

TABLE I. $(k_1 - k_2) \times 10^6$.

System	P	Exptl.	Calc.	Source
Lead:				
H ₂ -Air	0.4	232	211	Ref. 3
Steel:				
H ₂ -Air	0.365	206	210	3
SiC:				
H ₂ -CO ₂	0.428	210	173	2
H ₂ -Air	0.428	198	161	(Kannuliuk and Martin)
Air-CO ₂	0.428	12.1	11.5	
MgO:				
Air (700°C)	0.515	36.6	33.7	Calc. from 1,
Air (0°C)	0.872	12.4	12.7	F_2 const., $\tau = (3/P) - 2$

molecular conduction may be quite appreciable with these gases and fine powders even at one atmosphere. (This was referred to in a somewhat different manner in the first note.¹)

It should be noted that in addition to providing a means of comparing conductivities of fluids, information may be obtained as to the conductivity of solids. The requirement is that one of the fluids (the other could be air) be of reasonably high conductivity (e.g., liquid metals). Such information is definitely needed. For example, the data of Knapp⁵ for LiF and Al₂O₃ differ markedly from values recently reported. The writer has utilized the only data known to him as an example. Schumann and Voss give data at $P=0.4$ for lead granules with the fluids H₂O (1), H₂, air. Using Eq. (2) for H₂O (1) and air with $F_1=1$ and τ_2 (for air) as $(3/P)-2$, the writer obtained 9342×10^{-5} cg for lead (experimental value 8430×10^{-5}). This is considered good agreement since the conductivity of liquid water is only 153×10^{-5} .

Probably the accuracy of all such comparisons would be best with smooth particles of reasonably large size (but certainly below 4 mm, see Waddams⁶) and in other than open packing. Furthermore, any change in the surface of the grains should be avoided. Under such conditions F_1 probably would be 1. Radial flow methods would be quite convenient.

¹ H. S. Strickler, J. Chem. Phys. 17, 427 (1949).

² Wilhelm, Johnson, Wynkoop, and Collier, Chem. Eng. Progress 44 (2), 105 (1948).

³ T. E. W. Schumann and V. Voss, Fuel 13, 249 (1934).

⁴ J. B. Austin, Sympos. Thermal Insul. Materials, American Society for Testing Materials (1939).

⁵ W. J. Knapp, J. Am. Ceram. Soc. 26, 48 (1942).

⁶ A. L. Waddams, J. Soc. Chem. Ind. 206, 337T (1944).

Note on the Free Volume Equation of State for Hard Spheres

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(Received June 3, 1952)

BUEHLER, Wentorf, Hirschfelder, and Curtiss¹ have recently discussed in geometric terms the free volume of rigid spheres obtained from the classical Lennard-Jones-Devonshire model in which the nearest-neighbor molecules are fixed at their mean cell positions without, however, introducing the usual "smearing" to obtain spherical cell symmetry. Kirkwood,² in his analysis of the foundations of the free volume theory, has shown that this model corresponds to a first approximation to the solution of the following integral equation for the configurational distribution function $\varphi(\mathbf{r})$:

$$\begin{aligned} \varphi(\mathbf{r}) &= e^{\beta(\alpha - \psi(\mathbf{r}))}, \\ \psi(\mathbf{r}) &= \sum_i \int_{\text{cell}} V_{il}(\mathbf{R}_{il} + \mathbf{r} - \mathbf{r}') e^{\beta(\alpha - \psi(\mathbf{r}'))} dv', \\ e^{-\beta\alpha} &= \int_{\text{cell}} e^{-\beta\psi(\mathbf{r})} dv. \end{aligned} \quad (1)$$

We have omitted terms involving \bar{E} , the energy with all molecules at the centers of their cells, since they vanish for rigid spheres.

This choice of $\varphi(\mathbf{r})$ minimizes the configurational Helmholtz free energy per molecule given by

$$A^{(1)}/kT = \int_{\text{cell}} \varphi(\mathbf{r}) \log \varphi(\mathbf{r}) d\mathbf{v} + \beta/2 \sum_i \int_{\text{cell}} \int_{\text{cell}} V_{il}(\mathbf{R}_{il} + \mathbf{r} - \mathbf{r}') \varphi(\mathbf{r}) \varphi(\mathbf{r}') d\mathbf{v} dv', \quad (2)$$

subject to the assumptions: (1) representation of the potential energy by pairwise interactions; (2) a Hartree-like smoothing of the configurational probability density into a product of functions each depending on the position of a single molecule; (3) single occupancy of cells. The Lennard-Jones-Devonshire theory is obtained by placing $\varphi(\mathbf{r}) = \delta(\mathbf{r})$ on the right-hand side of (1) and in the second term on the right-hand side of (2). The sums in Eqs. (1) and (2), formally extending over all the molecules (except the first), may be limited to the nearest-neighbors in the case of hard spheres.

