

Transport Properties of Gases

K. E. Grew

Citation: The Journal of Chemical Physics 18, 149 (1950); doi: 10.1063/1.1747441

View online: http://dx.doi.org/10.1063/1.1747441

View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/18/1?ver=pdfcov

Published by the AIP Publishing

Articles you may be interested in

Transport Properties in Ionized Gases

AIP Conf. Proc. 11, 203 (1973); 10.1063/1.2948431

Transport Properties of Quadrupolar Gases

J. Chem. Phys. 46, 317 (1967); 10.1063/1.1840387

Transport Properties of Polar Gases

J. Chem. Phys. 35, 1676 (1961); 10.1063/1.1732130

Transport Properties in Gases

Phys. Today 10, 64 (1957); 10.1063/1.3060424

Calculation of Transport Properties of Gases

J. Chem. Phys. 17, 100 (1949); 10.1063/1.1747036



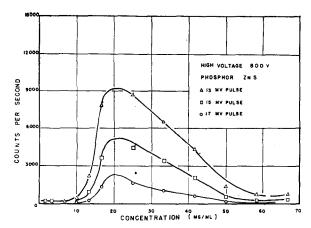


Fig. 1. Counting rate vs. concentration for the ZnS screens.

more opaque. Hence, elementary considerations would suggest that all of the counting rate-concentration curves should show maxima. Figures 1, 2, 3, and 4 show such curves. Figures 3 and 4

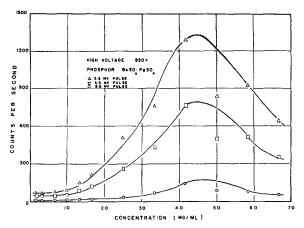


Fig. 2. Counting rate vs. concentration for the BaSO4: PbSO4 screens.

also show the percentage transmission of the phosphor screens for the wave-length for which the phosphor powder has the maximum emission. All of these curves were obtained under almost identical counting conditions. A polonium source of about 0.75 millicurie was used. The geometry was such that only a relatively small percentage (about 1 percent) of the total number of counts

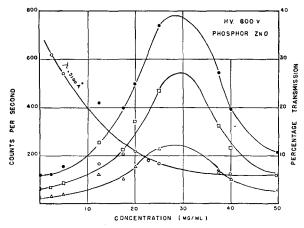


Fig. 3. Counting rate vs. concentration for the ZnO screens.

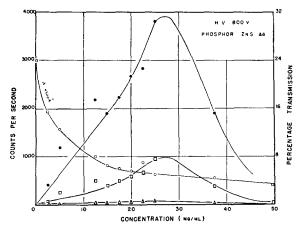


Fig. 4. Counting rate vs. concentration for the ZnS: Ag screens.

was intercepted. This arrangement was made purposely so that the mechanical recorder could follow the counts. The alphaparticles had about 4 Mev energy upon arrival at the screen. The scaler used was a Nuclear Instrument and Chemical Corporation model 162. The operating voltages are given in the graphs.

In general, it can be observed that a phosphor screen (about 0.5 mm thick) of about 30 mg/ml (30 mg of powder in 1 ml of plastic) gives best results. For the readers who are looking for a formula relating the counting rate to the concentration and spectral characteristics of the phosphor powder, the following relation is

Counting rate =
$$f(A) \left[\int_0^\infty g(\lambda) g'(\lambda) d\lambda \right] [j(c)e^{-\mu c}].$$

If the above relation, f(A) means some function of the activity (more than likely a constant fraction which considers the geometry). $g(\lambda)$ and $g'(\lambda)$ give the spectral characteristics of phosphor and cathode respectively and the integral $\int_0^{\infty} g(\lambda)g'(\lambda)d\lambda$ gives the extent to which these two overlap. The function j(c) takes care of the conversion efficiency and the effect of concentration on number of light pulses. If one divided the counting rate curve in Fig. 3 or 4 by the transmission curve, the result would be a curve showing the number of light pulses vs. concentration; this latter curve is essentially j(c). The absorption of the screens for their own radiation is essentially exponential. This accounts for the presences of $e^{-\mu c}$ in the formula percentage transmission curves in Figs. 3 and 4, also. Hence, it is possible to define each term in the equation (graphically) in terms of the data obtained.

