

Effect of Temperature on Mass Spectra

D. P. Stevenson

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locities, and then substitute these temperature dependent cross sections into the classical transport equations of Chapman⁵ and Enskog.⁶

One would not expect Amdur's indirect approach to be capable of the same accuracy as that of Hirschfelder, Bird, and Spotz. The method does seem, however, to permit greater flexibility in the choice of forms for the potential energy function and does not require numerical integrations. The good agreement between calculated and experimental values for the transport properties of the five rare gases (for example, for viscosities in the range 14°–550°K the average absolute deviation is 4.8 percent) would appear to justify the assumptions used to obtain quantities such as $S_{\eta, \kappa}$ and $S_{D(1,1)}$ as functions of v . This seems particularly likely since care was taken to use potential energy functions whose constants were not evaluated from experimental values of the transport properties which were being calculated.

¹ J. O. Hirschfelder, R. G. Bird, and E. L. Spotz, *J. Chem. Phys.* **16**, 968 (1948).

² I. Amdur, *J. Chem. Phys.* **15**, 482 (1947); **16**, 190 (1948).

³ E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), Chapter III.

⁴ H. S. W. Massey and C. B. O. Mohr, *Proc. Roy. Soc. A* **141**, 434 (1933).

⁵ S. Chapman, *Phil. Trans. Roy. Soc. A* **211**, 433 (1912); **A216**, 279 (1915); **A217**, 115 (1917).

⁶ D. Enskog, *Kinetische Theorie der Vorgänge in massig verdünnten Gasen*, (Inaug. Diss., Upsala, 1917).

The Transport Properties of Non-Polar Gases

J. S. ROWLINSON

Physical Chemistry Laboratory, Oxford University, England

November 4, 1948

IN the October issue of this Journal, Hirschfelder, Bird, and Spotz¹ (HBS) have published extensive tables for calculating the viscosity and thermal conductivity of gases whose molecules have a van der Waal's interaction potential of the form $E(r) = Ar^{-12} - Br^{-6}$. Their tables now enable such data to be analyzed with almost the same precision as has been applied to second virial coefficient data since 1924. The purpose of this note is to report an independent and almost simultaneous investigation of the same problem which, although different approximation methods were used, confirms the results of these authors.

The dynamics of an encounter were treated by a method similar to that of Burnett.² His treatment could not be followed exactly as some of his substitutions are valid for repulsive force-fields only. χ , the angle of deflection, was computed as a function of two variables α and q . In the notation of HBS, α is given by

$$\alpha = 1 + (1 + K)^{\frac{1}{2}} \quad (\text{cf. HBS Eq. (43)}),$$

where K is the ratio of the relative kinetic energy to the maximum energy of interaction. q is a measure of $1/b$, where b would be the distance of closest approach if $E(r)$ were everywhere zero, and is given by

$$y_m = q(\alpha/2)^{1/6}.$$

For head-on collisions, $q = 1$, and when molecules pass at infinite distance $q = 0$. For each value of α and q , χ was computed by Gauss' method of approximate quadrature,

using 6 ordinates. To avoid the complications of incipient "orbiting," the viscosity was only found for $kT/\epsilon \geq 0.5$ ($\text{HBS } kT/\epsilon \geq 0.3$). The largest value of χ was 475°. A function of $\sin^2 \chi$, denoted by J (as in Eq. (6) of Burnett and corresponding to $S^{(1)}(K)$ of Eq. (53) of HBS) was then found by integration by Gauss' method, using 5 ordinates in each of the following ranges of q , 1.00–0.95, 0.95–0.90, 0.90–0.40, and 3 ordinates in the range 0.40–0.00. Finally the J terms were summed by the most accurate of Burnett's formulae (4-terms). Empirical formulae were used to give J as $f(\alpha)$ and interpolation was used at many of the temperatures. It is readily seen that $\frac{1}{2} \sum n_s J_s$ should be identical with $W^2(2)$ of HBS. The two are compared in Table I.