It is the purpose of this note to point out that the system of Eqs. (1) may be solved exactly for rigid spheres. We consider a face-centered cubic lattice, and choose as the cell the dodecahedron Δ of Buehler *et al.* Let us denote the volume of this cell by v_Δ ; this is then the range of the integrations denoted in Eqs. (1) and (2). The nearest-neighbor distance and the volume per molecule v are related by $a^3 = \sqrt{2}v$. If r_0 denotes the diameter of the rigid spheres, the minimum volume per molecule is given by $v_0 = r_0^3/\sqrt{2}$.

Our solution for the system of Eqs. (1) is

$$\psi(\mathbf{r}) = \begin{cases} 0, & \text{if } \mathbf{r} \text{ in } \Delta', \\ \infty, & \text{if } \mathbf{r} \text{ not in } \Delta', \end{cases} \quad (3)$$

where Δ' is a dodecahedron similar to Δ , but with altitude $(a-r_0)/2$ instead of $a/2$. This simple solution was found by an attempt to use the iteration scheme suggested by Kirkwood;² the latter does not converge but oscillates around the solution (3). Since the collision spheres of the nearest-neighbors never intersect Δ' , we do not need to distinguish among the various cases discussed by Buehler *et al.*¹ The free volume v_f , defined as $v_f = e^{-\beta\alpha}$, is

$$v_f = v_{\Delta'} = (v^{\dagger} - v_0^{\dagger})^3, \quad (4)$$

and the equation of state is

$$pv/kT = 1 + \left(\frac{a}{r_0} - 1\right)^{-1}. \quad (5)$$

It is interesting that the equation of state (5) is the same as that obtained by the combined "smearing" and delta-function approximations (see reference 1). The correct free energy $A^{(1)}$ actually turns out to be greater than obtained in the usual first (delta-function) approximation because of an inconsistency in the latter: it is actually a combination of the first and next-higher approximations and corresponds to no actual $\varphi(\mathbf{r})$.

I would like to express my thanks to Professor J. G. Kirkwood, with whom I had the opportunity of discussing the material presented here before publication.

¹ Buehler, Wentorf, Hirschfelder, and Curtiss, J. Chem. Phys. 19, 61 (1951).

² J. G. Kirkwood, J. Chem. Phys. 18, 380 (1950).

Experimental Evidence for Anomalous Population Temperatures of OH in Flames*

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(Received June 3, 1952)

IT is the purpose of this note to present an evaluation of the experimental evidence for and against "anomalous" temperatures of OH in flames. Experimental studies have been carried out on low pressure flames^{1,2} and on flames burning at atmospheric pressure.^{1,3,4} The results have usually been interpreted by using

relations which are applicable only to isothermal systems. Attempts to correct for self-absorption have been made by using isointensity methods.³⁻⁵ For spectral lines with Doppler contour it has been demonstrated by quantitative calculations that the isointensity methods do not correct for self-absorption unless self-absorption is weak.⁶ In particular, Shuler's method,⁵ without allowance for the effect of frequency on intensity, has been shown to yield nonlinear plots for strong self-absorption and to be inferior to conventional procedures in the absence of self-absorption.⁶ Extensive studies on the effect of self-absorption in falsifying experimental data have been carried out by Cowan and Dieke.⁷ We have recently attempted to estimate absolute emission intensities for OH in low pressure flames⁸ by using data obtained by Oldenberg and Rieke.⁹

It is commonly acknowledged that the use of the customary isothermal relations may yield plots which are either nonlinear or, if linear, may yield meaningless results. Unfortunately, the matter has been allowed to rest at this point. Thus, it is not uncommon to use relations applicable to isothermal systems with negligible or small self-absorption and to base conclusions on what could be spurious effects. One might, therefore, abort further discussion by noting that claims for the validity of anomalous flame temperatures are based on experimental evidence which is practically uninterpretable in a quantitative and convincing manner. This last statement is especially true for observations made at atmospheric pressure of the "inner cone" of flames, i.e., of the region in which strong temperature gradients exist.† At atmospheric pressure the thickness of the flame front may be no larger than the slit-width of the spectrograph. A significant improvement over this type of investigation has been registered by the low pressure flames of Gaydon and Wolfhard since, at low pressures, temperature gradients normal to the direction of observation can be minimized.