*Part I in this series is the article by L. B. Robinson and J. R. Arnold [Rev. Sci. Inst. 20, 549 (1949)].
†This research has received partial support from a grant by the Research Corporation of New York and from the joint program of the AEC and ONR.

Transport Properties of Gases

K. E. GREW University College, Exeter, England November 18, 1949

N two valuable papers, 1,2 the second of which has only recently come to my notice, Hirschfelder, Bird, and Spotz have given theoretical values of the transport coefficients for gases whose molecules have force fields represented by

$$E(r) = 4e \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right],$$

where E is the potential energy of interaction of two molecules at distance r apart, r_0 is the separation when E is zero, and ϵ is the minimum energy. It is perhaps desirable to point out an error which appears in their comparison of those theoretical and experimental results relating to thermal diffusion.

Table I. Values of R_T calculated for the (12, 6) model compared with experimental values.

Gas mixture	Temp, °K	R_{T} HBS†	R _T	R _T experimental
He –Ne, 53.8% He	585.2 233.2 117.2	0.71 0.70 0.68	0.68 0.67 0.65	0.64 0.64 0.58
He-A, 51.2% He	585,2 233,2 117,2	0.73 0.71 0.63	0.67 0.65 0.58	0.66 0.63 0.55
He – Kr. 55.0% He	585.2 233.2 117.2		0.67 0.63 0.50	0.67 0.67 0.55
He −Xe, 53.6% He	585.2 233.2	0.75 0.70	0.71 0.66	0.66 0.66
Ne -A, 51.2% Ne	585.2 233.2 117.2	0.66 0.52 0.27	0.61 0.48 0.25	0.57 0.48 0.28
Ne –Kr, 53.0% Ne	585.2 233.2 117.2		0.61 0.43 0.16	0.64 0.47 0.30
Ne – Xe, 54.2% Ne	585.2 233.2	0.66 0.44	0.61 0.41	0.66 0.46
A-Kr, 53.5% A	585,2 232,2		0.50 0.18	0.61 0.18
A-Xe, 56.4% A	585,2 233,2	0.51 0.15	$0.48 \\ 0.14$	0.45 0.15
H ₂ -He, 53.6% H ₂	284	0.53*	0.62	0.41,*,a 0.60b
H ₂ -D ₂ , 50% H ₂	333	0.63	0.63	0.50,*. 0.52, 0.61

[†] HBS: values given by Hirschfelder, Bird, and Spotz.
* For mixtures containing 80% H₂.
* See reference 3.
b See references 7, 8, and 9.

The quantity used in the comparison is the thermal separation ratio R_T . Now the experimental values of R_T are calculated as the ratio $\alpha(\exp)/[\alpha(\infty)]_1$, where $\alpha(\exp)$ is the value of the thermal diffusion factor determined experimentally and $[\alpha(\infty)]_1$ is the theoretical value, in first approximation, for a mixture of molecules of the same masses, diameters and relative numbers as in the experimental mixture, but which interact as rigid elastic spheres. The diameters used in calculating $[\alpha(\infty)]_1$ are those found from the viscosity and the relation between viscosity and molecular diameter appropriate to rigid spheres. The corresponding theoretical value of R_T is the ratio $\alpha(12,6)/[\alpha(\infty)]_1$ where $\alpha(12,6)$ is the exact value of the thermal diffusion factor for the above model and $\lceil \alpha(\infty) \rceil_1$ is as just defined. It appears, however, that Hirschfelder, Bird, and Spotz, in calculating $[\alpha(\infty)]_1$ have used the "diameters" $2r_0$ found from the viscosity assuming that the molecular fields are of the (12, 6) type—and not rigid spheres, as should be done. The error introduced into R_T is in some cases appreciable, as can be seen in Table I. For isotopic mixtures the point does not arise, of course.

