

An Equation of State for Gases at High Pressures and Temperatures from the Hydrodynamic Theory of Detonation

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TABLE I.

Compound	Temperature T_w of line-width transition	Width ΔT of transition	Specific heat anomaly
NH ₄ Cl	133°K	16°	242.8°K
NH ₄ Br	108	16	235.2
NH ₄ I	< 95	—	230.7
NH ₄ IO ₃	120	7	—
NH ₄ CNS	100	20	—
NH ₄ NO ₃	< 95	—	212.8
(NH ₄) ₂ SO ₄	< 95	—	223.4

which the ammonium tetrahedra may be considered stationary. It has therefore been assumed in Table I that at sufficiently low temperatures the other ammonium salts will undergo similar line-width transitions.

It can be shown⁶ that the critical frequency above which relative nuclear motions should begin to narrow the absorption line is near the width, expressed as a frequency, of the broad line corresponding to the stationary nuclear configuration. We can account for the line width at temperatures just above the transition region by assuming hindered rotation or quantum-mechanical tunneling of the NH₄ tetrahedra at frequencies of the order of 100 kilocycles. Such a frequency will contribute negligibly to the specific heat.

The second-moment formula of Van Vleck has been used to investigate the nature of the rotation or tunneling of the ammonium tetrahedra above the line-width transition, and the results will be discussed in a more detailed account to be submitted to this journal.

In addition, the same theoretical considerations have been used in the interpretation of line-width transitions observed for the proton lines in a number of the simpler organic compounds. Also, the relation between the second-moment and interatomic distances in a stationary lattice has been used to determine molecular structure in several cases, including diborane, for which the experimental data support the ethylene-bridge structure. Reports of these experiments and findings are also in preparation.

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¹ G. E. Pake and H. S. Gutowsky, *Phys. Rev.* **74**, 979 (1948).

² F. Bitter and co-workers [*Phys. Rev.* **71**, 738 (1947)] have reported a qualitative observation that the proton line in NH₄Cl is slightly broader at low temperatures than at room temperature, but is consistently broad as is characteristic of normal solids.

³ G. E. Pake and E. M. Purcell, *Phys. Rev.* **74**, 1184 (1948).

⁴ J. H. Van Vleck, *Phys. Rev.* **74**, 1168 (1948).

⁵ N. Bloembergen, E. M. Purcell, and R. V. Pound [*Phys. Rev.* **73**, 679 (1948)] give, on page 704, the general nature of the relation.

An Equation of State for Gases at High Pressures and Temperatures from the Hydrodynamic Theory of Detonation

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September 13, 1948

IN regard to the criticisms of my paper^{1,2} by Dr. Stewart Paterson^{3,4} I find, after looking more carefully into my method (a) solution of the equations of the hydrodynamic theory, that Dr. Paterson is correct in pointing out that

method (a) is an unsatisfactory solution. In carrying out the solutions by method (a), I was including, rather naively, a step which had been introduced as a convenient short cut in earlier studies by method (b) which, although I failed to realize it, actually did depend on the nature of the solutions of method (b). The data reported in my paper,¹ while calculated by the procedure in question (although not as described in reference 1) are actually identical with those which would be obtained by the direct application of method (b). The slight difference between the two curves of Fig. 1 of my paper was due to the use of slightly different detonation velocities. This was, in fact, mentioned in the paper of reference 1. As far as I am concerned, Dr. Paterson and I are now in agreement on all essential points of discussion. As a matter of fact, the recent work of Paterson⁵ together with the arguments in reference 1, I believe, present strong evidence for the validity of the equation of state

$$pv = nRT + \alpha(v)p$$

for gases under the conditions encountered in the detonation of solid and liquid explosives.

¹ Melvin A. Cook, *J. Chem. Phys.* **15**, 518 (1947).

² Melvin A. Cook, *J. Chem. Phys.* **16**, 554 (1948).

³ Stewart Paterson, *J. Chem. Phys.* **16**, 159 (1948).

⁴ Stewart Paterson, *J. Chem. Phys.* **16**, 847 (1948).

⁵ Stewart Paterson, *Research* **1**, 221 (1948).

The Vapor Pressure and Melting Point of Graphite

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September 24, 1948

IN a letter to this Journal, L. H. Long has listed four types of experimental data which he believes will not admit a value of 170 kilocalories for the heat of sublimation of graphite. Careful examination of these data indicate that they are not capable of contradicting a heat of sublimation of 170 kilocalories, an atmospheric sublimation point of around 4600°K, or a melting point of over 5000°K.

(i) At temperatures above 3400°K where the carbon partial pressure is above 1 mm, the smoke due to carbon gas condensing in the cooler portions of an apparatus invalidates direct observations of the temperature by an optical pyrometer. Thus the temperatures given by Ribaud and Begue,¹ Basset,² and others who have worked in this high temperature range are much too low. In addition, their degassing procedures were poor. Both these effects produce results which make carbon seem more volatile than it really is.

(ii) Long lists various values for the melting point of carbon. However, Steinle³ has clearly shown that these previous workers had not actually reached the melting point. The pressure work of Basset² and Steinle³ show that the triple point of carbon occurs above 100 atmospheres. From the vapor pressures given by Brewer, Gilles, and Jenkins,⁴ this must mean that carbon melts above 5000°K.

