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THERMODYNAMIC FUNCTIONS FOR TRITIUM AND TRITIUM HYDRIDE. THE EQUILIBRIUM OF TRITIUM AND HYDROGEN WITH TRITIUM HYDRIDE. THE DISSOCIATION OF TRITIUM AND TRITIUM HYDRIDE.

Work done by:

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Report written by:

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ABSTRACT

The heat capacity, entropy, internal energy, and free energy are calculated to 2500° C. for tritium and tritium hydride. The distribution of tritium between the ortho and para states is considered. The equilibrium constant for the formation of tritium hydride from hydrogen and tritium is calculated from ~~298.1~~ 50 to 2500° K. The dissociation of tritium and tritium hydride into the atoms is discussed. The dissociation equilibria of hydrogen, deuterium, and deuterium hydride have been recalculated. The bearing of the radioactivity of tritium and tritium hydride on the attainment of thermodynamic equilibrium is briefly considered.

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Thermodynamic Functions For Tritium And Tritium Hydride. The Equilibrium of Tritium and Hydrogen With Tritium Hydride. The Dissociation of Tritium and Tritium Hydride.

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]. The present paper presents corresponding work for tritium and tritium hydride. The values refer to a mole of the ideal gas.

The general methods of such calculations are well known. In the present calculations partition functions and their derivatives have been calculated by direct summation over rotational and vibrational states. The energies of T_2 and HT are representable in the form.

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

The constants are listed in Table I. They were computed from the data for ordinary hydrogen as given by Jeppeson[3], who expresses the energy in a form slightly different from Eq. (1), through the theory of isotopic diatomic molecules[4]. The excellent agreement of the constants so calculated

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[1] Giauque, J. A. C. S. 52, 4826 (1930)

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

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TABLE I

MOLECULAR CONSTANTS OF T_2 AND HT

Constant	T_2 cm.$^{-1}$	HT cm.$^{-1}$
ω_e	3608.3	2553.8
$x_e \omega_e$	87.585	43.872
B_e	40.5747	20.3243
α_e	1.67048	0.59222
γ_e	0.030434	0.007636
$-\delta_e$	0.0024	0.00042
$-D_e$	0.02068	0.005190
β_e	0.369×10^{-3}	0.0655×10^{-3}
F_e	1.5378×10^{-5}	0.19328×10^{-5}

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with the observations of Jeppeson[5] in the case of HD lend confidence to the present procedure. The agreement in the case of D_2[2,6] is not quite so good. It is felt that, in general, the calculations are correct to the number of significant figures given except at the highest temperatures where the large values of v 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).

The constants in Table I were calculated taking the atomic weights (physical scale) of hydrogen and tritium to be 1.008130 and 3.017050[7]. The physical constants are otherwise those of the International Critical Tables[8] in order that these calculations may best be utilized in connection with the large body of similar calculations now existing. The experiments of Bloch, et al.[9] indicate the expected one-half unit of spin for the tritium nucleus.

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

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

[5] Jeppeson, Phys. Rev. 45, 480 (1934)

[6] Jeppeson, Phys. Rev. 49, 797 (1937)

[7] Mattauch, Phys. Rev. 57, 1155 (1940)

[8] International Critical Tables, Volume I, p. 16

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

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THE EQUILIBRIUM DISTRIBUTION OF MOLECULAR TRITIUM AMONG ORTHO AND PARA STATES

Like ordinary hydrogen, molecular tritium exists in ortho and para forms which occupy the odd and even rotational states, respectively, and which have the spin weights 3 and 1, respectively. The fraction of the molecules which is ortho attains the limiting value of 3/4 at moderate temperatures as may be seen from Table II and from Figure I. The limiting value is attained at lower temperatures than is the case for hydrogen and deuterium.

It is well known that both hydrogen and deuterium show a very slow attainment of ortho-para equilibrium in the absence of catalysts. It seems very likely that the radioactivity of tritium, giving rise to ionization, dissociation, and subsequent recombination, would provide an internal mechanism whereby pure tritium could attain ortho-para equilibrium at a much more rapid rate than pure hydrogen or deuterium. Assuming 10^3 bonds broken per disintegration and random recombination of fragments, the half-time for conversion by this mechanism should be of the order of a few days.

THE HEAT CAPACITY AND ENTROPY

The heat capacity at constant pressure of ortho, para, equilibrium, and normal tritium (room temperature ortho-para distribution) are given in Table III along with the corresponding total entropies which include the nuclear spin contribution of Rln4. Values are also given for HT. By 175°K. the four

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TABLE II

DISTRIBUTION OF MOLECULAR TRITIUM AMONG ORTHO AND PARA STATES

T, °K	% ortho	T, °K	% ortho
0	0.000	40	66.843
10	2.848	50	71.294
15	16.509	75	74.480
20	33.912	100	74.928
25	47.533	125	74.990
30	56.762	150	74.998
35	62.836	175	75.000

