

The Heat Capacity of Methane

D. S. Villars and G. Schultze (Phys. Rev. **38**, 998 (1931)) have recently published a paper on the rotational heat capacity of methane gas. By applying the results of Hund and Elert, they obtained the *a priori* probabilities of the rotational states and the series expression for $Q = \sum_i P_i e^{-\epsilon_{ri}/kT}$. According to Villars and Schultze, symmetry and nuclear spin result in the existence of three non-combining types of methane, quintet, triplet and singlet. They have calculated rotational heat capacities for each of the three varieties; for the metastable mixture of 5/16 quintet, 9/16 triplet and 2/16 singlet, and for the equilibrium mixture. The heat capacity of the metastable mixture is that of what we might call "ordinary" methane, while the equilibrium heat capacity is that which would obtain in the presence of some hypothetical catalyst. The results of Villars and Schultze indicate that the rotational heat capacity of methane reaches a maximum around 50°K and then falls off to about 0.6 R at 175°, where it is apparently still decreasing. This result was very surprising, since it seemed to us that the equipartition value of $3/2 R$ should have been

equation equally well at the boiling point and at room temperature led us to recalculate the results of Villars and Schultze.

Assuming methane to be a regular rigid tetrahedron, the rotational energy levels are given by the equation:

$$E_r = \frac{h^2}{8\pi^2 I} j(j+1).$$

From the definition, $\sigma = h^2/8\pi^2 I kT$, we have the following expression for the rotational heat capacity:

$$C_r = \sigma^2 \frac{d^2 \ln Q}{d\sigma^2} = \sigma^2 \left[Q \frac{d^2 Q}{d\sigma^2} = \left(\frac{dQ}{d\sigma} \right)^2 \right].$$

For I , the moment of inertia, we have used the Raman value, 5.17×10^{-40} gm cm² (Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929)), which was also used by Villars and Schultze. We have used the same *a priori* probabilities as those given by Villars and Schultze.

An evaluation of Q , $(dQ/d\sigma)$, $(d^2Q/d\sigma^2)$ by summing, and substitution in the above equation for C_r , gives the results in Table I, and

TABLE I. Rotational heat capacity of methane.

$T^\circ\text{K}$	Quintet C_r/R	Triplet C_r/R	Singlet C_r/R	Equilibrium C_r/R	5/16 Quintet 9/16 Triplet 2/16 Singlet C_r/R
3.84	0	0.035	0	0.499	0.020
7.68	0.006	0.481	0.003	0.941	0.290
12.80	0.276	0.981	0.030	1.347	0.642
19.20	1.354	1.328	0.219	1.733	1.198
25.60	2.255	1.457	0.537	1.838	1.592
30.72	2.432	1.487	0.794	1.798	1.696
38.40	2.198	1.498	1.101	1.688	1.667
43.89	1.971	1.499	1.250	1.621	1.615
51.20	1.747	1.500	1.374	1.563	1.561
61.44	1.589	1.500	1.456	1.527	1.527
76.80	1.516	1.500	1.492	1.504	1.504
153.60	1.500	1.500	1.500	1.500	1.500

reached by this temperature. If their results were correct, the experimental value of the entropy of methane at 298.1° would be considerably in error, since it has been obtained from the third law value at the boiling point by assuming the rotational heat capacity of the gas to be $3/2 R$ from the latter temperature to 298.1°K.

The fact that the experimental entropy agrees with that calculated from the Tetrode

those plotted in Figs. 1 and 2. In Fig. 1, the three curves represent the heat capacity of the three kinds of methane, while in Fig. 2, the two curves are for the equilibrium mixture and the metastable frozen mixture. Above the temperature range of the plots, the heat capacity curves are virtually straight lines, coincident with $C_r/R=1.5$.

