

maining coordinates remain at zero or if all the cross-terms of the dissociation energy matrix ( $D_{ij}$ ) are zero. Equation (9) can be written

$$D_k = D_{kk} + 2 \sum_j \alpha_j D_{kj}. \quad (10)$$

Assuming the  $\bar{D}_j$ 's positive, the  $\alpha_j$ 's will also be positive. Hence if  $D_{kk}$  is taken as the "pure" dissociation energy, then the observed value  $D_k$  will be greater or less than  $D_{kk}$  according as  $\sum_j \alpha_j D_{kj}$  is positive or negative. The  $D_{ij}$  can be expressed in terms of the  $d_{ij}$  by Eq. (6), giving an immediate relation between the dissociation energy of a bond and interaction constants involving it with other stretching coordinates in the potential function. Often, one interaction may be of over-riding importance; for a single interaction

$$D_k = D_{kk} + 2\alpha_j D_{kj} \\ = D_{kk} + 2[(D_{kk}D_{jj})/(d_{kk}d_{jj})]d_{kj}, \quad (11)$$

where  $\alpha_j$  is assumed of order unity (the treatment is of course only approximate). It may be noted that a relative strengthening of a linkage in a given molecule should be associated with a positive stretching-stretching interaction constant; there is some evidence for this. (See, for example, Duchesne, reference 1.)

<sup>1</sup> J. Duchesne, Acad. Roy. Belg. Classe sci. **26**, 1-44 (1952).

## The Possibility of a Theoretical Calculation of the Critical Temperature

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IN order to calculate theoretically the critical temperature of a substance we accept the following hypothesis.

The critical point of a substance arises from the fact that at the critical temperature ( $T_c$ ) the average kinetic energy ( $K_c$ ) is equal to the average (negative) potential energy ( $U_c$ ).

From this hypothesis we obtain the relation

$$3/2RT_c = -U_c \quad \text{or} \quad T_c = -2/3RU_c.$$

It is difficult to calculate exactly the value of  $U_c$ ; therefore we try to make some rather crude estimates for the case of the inert gases.

According to London<sup>1</sup> for nonpolar atoms and molecules  $U$  is proportional to  $\alpha^2 I/r^6$ ;  $r^2$  is of course proportional to  $V_c$ . Using these formulas we see that the quotient  $Q = V_c T_c / \alpha^2 I$  must be a constant. It will be noted that  $Q$  is reasonably constant, except of course for helium. (Helium is "blown up" by its quantum-mechanical zero point energy.)

It is possible to deduce from the Lennard-Jones potential for the crystal energy  $E$  that the attractive potential energy, when a state of equilibrium has been reached, is equal to twice the repulsive (Born) energy; viz.,  $E = -A/r^6 + B/r^{12}$  and  $(dE/dr)_{eq} = 0$  gives for the state of equilibrium

$$E_{eq} = -(A/r_{eq}^6)(1 - \frac{1}{2}) \quad \text{or} \quad U_{eq} = 2E_{eq}.$$

( $E_{eq}$  is equal to the sublimation energy.)

The critical volume  $V_c$  is about three times the volume of the solid  $V_0$ . One obtains for  $U_c$ :  $U_c = (V_0/V_c)^2 U_{eq}$ . (At the critical temperature the repulsive energy is about one percent of the total potential energy and can therefore be neglected.)

For  $T_c$  we get  $T_c = -2/3R(V_0/V_c)^2 U_{eq}$  or substituting the values for  $V_0/V_c$ ,  $R$  and  $U_{eq}$ :  $T_c = (2/27)E_{eq}$ . This relation was already known empirically.<sup>1</sup> The results are given in Table I.

