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LA-701

Series A

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THERMODYNAMIC FUNCTIONS FOR TRITIUM DEUTERIDE.

THE DISSOCIATION OF TRITIUM DEUTERIDE.

EQUILIBRIA AMONG THE ISOTOPIC HYDROGEN MOLECULES.

Work done by:	Report written by:
Bengt Carlson, Group Leader	W. M. Jones
Josephine Elliott	
Bertha Fagan	
Max Goldstein	
Margaret Johnson	
Nell Lane	

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ADDENDUM

Under "Work done by" on the title page of LA-701, the name of W. M. Jones has been omitted. The corrected form of the acknowledgement should read:

Work done by:

Bengt Carlson
Josephine Elliott
Bertha Fagan
Max Goldstein
Margaret Johnson
W. M. Jones
Nell Lane

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Abstract

The heat capacity, entropy, internal energy and free energy are calculated to 2500° K for tritium deuteride. The dissociation of tritium deuteride is considered. Equilibria of the isotopic hydrogens among themselves are calculated.

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Thermodynamic Functions for Tritium Deuteride.

The Dissociation of Tritium Deuteride.

Equilibria Among the Isotopic Hydrogen Molecules.

Accurate calculations of the thermodynamic properties of hydrogen have been carried out by Giauque[1] and similar calculations have been made for deuterium and deuterium hydride by Johnston and Long.[2] Recently similar calculations have been made for tritium and tritium hydride.[3] In the present report similar data are given for tritium deuteride. Values refer to one mole of the ideal gas at one atmosphere.

The energy of the tritium deuteride molecule is representable in the form

$$E_{J,\nu} = \omega_e(v+\tfrac{1}{2}) - X_e\,\omega_e(v+\tfrac{1}{2})^2 + \left[B_e - \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2 + \delta_e(v+\tfrac{1}{2})^3\right] J(J+1) + \left[D_e + \beta_e(v+\tfrac{1}{2})\right] J^2(J+1)^2 + F_e J^3(J+1)^3 \qquad (1)$$

The constants are listed in Table I. They were computed from the data for ordinary hydrogen, as given by Jeppeson[4], who expresses the energy in a form slightly different from Eq. (1), through the theory of isotopic diatomic molecules[5]. The

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[1] Giauque, J.A.C.S. 52, 4826 (1930); see also C. O. Davis and H. L. Johnston, J.A.C.S. 56, 1045 (1934).

[2] Johnston and Long, J. Chem. Phys. 2, 389, 710 (1934).

[3] LA-656. –

[4] Jeppeson, Phys. Rev. 44, 165 (1933).

[5] Jevons, Report on Band Spectra of Diatomic Molecules, Cambridge University Press (1932).

[redacted]

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partition function and its derivatives were evaluated by direct summation over rotational and vibrational states.

It is felt that in general the calculations are correct to the number of significant figures given, except perhaps at the highest temperatures where the large values of ν and, particularly, of J needed for the convergence of the summations lie outside the range employed by Jeppeson in fitting the constants of Eq. (1).

Table I

Molecular Constants for DT

ω_e	2853.8 cm^{-1}
$X_e \omega_e$	54.786
B_e	25.380
α_e	0.82641
γ_e	0.011908
$-\delta_e$	0.00073
$-D_e$	0.008093
β_e	0.1142×10^{-3}
F_e	0.37637×10^{-5}

The constants of Table I were calculated taking the atomic weights of deuterium and tritium to be 2.014722 and 3.017050 (physical scale).[6] The physical constants are otherwise

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[6] Mattauch, Phys. Rev., 57 1155 (1940); Livingston and Bethe, Rev. Mod. Phys. 9, 373 (1937).

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those of the International Critical Tables[7] in order that the present calculations may best be utilized with the large body of similar calculations now existing (see Appendix, however). The spin of the deuterium nucleus is unity and that of the tritium nucleus is one-half unit.[8]

Heat Capacity and Entropy

The heat capacity at constant pressure and the entropy for tritium deuteride are given in Table II. The entropy includes the nuclear spin contribution of Rln 6. Fig. 1 shows the internal portion of C_v/R at low temperatures for DT, HT, and HD[2,3].

Internal Energy and Free Energy

The internal energy and the free energy, both given with respect to the state in which $\nu = J = 0$, are presented in Table III. The internal energy does not include the translational contribution of 3/2 RT. The $-\left(\frac{F^o - E^o_0}{T}\right)$ tabulations include the nuclear spin contribution of Rln 6.

The values of S^o in Table II and the values of $-(F^o - E^o_0)/T$ in Table III must each be decreased numerically by Rln 6 = 3.560 when they are combined with similar data for other molecules which do not include the nuclear spin contribution. The neglect of spin is, however, a high temperature approximation, and it is not permissible in dealing with equilibria involving a molecular hydrogen below about 175°K.