Carbon can be melted in contact with tantalum carbide at temperatures above 3300°C, but this is due to the eutec-

tic between C and TaC as shown by Ellinger.⁵ A melting point over 5000°K for carbon is consistent with Steinle's work which showed that there was a large temperature gradient from the interior of the carbon rods, where melting took place, to the exterior where a lower temperature was read.

(iii) At 4000°K, the partial pressure of carbon is almost 0.1 atmosphere which should be sufficient to maintain an arc.

(iv) The work of Mott⁶ only demonstrates that carbon is more volatile than tungsten. This is consistent with the boiling point of around 6000°K for tungsten which is given by Kelley.⁷ The volatilization which limited the thin carbon tube used by Brewer, Gilles, and Jenkins⁴ to a top temperature of 3000°K is consistent with the partial pressure of around 0.03 mm. As a result of faster vaporization from the hottest sections, these sections become thinner, which increases the electrical resistance and thus increases the temperature of these hot rings still further. Thus temperatures above 3000°K are reached, and these hot rings lose carbon rapidly enough to cause breaking of the tube at the weak ring which results after loss of a fraction of a mm thickness of carbon. These results are quite consistent with the vapor pressures given by Brewer, Gilles, and Jenkins.

The data discussed above and other data which present direct evidence on the vapor pressure of graphite have been carefully examined, and no experiments have been found that are capable of excluding 170 kilocalories as the heat of sublimation of graphite.

¹ G. Ribaud and J. Begue, *Comptes Rendus* **221**, 73 (1945).

² J. Basset, *Brennstoff-Chemie* **23**, 127 (1942).

³ H. Steinle, *Zeits. f. angew. Mineral.* **2**, 28, 344 (1940).

⁴ L. Brewer, P. W. Gilles, and F. A. Jenkins, *J. Chem. Phys.* **16**, 797 (1948).

⁵ F. H. Ellinger, *Trans. Am. Soc. Metals* **31**, 89 (1943).

⁶ W. R. Mott, *Trans. Am. Electrochem. Soc.* **34**, 255 (1918).

⁷ K. K. Kelley, *Bur. of Mines Bull.* **383** (1935).

Notes on the Properties of Synthetic Rutile Single Crystals

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July 19, 1948

THE synthesis of large single crystals of rutile by the Titanium Division, National Lead Company, was announced recently.¹ It appears desirable to call attention to the exceptionally high dielectric constants which can be obtained in these crystals by proper treatment.

The color of the crystals is opaque black after they come from the furnace. This opaque black color can be changed gradually to transparent blue and finally to yellow by treatment in an oxygen atmosphere at 1000°C. The color differences presumably are related to the titanium/oxygen ratio; the yellow variety corresponds to Ti/O value of $\frac{1}{2}$. A reversal of the color changes can be effected by treatment in hydrogen at 600° to 800°C.

In order to determine the effect on the electrical properties caused by varying oxygen proportions in the lattice of rutile, a series of dielectric constant and resistivity measurements were made on the single crystal material.

A General Radio 716B capacity bridge was used with a simple crystal holder to measure the dielectric constant. The bridge was driven by a 1000-cycle oscillator, and all values of the dielectric constant are 1000-cycle values.

The resistivity of the specimens was measured using the voltage-current method. For the high resistivities an electrometer and high voltage supply were used; for the low resistivities a simple ohmmeter sufficed.

An oriented sample, 0.26×0.155×0.185 cm, in the completely oxidized condition was measured in the three principal crystallographic directions with the following results:

Crystallographic direction	Dielectric constant
X	89
Y	92
Z	180

Two unoriented rectangular samples, 0.6×0.8×0.25 cm and 0.9×0.5×0.19 cm, were completely oxidized and then subjected to a series of treatments in hydrogen for short periods. Measurements of the dielectric constant and resistivity were made after each reduction treatment. Typical data are given in Table I.

TABLE I.

Reduction exposure	Temp. °C	Time of treatment	Color	Dielectric constant	Resistivity (ohm cm)
First	600	5 min.	faint blue	2.34×10^4	4.73×10^5
Second	600	5 min.	faint blue	3.01×10^4	7.12×10^5
Third	600	5 min.	faint blue	2.22×10^4	9.5×10^5
Sixth	600	5 min.	faint blue	1.79×10^4	9.5×10^5

Subsequent treatment at 800°C for 30 minutes yielded a material of metallic luster having a blue color but also opaque when resistivity was low. The dielectric constants for the principal directions in the crystal initially increase proportionally upon reduction, but finally approach a common value in the well reduced material. The properties of the black original furnace material are apparently identical with the well reduced blue material. (Exploratory experiments show that the reduced material is not ferroelectric.)

A reasonable explanation of the observed effects might be based on the idea that the reduced material can be regarded as an irregular sandwich of a conducting surface region and a dielectric interior with indefinite boundaries. In this case the existence of a space charge polarization would account for the major portion of the observed change in properties.² Such regions could also account for the variation of the dielectric constant and resistivity of the basal plane.

These data are preliminary in character, but are considered of sufficient novelty to be presented pending a more thorough study of the electrical and photo-conductive properties.

¹ Science News Letter, October 1947.

² Table of Dielectric Materials, Report V, Contract OEMar-191 NDRC, Laboratory for Insulation Research, MIT, p. 18 (1944).