In principle it is possible to deduce  $U_c = -A/r^6 - B/r^{12}$  from the known values for polarizabilities, ionization energies, and diamagnetic susceptibilities using the formulas of London or Slater and Kirkwood. From the mere existence of a number of

TABLE I.<sup>a</sup>

|       | $T_c(\text{exp})$<br>°K | $T_c(\text{calc})$<br>°K | $V_c(\text{exp})$<br>cm <sup>3</sup> /mol | $Q$<br>arbr. un. | $-E$<br>cal/mol     | $-U_c$<br>cal/mol   | $r$<br>cryst. A | $r$<br>calc A |
|-------|-------------------------|--------------------------|---|------------------|---------------------|---------------------|-----------------|---------------|
| 2 He  | 5.2                     | ...                      | 57.8                                      | 17.4             | ...                 | ...                 | 1.79            | 1.66          |
| 10 Ne | 44.4                    | 43.7                     | 41.7                                      | 26.4             | 590                 | 131                 | 1.60            | 1.48          |
| 18 Ar | 150.7                   | 150.3                    | 75.3                                      | 24.3             | 2030                | 451                 | 1.91            | 1.81          |
| 36 Kr | 209.4                   | 207.3                    | 92.1                                      | 25.7             | 2800                | 622                 | 1.97            | 1.93          |
| 54 Xe | 289.7                   | 289.0                    | 113.8                                     | 25.6             | 3900 <sup>b</sup>   | 867                 | 2.18            | 2.08          |
| 86 Rn | 377.6                   | ...                      | 145 <sup>c</sup>                          | (25.6)           | (5100) <sup>d</sup> | (1134) <sup>d</sup> | ...             | 2.26          |

<sup>a</sup> The numerical values have been mainly taken from reference 1 and N. V. Sidgwick, *The Chemical Elements and Their Compounds* (Clarendon Press, Oxford, 1950).

<sup>b</sup> Less accurate value.

<sup>c</sup> Calculated using 25.6 for  $Q$ .

<sup>d</sup> Calculated using  $T_c(\text{exp})$ .

formulas for the attractive energy the conclusion can be drawn that there remains a considerable degree of uncertainty in the calculated value of  $U$ .

By making a number of more or less arbitrary assumptions (coordination number, distances, powers of  $r$  included) it is possible to obtain the right, however, not a scientific, result. The virial theorem gives the relation  $Z = 3PV - 2K$ ;  $Z$  is the virial of the intermolecular forces. In classical statistics  $K = (3/2)RT$ . For  $Z$  Lorentz<sup>2</sup> and Boltzmann<sup>3</sup> have obtained the expression  $Z = 3U + 8K(V_a/V)$ .  $V_a$  is the total volume of the atoms (molecules). If  $a$  is the radius of the atom,  $V_a = 4/3\pi Na^3$ . At the critical point  $K_c = -U_c$ ; therefore we may write  $P_c V_c = RT_c [(4V_a/V_c) - \frac{1}{2}]$  or  $P_c = -(2/3)(U_c/V_c)[(4V_a/V_c) - \frac{1}{2}]$ . From a given value of  $V_c$  it is therefore possible to deduce theoretically  $T_c$  as well as  $P_c$ . We use this relation to compute a value for the radii of the atoms of the inert gases, taking the average value 0.292 for the critical coefficient  $P_c V_c / RT_c$ . Taking into account the fact that the radius of an atom is not a well-defined quantity the agreement between the computed value (eight column) and the value from x-ray analysis (seventh column) is satisfactory. This agreement is, however, not a good proof of the hypothesis, for the radius is very insensitive for changes in the value of the critical coefficient.

<sup>1</sup> F. London, Z. phys. Chem. **B11**, 222 (1931).

<sup>2</sup> H. A. Lorentz, Wied. Ann. **12**, 127, 660 (1881).

<sup>3</sup> L. Boltzmann, *Gastheorie* (1898), p. 149.

## On the Validity of Anomalous Population Temperatures in Flames\*

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IT should be obvious to anyone reading our recent papers objectively that our "principal thesis" was (a) to examine the origin of the basic relations involved in the customary procedure for the determination of population temperatures in flames, with emphasis on the effect of spectral line shape on the final equations,<sup>1</sup> and (b) to present experimental data on low pressure combustion flames<sup>2</sup> which support the earlier experimental findings of Gaydon and Wolfhard.<sup>3</sup> We noted that the usual equations hold only if  $(P_r)_{\max} X \ll 1$ , and pointed out some time ago<sup>4</sup> that this condition is equivalent to the absence of self-absorption. Furthermore, contrary to Shuler's interpretation of our remarks,<sup>5</sup> use of the best available intensity data, namely, the data obtained by Oldenberg and Rieke,<sup>6</sup> led us to the conclusion that the condition  $(P_r)_{\max} X \ll 1$  is apparently not satisfied in representative low pressure combustion flames. We therefore arrived at the conclusion that anomalous population temperatures reported for low pressure combustion flames<sup>3</sup> may be the result of misinterpretation of experimental data.