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[7] International Critical Tables, McGraw-Hill Book Company (1926).

[8] Bloch, Packard, Graves and Spence, Phys. Rev. 71 373 (L), 551 (L) (1947).

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Table II

HEAT CAPACITY AND ENTROPY (INCLUDING NUCLEAR SPIN) OF TRITIUM DEUTERIDE IN CAL. DEG.$^{-1}$ MOLE.$^{-1}$

T, °K	C_p^o	S^o	T, °K	C_p^o	S^o
0	0.000	0.000	250	6.973	39.369
10	5.203	17.551	275	6.975	40.033
15	6.065	19.812	298.1	6.977	40.597
20	6.806	21.669	300	6.977	40.640
25	7.106	23.227	400	6.994	42.649
30	7.147	24.529	500	7.039	44.215
35	7.109	25.628	600	7.124	45.504
40	7.064	26.574	700	7.243	46.611
50	7.010	28.144	800	7.383	47.587
75	6.975	30.977	900	7.533	48.465
100	6.969	32.983	1000	7.682	49.268
125	6.968	34.538	1250	8.021	51.019
150	6.968	35.808	1500	8.296	52.507
175	6.969	36.883	2000	8.685	54.950
200	6.970	37.813	2500	8.943	56.917
225	6.972	38.634			

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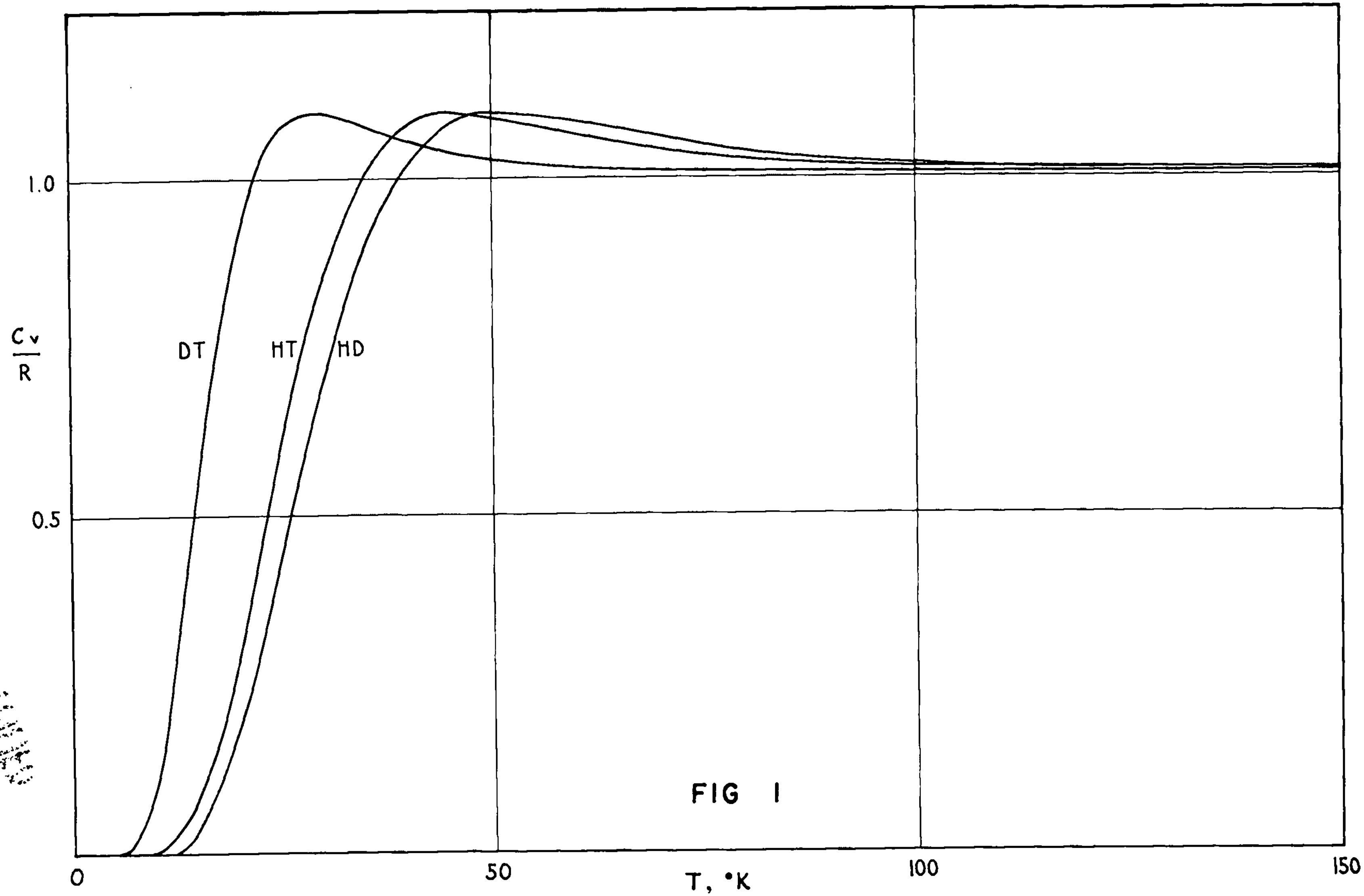