Our results differ considerably from those of Villars and Schultze. Below 40°, the two

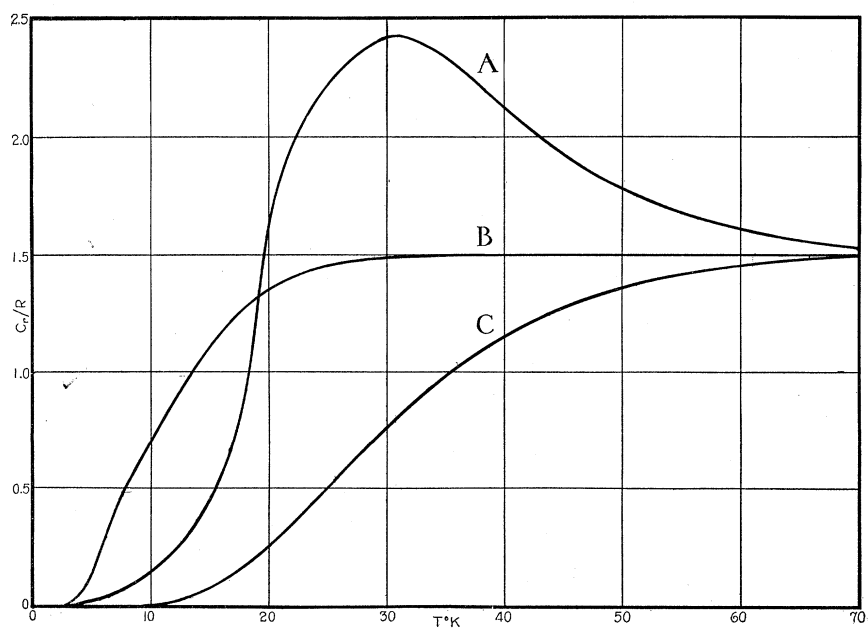


Fig. 1. Rotational heat capacities of methane. *A*, quintet. *B*, triplet. *C*, singlet.

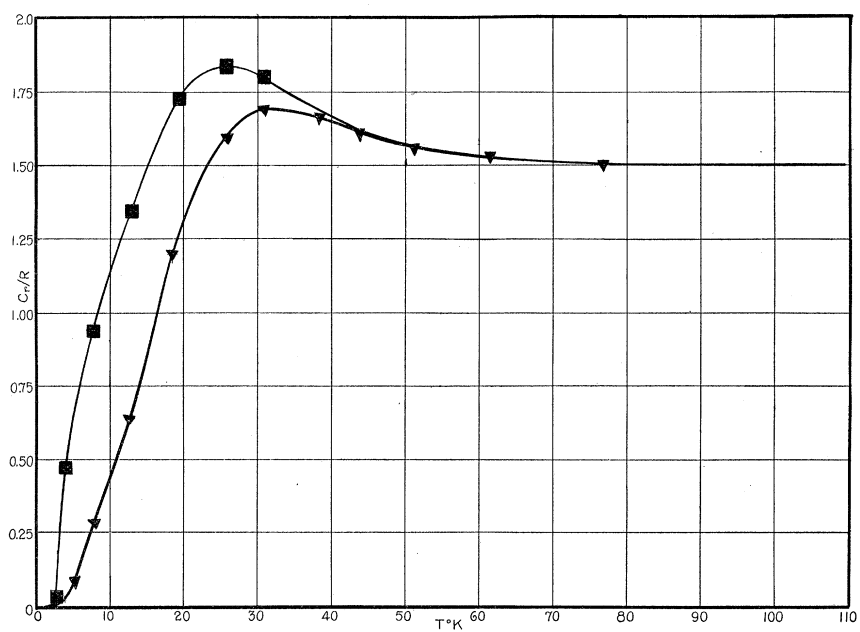


Fig. 2. Rotational heat capacities of methane. Squares, equilibrium. Triangles, frozen.

sets of results agree fairly well, except for the case of the equilibrium mixture, but at higher temperatures the difference is very marked. As may be seen from Fig. 2, according to our calculations, the heat capacity after reaching a maximum, descends asymptotically toward the equipartition value, which it reaches, within a few thousandths of a calorie, at a temperature of 100°K. We have been unable to discover the source of the large deviation, but suspect it lies in the evaluation of the sums involved.