It may be pointed out too that some of the experimental values of R_T given by Hirschfelder, Bird, and Spotz are questionable. The values quoted for hydrogen-deuterium and hydrogen-helium mixtures— R_T =0.50 and 0.41 respectively—are those found by Murphey.3 There is some uncertainty about both. For hydrogendeuterium Waldmann's results lead to $R_T = 0.52$, while Heath, Ibbs, and Wilds agree with Grews in finding $R_T = 0.60 \pm 0.01$. For hydrogen-helium mixtures the results of Elliott and Masson,7 of v. Itterbeek, v. Paemel, and v. Lierde, and of Grew, all indicate a value $R_T = 0.60$. For hydrogen-carbon dioxide mixtures there are several independent measurements giving $R_T = 0.44$ at 300°K and 0.57 at 600°K (Lugg, 10 Blüh, Blüh, and Puschner, 11 Bastick, Heath, and Ibbs12).

The effect of these corrections is in most cases to bring the theoretical and experimental values nearer to each other. It must be remembered, however, in drawing conclusions as to the suitability of the (12, 6) model that the theoretical values of $\alpha(12, 6)$ actually used in the calculation of R_T are first approximations only, and not exact values. It would be interesting to have the error of the first approximation determined, for then thermal diffusion measurements could, it seems, give rather precise information about molecular fields of force.

```
1 Hirschfelder, Bird, and Spotz, J. Chem. Phys. 16, 968 (1948).
2 Hirschfelder, Bird, and Spotz, Chem, Rev. 44, 205 (1949).
3 B. F. Murphey, Phys. Rev. 72, 834 (1947).
4 Waldmann, Zeits. f. Physik 124, 2 (1947).
5 Heath, Ibbs, and Wild, Proc. Roy. Soc. 178Å, 380 (1941).
6 K. E. Grew, Proc. Roy. Soc. 178Å, 390 (1941).
7 Elliott and Masson, Proc. Roy. Soc. 108Å, 378 (1925).
8 v. Itterbeek, v. Paemel, and v. Lierde, Physica 13, 231 (1947).
9 K. E. Grew, Proc. Phys. Soc. 62, 655 (1949).
10 Lugg, Phil. Mag. 8, 1019 (1929).
11 Blüh, Blüh, and Puschner, Phil. Mag. 24, 1103 (1937).
12 Bastick, Heath, and Ibbs, Proc. Roy. Soc. 173Å, 543 (1939).
```

The Crystal Structure of Urea-Hydrocarbon and Thiourea-Hydrocarbon Complexes

A. E. SMITH Shell Development Company, Emeryville, California November 14, 1949

HE formation of crystalline complexes of urea with straight chain hydrocarbons, fatty acids and other compounds was first reported by Bengen¹ and was further discussed by Zimmerschied² and co-workers. It is the purpose of this communication to report the results of an x-ray investigation of the crystal structure of both urea and thiourea complexes and to describe their molecular configuration and its relation to their stability.

Complete Weissenberg data were taken for single crystals of cetane-urea and 1, 10-dibromodecane-urea complexes. Powder patterns were also taken of urea complexes of C₁₀-C₅₀ hydrocarbons and various straight chain alcohols, acids and esters. All gave essentially identical powder patterns. The unit cell is hexagonal; $a_1 = 8.24$ A, c = 11.0Å, space group C6₁2, six urea molecules per unit cell. The urea molecules form spirals with the hydrocarbon molecules situated at the center (Fig. 1). Spirals of hydrogen bonds between the O and NH2 groups of adjacent urea molecules account largely for the stability of the structure (Fig. 2). The shorter N-H-O bonds are about 2.93A in length and are planar with the urea molecule; the longer H bonds are about 3.03A General factors determining the stability of molecular complexes have been discussed by H. M. Powell.⁸

The hydrocarbons are at the special positions (0, 0, Z) in a zigzag planar configuration with the long axis of the molecule parallel to Co. The molecules are randomly distributed with the plane of the molecule at positions perpendicular to the a axis and at multiples of 120° to this position. The Z positions of the carbon

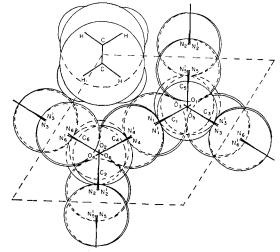


Fig. 1. Centane-urea complex, contents of unit cell projected onto (001) plane showing packing arrangement.

See reference 4. d See references 5 and 6.