FIG 1

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Table III

INTERNAL ENERGY AND FREE ENERGY

T, °K	$E^o - E^o_o$ cal.mole^{-1}	$-\left(\frac{F^o - E^o_o}{T}\right)$ cal.deg^{-1}mole^{-1}	T, °K	$E^o - E^o_o$ cal.mole^{-1}	$-\left(\frac{F^o - E^o_o}{T}\right)$ cal.deg^{-1}mole^{-1}
10	.334	12.550	250	475.03	32.502
15	3.54	14.609	275	525.20	33.156
20	11.06	16.149	298.1	571.61	33.712
25	21.16	17.414	300	575.42	33.755
30	32.02	18.494	400	777.10	35.739
35	42.84	19.437	500	981,72	37.284
40	53.43	20.271	600	1192.8	38.549
50	74.09	21.695	700	1414.2	39.624
75	124.59	24.349	800	1648.7	40.559
100	174.70	26.269	900	1897.7	41.390
125	224.72	27.773	1000	2161.8	42.139
150	274.73	29.009	1250	2884.	43.744
175	324.76	30.059	1500	3683.	45.084
200	374.82	30.971	2000	5452.	47.257
225	424.91	31.778	2500	7379.	48.998

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THE DISSOCIATION OF TRITIUM DEUTERIDE

Values of $-\left(\frac{F^o - E^o_0}{T}\right)$ for DT, D, and T may be employed in the calculation of the dissociation constant K for the process $DT \rightleftharpoons D + T$ through the relationship

$$-R \ln K = \Delta\left(\frac{F^o - E^o_0}{T}\right) + \frac{\Delta E^o_0}{T} \qquad (2)$$

The values of $-\left(\frac{F^o - E^o_0}{T}\right)$ for D and T were taken from references 2 and 3, respectively. The quantity ΔE^o_0 is greater than $D_0(H_2)$ by the difference is the zero point energies of H_2 and DT, and has the value 104,970 ± 20 cal. This figure is based on the value 36,116 ± 6 $cm.^{-1}$ for $D_0(H_2)$[9] and the I.C.T. physical constants. The equilibrium constants are presented in Table IV along with the constants[1,2,3] for the dissociation of the other isotopic hydrogens.

The percentage dissociation at a total pressure of one atmosphere may be calculated from the equilibrium constant and is given in Table V along with similar data for the other hydrogens[1,2,3].

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[9] Beutler, Z. Physikal Chem. B29 315 (1935); Beutler & Jünger, Z. Physik 101, 304 (1936).

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Table IV

DISSOCIATION CONSTANTS FOR DISSOCIATION OF ISOTOPIC HYDROGEN MOLECULES IN ATMOSPHERES

T, °K	1000	1500	2000	2500
H_2	6.45×10^{-18}	3.60×10^{-10}	2.96×10^{-6}	6.92×10^{-4}
HD	2.48	1.57	1.36	3.28
D_2	3.71	2.70	2.49	6.17
HT	2.26	1.49	1.32	3.21
DT	1.67	1.28	1.21	3.03
T_2	3.01	2.44	2.35	5.94

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Table V

PERCENTAGE DISSOCIATION OF ISOTOPIC HYDROGEN MOLECULES AT A TOTAL PRESSURE OF ONE ATMOSPHERE

T, °K	1000	1500	2000	2500
H_2	12.7×10^{-8}	9.5×10^{-4}	8.6×10^{-2}	1.31
HD	7.9	6.3	5.8	0.91
D_2	9.6	8.2	7.8	1.24
HT	7.5	6.1	5.7	0.90
DT	6.5	5.7	5.5	0.87
T_2	8.7	7.8	7.7	1.22

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EQUILIBRIA AMONG THE ISOTOPIC HYDROGENS