If we neglect, for the time being, the unhappy circumstance that we always observe regions of active combustion through cooler gas layers, there are, to begin with, discrepancies between the conclusions reached by different investigators. For example, Shuler¹⁰ quotes Dieke and Crosswhite as having shown that the "anomalous" intensity distributions of OH observed in some atmospheric pressure flames are principally the result of self-absorption. On the other hand, Gaydon,¹¹ in summarizing the available information on OH, speaks of effective rotational temperatures for OH around 5700°K at atmospheric pressure and still higher temperatures at very low pressures. The important pioneering work of Gaydon and Wolfhard on low pressure flames has been checked recently; however, the experimental conditions were such that the observed "anomalies" could be explained readily on the basis of self-absorption.²

Shuler,¹⁰ in quoting Broida's anomalous rotational temperatures in flames burning at atmospheric pressure, expresses the opinion that "corrections" for self-absorption can be made simply by measuring the intensity of absorption by the flame for continuous radiation. This argument is very weak, however, since absorption measurements for continuous radiation bear a close relation to self-absorption only if the experimental slit-width is small compared to the width of the spectral lines under study. This condition is probably not satisfied in Broida's work in spite of Broida's excellent spectrographic techniques.

The preceding discussion emphasizes the fact that there is at present no direct and unequivocal evidence for the existence of "anomalous" rotational or vibrational temperatures of OH in flames. On the other hand, indirect support for the existence of "anomalies" has been obtained, particularly by Gaydon and Wolfhard.¹ Nevertheless, in view of the ever-present problems arising from the existence of temperature gradients in the field of view and the equally unavoidable possibility for falsification of data as the result of self-absorption, the indirect and inferential evidence is never quite satisfying. Furthermore, even in the absence of analytical treatments on the combined effects of self-absorption and temperature gradients in producing distortions,

it is frequently possible to offer plausible explanations for observed data without the invention of "anomalous" rotational temperatures for OH. For example, a decrease in apparent population temperature from the base to the top of a flame may indicate either higher temperatures of OH or else higher concentrations of OH at the base of the flame.‡ Similarly, "normal" temperatures for OH in H₂-O₂ flames but "abnormal" temperatures in the same flames containing a trace of acetylene may indicate either chemiluminescence or else the *initial* production of large quantities of OH as the result of introduction of the acetylene. The calculations on the effect of self-absorption in conventional plots used for the determination of population temperatures in flames,⁶ have shown clearly that the apparent rotational temperatures are a very sensitive function of the absolute concentration of OH. Hence, even a relatively small excess of OH at the base of a flame could be responsible for a relatively high value of the population temperature. Perhaps the strongest case for the reality of the "anomalies" can be made on the basis of the increase in rotational temperature with a decrease of pressure. But even this result is not unambiguous without a careful quantitative study of the optical system, of changes in the field of view and of temperature gradients with pressure, etc. Although we have no objections, in principle, against "anomalous" temperatures and no prejudice other than that we believe that "anomalies" should be established beyond any reasonable doubt, it is our considered opinion that the available experimental evidence in support of abnormal rotation or vibration of OH in the ²Σ state in flames is not overwhelming.

* Supported by the ONR under Contract Nonr-220(03), NR 015 210.

† No criticism is intended of the valuable work on species identification or basic spectroscopy in which the flame functions only as a means for obtaining suitable conditions for observation of spectra.

‡ Absorption data obtained by Gaydon and Wolfhard show the converse behavior (see reference 1). However, these absorption measurements were performed under such conditions that no quantitative conclusions can be derived from them. The rotational half-width of OH at a pressure of a few mm of Hg must be far less than a few tenths of a wave number. The very important work by Gaydon and Wolfhard on the use of a Fabry-Perot interferometer to obtain line contours for CH suggests that in low pressure flame the spectral lines exhibit a Doppler contour, which is in accord with expectations.

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⁵ K. E. Shuler, J. Chem. Phys. **18**, 1466 (1950).

⁶ S. S. Penner, Technical Report No. 5, Contract Nonr-220(03), NR 015 210, April 1952; for a summary of this work see J. Chem. Phys. **20**, 1334 (1952).

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⁸ S. S. Penner, J. Chem. Phys. **20**, 507 (1952).

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Ionic Hydration: An Isotopic Fractionation Technique*

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(Received May 27, 1952)

THE determination of ionic hydration is beset with semantic and experimental difficulties.¹ Following Redlich's discussion² of molecules *versus* ion pairs, we propose to regard ionic hydrates, A(H₂O)_n[±], as existing as definite species in solution if, and only if, characteristic internal vibrations can be detected by spectral or other effects. It has been shown³ that ions may cause appreciable fractionation of the oxygen isotopes in the water in which they are dissolved. We wish to present some preliminary results indicating the connection between this effect and ionic hydration.