

The Partition Function of a Gas of Hard Elastic Spheres

O. K. Rice

Citation: [The Journal of Chemical Physics](#) **10**, 653 (1942); doi: 10.1063/1.1723636

View online: <http://dx.doi.org/10.1063/1.1723636>

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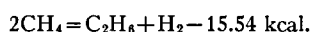
The Carbon-Carbon Bond Strengths in Ethane, Propane, and *n*-Butane

E. R. VAN ARTSDALEN

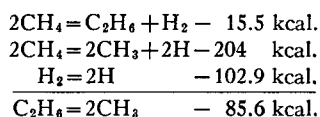
Department of Chemistry, Lafayette College, Easton, Pennsylvania
August 19, 1942

RECENTLY the carbon-hydrogen bond strengths in methane and ethane were determined from kinetic data by Andersen, Kistiakowsky, and Van Artsdalen¹ who gave values which agree very well with those obtained by Stevenson² from measurements of electron impact potentials. In the calculation of the carbon-hydrogen bond strengths the various energy relations were not corrected to absolute zero. When this is done, one finds that the CH₃-H bond strength, in round numbers, is 101 kcal. at 0°K, 102 kcal. at room temperature, as reported, and 103 kcal. at 450–475°K.

The heat of dissociation of carbon-hydrogen bonds may be combined with other established thermal data to calculate carbon-carbon bond strengths in several simple hydrocarbons. From thermal data tabulated by Rossini³ one obtains the following at 298.16°K:



This can be combined with the value of 102±1 kcal. for the strength of the CH₃-H bond and with the value for the heat of dissociation of hydrogen⁴ to obtain a value for the CH₃-CH₃ bond strength. Thus at 298.16°K

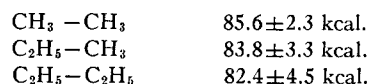


The probable error is ±2.3 kcal.

This value is in good agreement with that calculated by Stevenson.² Trenner, Morikawa, and Taylor⁵ obtained 97.6 kcal. employing their value of 108 kcal. for the CH₃-H bond strength. It seems certain that the carbon-carbon bond strength in ethane must be lower than the carbon-hydrogen bond strength in ethane (98±2 kcal.) to account for pyrolytic products. Rice and Johnston⁶ estimated from activation energies of free radical formation at high temperature a C-C bond of 74 kcal. Because chain decomposition appears to be less frequent than had

been thought, Kistiakowsky⁷ suggested that the true bond strength is higher than 74 kcal.

Similar calculations may be made to determine the carbon-carbon bond strength in propane and the center bond in normal butane. The necessary data (heats of formation of the hydrocarbons, C-H bond strengths in CH₄ and C₂H₆, and the heat of dissociation of H₂) are given in the above references. This method of calculating carbon-carbon bonds may be applied wherever the appropriate carbon-hydrogen bonds and heats of formation of the hydrocarbons are known. The following resumé of values for 298.16°K is obtained:



Lowering of the C-C bond strength with increasing chain length is observed in agreement with expectation. It is noted that a CH₂ increment lowers the bond strength about 1.5 kcal. However, qualitative rather than quantitative significance should be attached to this because of the rather large probable errors.

¹ Andersen, Kistiakowsky, and Van Artsdalen, *J. Chem. Phys.* **10**, 305 (1942).

² D. P. Stevenson, *J. Chem. Phys.* **10**, 291 (1942).

³ F. D. Rossini, *Chem. Rev.* **27**, 1 (1940).

⁴ Bichowsky and Rossini, *Thermochemistry* (Reinhold, 1936).

⁵ Trenner, Morikawa, and Taylor, *J. Chem. Phys.* **5**, 203 (1937).

⁶ Rice and Johnston, *J. Am. Chem. Soc.* **56**, 214 (1934).

⁷ G. B. Kistiakowsky, *J. Phys. Chem.* **41**, 175 (1937).

The Partition Function of a Gas of Hard Elastic Spheres

O. K. RICE

University of North Carolina, Chapel Hill, North Carolina
September 8, 1942

TONKS¹ has derived the equation of state of a one-dimensional gas consisting of *N* hard elastic spheres of radius *σ*, constrained to move along a line of length *l*. The partition function, found readily from his work, is

$$Q = [(2\pi mkT/h^2)^{1/2} e(l/N)(1-\theta)]^N, \quad (1)$$

where $\theta = N\sigma/l$. The factor e^N , occurring because the whole effective length $l(1-\theta)$ can be shared, gives rise to a "communal entropy" of Nk .

In three dimensions Tonks considers separately the dilute and the concentrated gas. For the former he uses an equation of state of the virial type, Eq. T(31). (T refers to Tonks' equations.) For the concentrated gas, Tonks obtains an equation of state, Eq. T(32), by an ingenious argument, which is equivalent to using as the partition function

$$Q = [(2\pi mkT/h^2)^{3/2} v^3 (1-\theta^3)]^{3N}, \quad (2)$$

essentially the cube of Eq. (1), with v^3 (v =volume per molecule) taking the place of l/N , and θ^3 replacing θ . In Eq. (2), $\theta = \sigma^3/2^3v$; thus the free volume $v(1-\theta^3)^3$ vanishes when the spheres are in contact in a face-centered cubic lattice. To bridge the gap between Eq. T(31) and Eq. T(32), Tonks gives an interpolation formula, Eq. T(33).