From the tabulations of $-\left(\frac{F^{o}-E^{o}_{o}}{T}\right)$ and the zero point energies of the molecules involved, equilibrium constants may be evaluated from a relationship of the form of Eq. 2 for the following equilibria:

$$H_2 + T_2 = 2\,HT \tag{1}$$

$$D_2 + T_2 = 2\,DT \tag{2}$$

$$T_2 + HD = HT + DT \tag{3}$$

$$H_2 + DT = HD + HT \tag{4}$$

$$D_2 + HT = HD + DT \tag{5}$$

$$H_2 + D_2 = 2HD \tag{6}$$

The free energy functions for T-containing molecules are from LA-656 and this report, those of D_2 and HD from reference 2, while those for H_2 at and above room temperature are from reference 1. For values of the free-energy function for H_2 below room temperature the data used is that of Urey and Rittenberg[10], corrected to I.C.T. constants. The constants for (1) are from LA-656. It will be noted that these constants are not all independent and that $K_1 = K_3 K_4$, $K_6 = K_4 K_5$, and $K_2 = K_3 K_5$. Table VI gives the equilibrium constants as a function of temperature. The approach to the classical values of 4 or of 2 may be noted at high T.

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[10] Urey and Rittenberg,J. Chem. Phys 1, 137 (1933).

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Table VI

EQUILIBRIUM CONSTANTS FOR ISOTOPIC EQUILIBRIA

T, °K	K_1	K_2	K_3	K_4	K_5	K_6
2500	3.99	4.00	2.00	1.99	2.00	3.97
2000	3.98	4.00	2.00	1.99	2.00	3.97
1500	3.94	4.00	2.00	1.98	2.00	3.96
1250	3.90	4.00	1.99	1.96	2.01	3.94
1000	3.81	3.99	1.98	1.93	2.02	3.90
900	3.76	3.98	1.97	1.91	2.03	3.87
800	3.68	3.98	1.95	1.88	2.04	3.83
700	3.59	3.97	1.94	1.85	2.05	3.78
600	3.45	3.96	1.91	1.80	2.06	3.72
500	3.26	3.93	1.88	1.73	2.09	3.62
400	2.99	3.88	1.82	1.64	2.13	3.48
300	2.58	3.82	1.74	1.48	2.19	3.26
298.1	2.57	3.82	1.74	1.48	2.20	3.26
250	----	3.77	1.67	----	2.26	----
200	1.948	3.69	1.58	1.24	2.34	2.90
150	----	3.57	1.33	----	2.68	----
100	0.947	3.32	1.18	0.802	2.82	2.26
50	0.242	2.60	0.687	0.353	3.78	1.33
25	----	1.95	0.282	----	6.94	----

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Appendix

In the computation of thermodynamic functions from the spectroscopic energy levels, the latter are given in cm^{-1} and a conversion to calories is achieved by a factor, say β. Thus $Q = \sum p_i e^{-\beta\epsilon_i/RT} = \sum p_i e^{-\alpha\epsilon_i/T}$, where ϵ_i is in cm^{-1}. The factor α may be subject to small changes as more reliable values of the physical constants become available. It may be desired to put calculations, made originally for some value of α, on the basis of a new value. There are given below simple expressions giving the corrections ΔQ, $\Delta(E^o - E^o_0)$, ΔS^o, and $\Delta\left\{-\left(\frac{F^o - E^o_0}{T}\right)\right\}$ to be added algebraically to Q, $E^o - E^o_0$, S^o, and $-\left(\frac{F^o - E^o_0}{T}\right)$, corresponding to a change from α to $\alpha + \Delta\alpha$:

$$Q = \sum p_i e^{-\alpha\epsilon_i/RT}, \quad \frac{dQ}{d\alpha} = \frac{1}{\alpha RT} \sum p_i \alpha \epsilon_i e^{-\frac{\alpha\epsilon_i}{T}}$$

$$= -\frac{Q}{\alpha RT}(E^o - E^o_0)$$

or

$$\frac{\Delta Q}{Q} = -\frac{(E^o - E^o_0)}{RT} \cdot \frac{\Delta\alpha}{\alpha} \qquad (1)$$

Similarly

$$\Delta(E^o - E^o_0)/E^o - E^o_0 = \left[1 - \frac{C^o T}{E^o - E^o_0}\right] \frac{\Delta\alpha}{\alpha} \qquad (2)$$

$$\Delta S^o = -C^o \frac{\Delta\alpha}{\alpha} \qquad (3)$$

$$\Delta\left\{-\left(\frac{F^o - E^o_0}{T}\right)\right\} = -\left(\frac{E^o - E^o_0}{T}\right)\frac{\Delta\alpha}{\alpha} \qquad (4)$$

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The portions of the thermodynamic functions and their corrections referred to are those which correspond to the partition function in question. The functions corresponding to the original set of physical constants may be utilized in calculating the corrections, which are quite small. The correction to C^o may be found by graphical or numerical differentiation of $\Delta(E^o - E^o_0)$ with respect to T.

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