TABLE I.

kT/ϵ	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.6
$\frac{1}{2} \sum n_s J_s$	2.300	2.085	1.916	1.773	1.651	1.554	1.410	1.312	1.241
$W^2(2)$	2.257	2.065	1.908	1.780	1.675	1.587	1.452	1.353	1.279
kT/ϵ	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.5	4.0
$\frac{1}{2} \sum n_s J_s$	1.190	1.105	1.118	1.083	1.064	1.042	1.022	0.9864	0.9547
$W^2(2)$	1.221	1.175	1.138	1.107	1.081	1.058	1.039	0.9999	0.9700
kT/ϵ	4.5	5.0	5.5	6.0	7.0	8.0	9.0	10.0	
$\frac{1}{2} \sum n_s J_s$	0.9403	0.9262	0.9074	0.8950	0.8740	0.8562	0.8406	0.8265	
$W^2(2)$	0.9464	0.9269	—	0.8963	0.8727	0.8538	0.8379	0.8242	

The viscosity may be calculated from either of these functions by using Eq. (7) of HBS. No attempt was made to compute the small correction factor V , as $(V-1/V)$ is less than the probable error in $W^2(2)$.

In view of the length and complexity of these calculations, and the different methods used in each laboratory, the agreement is very satisfactory. The differences are small and irregular, and are almost certainly due to inaccuracy in the interpolation formulae used in this work and to the use of methods which were essential in a single-handed computation.

¹ J. O. Hirschfelder, R. B. Bird, and E. L. Spotz, *J. Chem. Phys.* **16**, 968 (1948).

² D. Burnett, *Proc. Camb. Phil. Soc.* **33**, 363 (1937).

Effect of Temperature on Mass Spectra

D. P. STEVENSON

Shell Development Company, Emeryville, California

November 1, 1948

IN a recent communication with a title similar to that of the present one, Fox and Hipple¹ describe the effect of temperature on the mass spectrum of isobutane. It is the object of this note to indicate the nature and origin of their observations.

An increase of temperature has two observable effects on the mass spectra of the substances thus far studied. These are:

1. The specific intensity of all ions decrease with increasing temperature.
2. The specific intensities of the "parent ion" decrease more rapidly with temperature than do the specific intensities of fragmentary ions, and within the accessible temperature range (75–350°C) this effect is more pro-

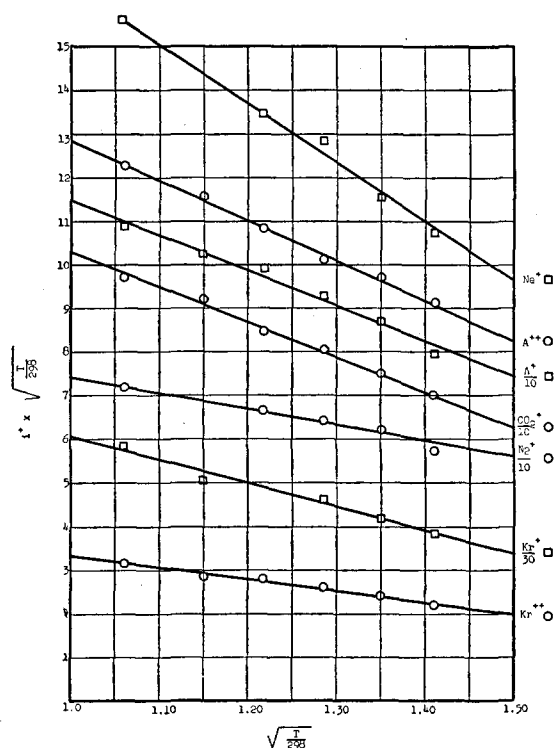


FIG. 1. The variation of specific ion currents (i^*) with absolute temperature (T) for various simple ions (Westinghouse type LV mass spectrometer, 75-volt ionizing electrons). Although the specific current units are arbitrary, the same units have been used for all substances and thus are consistent with the relative sensitivities of the various substances. The temperatures have been normalized to "room temperature" (25°C) to provide a more convenient scale.

nounced for complex than for simple molecules. The largest effects have been found in the mass spectra of branched chain paraffins.

Both 1 and 2 have their origin in the increase in energy of the molecules associated with the increase in temperature. The increase in kinetic energy ($\frac{3}{2}kT$) is the source of effect 1, while the increase in internal (vibrational) energy brings about effect 2.