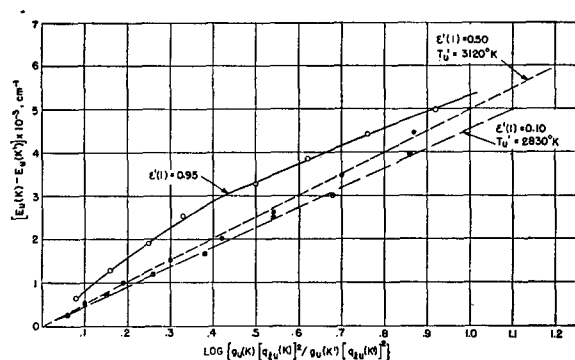


FIG. 1. Plot of  $[E_u(K) - E_u(K')] \text{ vs } \log \{g_u(K) [q_u(K)]^2 / g_u(K') [q_u(K')]^2\}$  for lines with equal total intensities at 3000°K as a function of  $\epsilon'(1)$  for the  $P_1$ -branch, (0,0)-band,  $2\Sigma \rightarrow 2\Pi$  transitions of OH.

Since we have done no experimental work on flames burning at atmospheric pressure, no reference was made to the attempts to correct for self-absorption in flames of this type. However, since Shuler<sup>5</sup> has furnished us with a résumé of what he considers to be important with regard to the study of flames burning at atmospheric pressure, it may be desirable if we indicate our position with regard to this work. First of all, we wish to call attention to the many important contributions made by Dieke and his collaborators to the development of valid techniques for the determination of population temperatures.<sup>7</sup> This work appears to have been done competently and with care. To the best of our knowledge, Dieke has not emphasized the occurrence of "anomalous" temperatures. We have not attempted investigations of flames burning at atmospheric pressure (1) because we were fortunate in having at our disposal the very excellent low pressure flame apparatus constructed by Gilbert,<sup>2</sup> and (2) because we did not feel in a position to carry out an unambiguous analysis of data obtained by examination of very narrow reaction zones, particularly if the field of view contains strong temperature gradients.

A straightforward quantitative study has been carried out recently<sup>8</sup> on the effect of self-absorption in an isothermal system at 3000°K on the observable experimental data by using the quantity

$$\epsilon'(1) = 1 - \exp(-P_{\max}X)$$

for the first line of the  $P_1$ -branch, (0,0)-band,  $2\Sigma \rightarrow 2\Pi$  transitions of OH, as a variable parameter. These detailed calculations lead to the conclusions enumerated below.

(1) Apparent population temperatures between 3000 and 19,000°K are obtained in conventional plots from the lines with  $9 \leq K \leq 18$  as  $\epsilon'(1)$  is varied from 0.1 to 0.99.

(2) Self-absorption must occur in absorption experiments for an isothermal system whenever it occurs in emission experiments since the spectral emissivities and absorptivities are identical. Nevertheless, it appears to be possible to correlate the results of absorption experiments by conventional plots even under conditions in which self-absorption is not negligible. However, the temperatures calculated<sup>9</sup> from the slopes are not reliable.<sup>8</sup>

(3) As is implied by the work of Cowan and Dieke,<sup>7</sup> the iso-intensity method of Shuler<sup>10</sup> is not always a valid procedure, since the effects of self-absorption do not necessarily cancel in first order. This last statement is amplified by the curves shown in Fig. 1, which were constructed according to Shuler's method.<sup>10</sup> Reference to Fig. 1 shows that the temperatures calculated from the slopes differ slightly from the known temperature of 3000°K for small values of  $\epsilon'(1)$  and that the curves become nonlinear for large values of  $\epsilon'(1)$ . The absolute intensity estimates obtained by Oldenberg and Rieke<sup>6</sup> are consistent with  $0.3 \leq \epsilon'(1) \leq 0.99$  for representative flames at 3000°K.

