*1,3*) for 12 gases. A convenient source of values of dipole moments of some 350 substances in the vapor state (worked out from dielectric constants, molecular beam, and spectroscopic studies rather than from *P-V-T* measurements) is the tabulation of Maryott and Buckley (*5*). A further source of material on this subject is Sutton's report (*8*), unfortunately not available at this time.

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