For the sake of completeness, we have calculated the vibrational heat capacity at room temperature. Use is made of the same equation as in rotation, namely $C/R = (\sigma^2 d^2 \ln Q / d\sigma^2)$, but in this case we substitute vibrational energies in the expression for Q . With the

frequency assignments of Dennison (D. M. Dennison, *Astrophys. J.* **62**, 84 (1925)) and assuming simple harmonic motion, we obtain $C_v^{(298.1)}/R = 0.296$. For the heat capacity of methane at room temperature, therefore, we have $3/2 R$ for translation, $3/2 R$ for rotation, R for $C_p - C_v$ and $0.296 R$ for vibration. Thus

$$C_p^{298.1} = 8.54 \text{ cal. mole}^{-1}.$$

The International Critical Tables gives $C_p = 8.47$ at 15°C, and at this temperature our calculated value would be 8.45.

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An Estimation of the Spectrum of the Element of Atomic Number 87

During the past two years I have been examining the optical spectra of mineral concentrates in an effort to identify the *raies ultimes* of the missing alkali element, eka-caesium. A comparison of alkali spectra shows that the principal series spectrum of this element will be characterized by a widely separated doublet in the red region, and a closer doublet in the violet. K. T. Bainbridge,¹ basing his computations on the similarity of the spectrum of Ra II with that of unionized eka-caesium, has estimated the wavelength of the $1^2S-2^2P_2$ line to be $7600 \pm 200\text{\AA}$, and that the component of lesser intensity, $1^2S-2^2P_1$, is further in the red at $8720 \pm 200\text{\AA}$. F. H. Loring² has made another estimate, based on Hick's equation for series spectra, which lead to values of 8061\AA for the $1^2S-2^2P_2$ line, and 4831\AA as the wave-length of the $1^2S-3^2P_2$ line. Both estimates of the $1^2S-2^2P_2$ line place it in a region of poor photographic sensitivity, indicating that for purposes of identification, the $1^2S-3^2P_2$ transition, though theoretically not the most persistent line in the spectrum of the element, will be more important than the true *raie ultime* in the red. As the approximated wave-lengths of the red line differ considerably from each other, corresponding doubt is placed on the estimate made by Loring of the wave-length of the line in the violet region. In general, a more exact knowledge of the position of the individual lines, together with independent estimates of the doublet separations, are desirable.

Unfortunately, the methods which led to the exact elucidation of the spectra of stripped atoms of the initial series of the periodic table are not applicable to the present case owing to the paucity of analyzed spectra in the 7th period. Spectral regularities in a group of elements, as observed by Ramage³ among the atomic weights of the alkalis, or by Hicks' for their atomic volumes,⁴ cannot be used for extrapolating the spectrum of eka-caesium because of a lack of generality in the correlations.

In an effort to estimate the spectrum of the missing alkali, I observed that for any spectral term T , in a periodic group of elements, the quantum defect Q , is roughly a linear function of the total quantum number n , of the valence electron. If Q is known, T can be calculated from the relationship: (1) $T = r^2 R / (n - Q)^2$, where R is the Rydberg constant and $r - 1$ is the degree of ionization of the atom. Though this relationship is not precise, it is singularly free from manifest exceptions (see Fig. 1). This generality has been tested and found to be true for the S , P , D , F , G and H levels of the neutral alkali atoms, the singlet and triplet S and P levels in the spectra of the

¹ K. T. Bainbridge, *Phys. Rev.* **34**, 752 (1929).

² F. H. Loring, *Chem. News* **140**, 178, 202, 242 (1930).

³ Ramage, *Proc. Roy. Soc.* **A70**, 1 (1902).

⁴ W. N. Hicks, *Proc. Roy. Soc.* **A83**, 226 (1910).