On the basis of our present knowledge of his work and the results of our calculations, we do not feel that we can accept

Shuler's "anomalous" vibrational temperatures<sup>11</sup> as valid experimental evidence without (1) convincing proof that all necessary corrections for temperature gradients in the field of view have been applied, preferably by use of the methods of Cowan and Dieke,<sup>7</sup> and (2) a quantitative demonstration, using the absolute intensity estimates of Oldenberg and Rieke,<sup>6</sup> that the effects of self-absorption do not produce significant distortion of the experimental data.

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<sup>1</sup> S. S. Penner, *J. Chem. Phys.* **20**, 507 (1952). It should be noted that, in general, peak intensity ratios are obtained if the instrumental slit width is small compared to the line width, whereas total intensity ratios are measured when the instrumental slit width is large compared to the line width.

<sup>2</sup> Penner, Gilbert, and Weber, *J. Chem. Phys.* **20**, 522 (1952); M. Gilbert, *Jet Propulsion Laboratory Report No. 4-54*, August, 1949.

<sup>3</sup> A. G. Gaydon and H. G. Wolfhard, *Proc. Roy. Soc. (London)* **194A**, 169 (1948), and later publications.

<sup>4</sup> S. S. Penner, Technical Report No. 2, Contract Nonr-220(03), NR 015 210, November 1951; Technical Report No. 4, February, 1952.

<sup>5</sup> K. E. Shuler, *J. Chem. Phys.* (to be published).

<sup>6</sup> O. Oldenberg and F. F. Rieke, *J. Chem. Phys.* **6**, 439 (1938); R. J. Dwyer and O. Oldenberg, *J. Chem. Phys.* **12**, 351 (1944). The numerical values of maximum absorption coefficients listed in Table II of reference 1 must be used in conjunction with optical densities  $X$  which represent the population of molecules in the lower energy level involved in a given energy transition.

<sup>7</sup> R. D. Cowan and G. H. Dieke, *Revs. Modern Phys.* **20**, 418 (1948); G. H. Dieke and H. M. Crosswhite, *Bumblebee Report No. 87*, November, 1948.

<sup>8</sup> S. S. Penner, Technical Report No. 5, April, 1952 (to be published).

<sup>9</sup> H. P. Broida, *J. Chem. Phys.* **19**, 1385 (1951).

<sup>10</sup> K. E. Shuler, *J. Chem. Phys.* **18**, 1466 (1950).

<sup>11</sup> H. P. Broida and K. E. Shuler, *J. Chem. Phys.* **20**, 168 (1952).

## On the Validity of Spectroscopic Temperature Determinations in Flames

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IT is the purpose of this note to call attention to the fact that some of the points raised recently by Penner<sup>1</sup> have been discussed in the literature several times previously. The conclusions reached by Penner as to the validity of some of the reported results of spectroscopic studies of flames should be considered in that context.

It is the principal thesis of Penner's papers<sup>1</sup> that the relations usually employed in the determination of "population temperatures" in flames from emission spectra are valid only if  $(P_\nu)_{\max}X \ll 1$ , i.e., if the product of the maximum value of the spectral absorption coefficient and the optical density of the emitter is much less than unity. This condition is equivalent to the requirement that the self-absorption of a given chemical species must be very small in order for accurate quantitative intensity measurements of emission lines to be feasible. This point has been discussed already by Cowan and Dieke<sup>2</sup> and Dieke and Crosswhite,<sup>3</sup> and the workers in the field of kinetic spectroscopy of flames are cognizant of the necessity of taking account of this self-absorption in the interpretation of their results.

For example, Dieke and Crosswhite<sup>4</sup> have shown that the "anomalous" intensity distributions of OH observed in some atmospheric pressure flames are principally due to self-absorption; when the appropriate intensity corrections are made on the basis of direct absorption measurements, the intensity distributions quite often become "normal" and lead to reasonable rotational flame temperatures. Broida<sup>5</sup> has used direct absorption measurements to correct for self-absorption in his OH emission study. The anomalous intensity distributions observed by him, after these corrections were made, thus cannot be attributed to an erroneous interpretation of experimental data due to lack of self-absorption corrections. The author<sup>6</sup> has used a modification of the iso-intensity method of Dieke and Crosswhite<sup>4</sup> in the analysis of his data on OH radicals. With this method, as has been pointed out repeatedly,<sup>3,6</sup> it is possible to avoid the complication introduced by