The increase in kinetic energy of the molecules results in a decrease in the average number of molecules in the ionization chamber since the flow of gas through the mass spectrometer tube is effusive. This results in the ion current being proportional to $T^{-1/2}$. The increase of kinetic energy further results in the ions being formed with greater initial kinetic energy and since the discrimination losses in the ion source increase as $T^{1/2}$, the observed ion current decreases as $(1 - \alpha T^{1/2})$, where α is a function of the ion source geometry, the ion accelerating fields, and the magnetic fields across the ionization chamber.² Thus the decrease of ion current with temperature is expressed as

$$i(T) = i_0 T^{-1/2} [1 - \alpha T^{1/2}]. \quad (\text{A})$$

Equation A has been found to represent the temperature variation of the ion currents in the mass spectra of neon, argon, krypton, nitrogen, and carbon dioxide over, $335 \leq T \leq 593^\circ\text{K}$. This may be seen from Fig. 1, where

$i \times (T/298)^{1/2}$ is plotted against $(T/298)^{1/2}$ for selected ions. It will be noted that for the rare gases (argon and krypton), the formula for the temperature variance of specific ion current fits singly and double charged ions equally well.

The increase in internal energy that accompanies increasing temperature results in an increased fraction of the molecules of a substance being in configurations which permit excitation to energy levels above dissociation limits of the states of the molecule-ion. This results in a larger fraction of the molecule-ions produced by electron impact dissociating, and thus the parent ion forms a smaller fraction of the total ion current. This effect, (2), is related to the greater probability of the breaking of C-H bonds than of C-D bonds in deuterio-hydrocarbons.³

In Table I there are given the ratios, $i_p^+/\sum i_n^+$, where i_p^+ = specific intensity of parent ion, i_n^+ = specific intensity of any ion, and the summation is over all ions, including i_p^+ , in the mass spectra of a number of hydrocarbons for $T = 340, 440$, and 540°K . This ratio equals the fraction of

TABLE I. Effect of temperature on the fraction of the mass spectra due to parent ions.

Substance	p^a	75-volt ionizing electrons		
		$T = 340$	440	540°K
Methane	16	0.572	0.555	0.542
Acetylene	26	0.796	0.792	0.788*
Acetylene- d_2	28	0.829	0.821	0.820*
Ethane	30	0.164	0.152	0.135
Propane	44	0.154	0.132	0.108
<i>n</i> -Butane	58	0.095	0.071	0.048
<i>i</i> -Butane	58	0.0295	0.0204	0.0117

^a p = molecular weight of parent ion.

* $T = 575^\circ\text{K}$.

ions formed which do not dissociate. These data were obtained with a Westinghouse type LV mass spectrometer, i.e., the same type used by Fox and Hipple.¹ The spectra were recorded by varying the magnetic field, and the ion intensities were not corrected for ion source discrimination. As would be expected, the less rigid the molecule the greater is the effect of temperature on the probability of dissociation of the molecule ion, i.e., the smaller the fraction of ions which do not dissociate.

¹ R. E. Fox and J. A. Hipple, J. Chem. Phys. 15, 208 (1947).

² For discussions of ion source discrimination, see Norman D. Coggeshall, J. Chem. Phys. 12, 19 (1944); H. W. Washburn and C. E. Berry, Phys. Rev. 70, 559 (1946).

³ The differences in the mass spectra of such isotopic molecules arise in part from the greater amplitude of the zero-point vibrations of the -H bonds than of the -D bonds. See Evans, Bauer, and Beach, J. Chem. Phys. 14, 701 (1946); N. Bauer and J. Y. Beach, J. Chem. Phys. 15, 150 (1947); David P. Stevenson, J. Chem. Phys. 15, 409 (1947).

The Phase Transition and the Piezoelectric Effect of KH_2PO_4

T. NAGAMIYA AND S. YOMOSA

Department of Physics, Osaka University, Japan

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A NOMALOUS behaviors of the dielectric constants^{1,2} and the phase transition³ at 122°K of KH_2PO_4 were treated by the methods of statistical mechanics by Slater⁴ and others.^{5,6} In this crystal, PO_4 groups are linked by hydrogen bonds which are directed nearly parallel to the