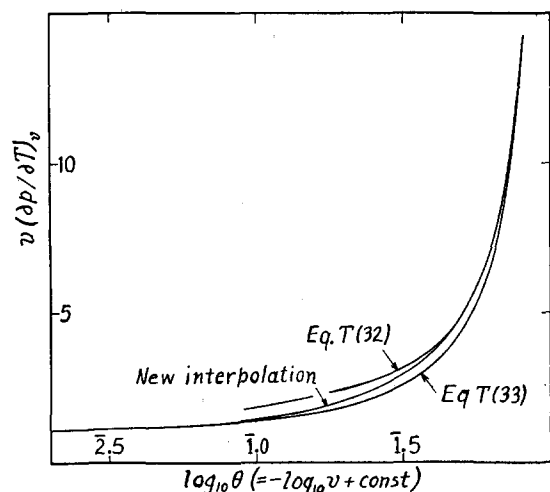


FIG. 1.

In Eq. (2) the factor e^{3N} corresponds to the large communal entropy $3kN$, because lengths are shared in the three directions of space, rather than volume being shared as such. That such a large communal entropy can exist does not seem to have been explicitly pointed out before, though it is implicit in an earlier note by the writer.² In the dilute gas, the communal entropy is only kN . Thus the change of entropy per mole from a small volume v_1 to a large volume v_2 will be

$$\Delta S = RT \ln [v_2/v_1(1-\theta^3)^3] - 2R. \quad (3)$$

ΔS can also be calculated by integrating the thermodynamic equation $v(\partial p/\partial T)_v = (\partial S/\partial \ln v)_T$, using Eq. T(33) (see Fig. 1). This gives a ΔS about 1 entropy unit smaller than does Eq. (3), despite the $-2R$ in the latter. A better interpolation is shown in Fig. 1; this assumes that Eq. (2) holds to somewhat lower values of θ than does use of Eq. T(33). The agreement that can thus be obtained shows the essential consistency of Tonks' ideas and seems to offer support to the correctness of the large communal entropy inherent in Eq. (2).

¹ L. Tonks, Phys. Rev. **50**, 955 (1936).

² O. K. Rice, J. Chem. Phys. **9**, 121 (1941).

The Partition Function of a Simple Liquid

O. K. RICE

University of North Carolina, Chapel Hill, North Carolina
September 8, 1942

IF we neglect the mutual potential energy of the atoms and consider only the thermal energy, a face-centered cubic solid bears a resemblance to a close-packed gas of hard spheres. We can get an effective value θ_0 for θ of Eq. (2) (preceding note) by equating Q to the thermal

part of the partition function for the solid, eT^3/Θ^3 (where Θ is the Debye characteristic temperature). Θ may be obtained as a function of interatomic distance, if the intermolecular potential energy is known.

This may be extended to the liquid, if we consider it to be formed from the solid by introduction of holes through removal of atoms; these holes then contribute to the free volume.¹ If there are N atoms and n holes, we write $\theta = \theta_0 N/(n+N)$, where θ_0 is the value for the solid with the same interatomic distance, obtained as in the preceding paragraph. We substitute θ into Eq. (2), noting also that the molecular volume has been increased by a factor $(n+N)/N$.

This procedure gives only that part of the partition function due to the thermal motion. We must consider, also, the energy necessary in order to produce a hole, already discussed in previous work.² But, in addition, in order that these holes should actually be used, it is necessary for the atoms to move past each other, with fluctuations in the distances between nearest neighbors. These fluctuations show up in the atomic distribution curves obtained from x-ray investigations, which show a broader band of nearest-neighbor distances than can be accounted for by thermal motion alone. This results in a further increase in the average potential energy, whose order of magnitude in the liquid can be estimated from the atomic distribution curves. In order that the holes should be effectively used, the increase in entropy gained therefrom must more than counterbalance the increase of energy due to both causes noted above.

These ideas have been applied to argon. In doing this the free energy is minimized using n/N as an additional parameter. The picture appears to work very well in explaining the properties of the liquid at the normal melting point. At 193°K, the theory makes the liquid appear to be too compressible. This seems to be due in large part to two causes. (1) The potential energy curve previously deduced³ and used in these calculations probably does not rise steeply enough at small distances. (2) It will be recognized that if a close-packed model gas of hard elastic spheres contains only a few holes, these holes cannot be used to increase the freedom of motion, since they are blocked off by surrounding spheres. As the number of holes increases, a point will rather suddenly be reached where they can be shared. In our model of a liquid, some similar effect will occur. This matter will be discussed in a fuller report, in the light of the data and the detailed calculations.

The entropy of the liquid obtained on this model agrees fairly well with that calculated by the method given in a previous note.¹ It is slightly smaller, which is perhaps in the wrong direction, but it increases somewhat more slowly with n/N , and in this respect appears to give a better indication of the behavior of the liquid.

¹ Compare O. K. Rice, J. Chem. Phys. **9**, 121 (1941).

² O. K. Rice, J. Chem. Phys. **7**, 883 (1939).

³ O. K. Rice, J. Am. Chem. Soc. **63**, 3 (1941).