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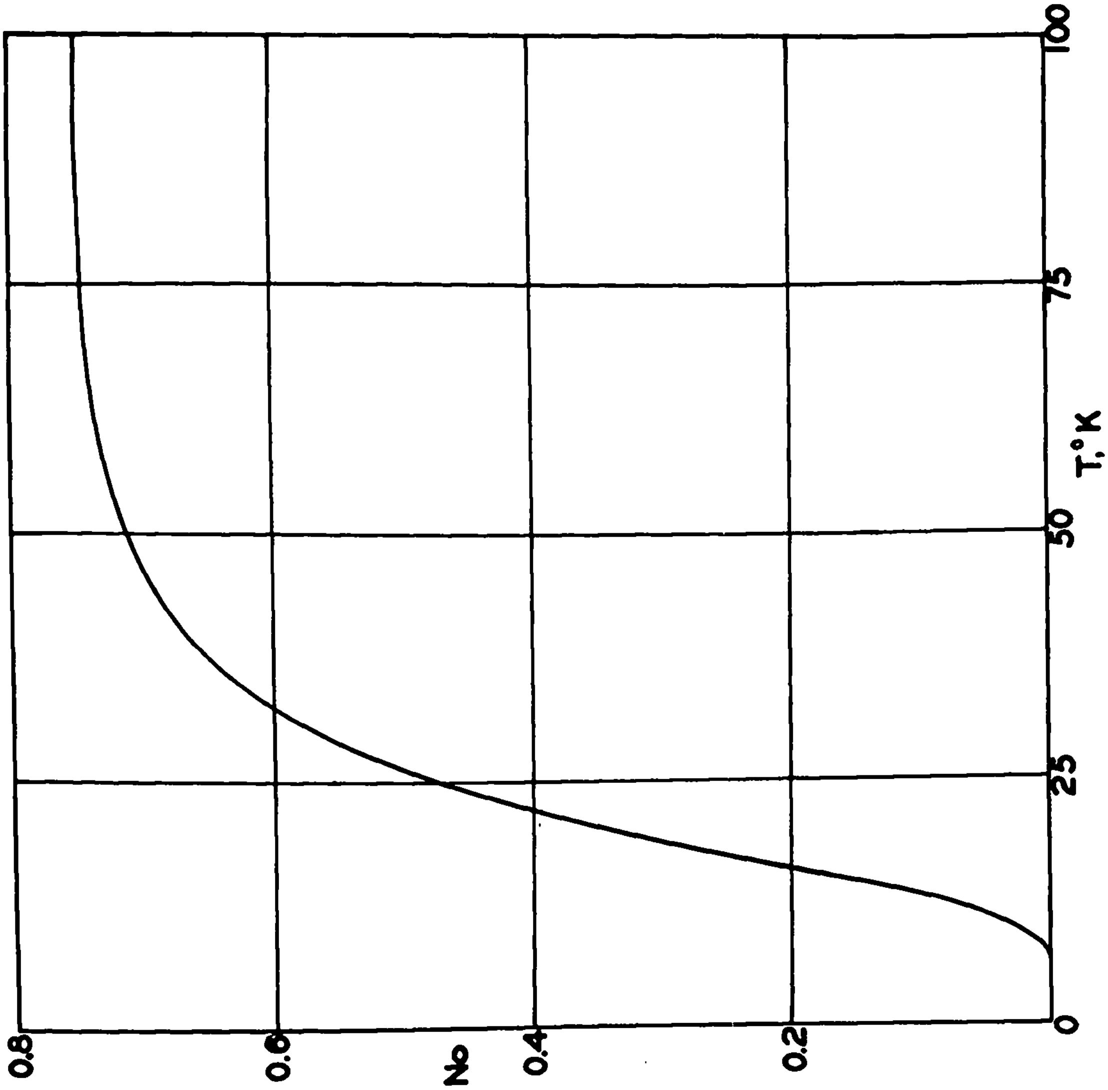

Fig. 1: Fraction of tritium molecules in odd rotational states as a function of temperature.

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types of T_2 have attained identical heat capacities, and the entropies of normal and equilibrium tritium have become identical. Moreover, above this temperature, the entropies of para and of ortho tritium are less than the entropy of equilibrium or of normal tritium by very nearly $R\ln 4 = 2.754$ e. u. and $R\ln 4/3 = 0.572$ e. u., respectively. This simplifies Table III. Figures 2 and 3 show the internal portion of C_V/R at low temperatures. The characteristic features are owing to rotation.

It is well known that calorimetric measurements performed on H_2 in the absence of a catalyst give rise to an entropy lower than the computed value by $R\ln 4 + 3/4R\ln 3$. These two terms correspond to nuclear spin degeneracy and to failure of ortho-para equilibration to occur in the time of experiment, respectively. This "discrepancy" is well understood and has been considered in detail by Giauque[1]. A similar situation exists for D_2[2,10].

Granting that the calorimetric measurements could be made, we may speculate on the "discrepancy" which would exist between the experimental and computed entropies for T_2 gas. The term $R\ln 4$ would remain even if measurements could be made at a small fraction of one degree Kelvin. If the estimate of a few days for the half time of the ortho-para conversion is accepted, then the remaining discrepancy might be a fair fraction of the corresponding term in H_2, $3/4R\ln 3$.

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[10] Clusius and Bartholomé, Z. physikal. Chem. B30, 237 (1935)

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TABLE III

HEAT CAPACITIES AND ENTROPIES (INCLUDING NUCLEAR SPIN) OF T_2 AND HT IN CAL. MOLE^{-1} DEG.$^{-1}$

T, °K	C_p^o for tritium				S^o for tritium				C_p^o for HT	S^o for HT
	o-T_2	p-T_2	e-T_2	n-T_2	o-T_2	p-T_2	e-T_2	n-T_2		
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10	4.967	4.967	6.770	4.967	18.860	14.495	14.876	18.886	4.977	16.043
15	4.967	4.981	8.970	4.971	20.874	16.510	18.121	20.901	5.143	18.083
20	4.967	5.104	8.689	5.001	22.304	17.956	20.703	22.334	5.611	19.620
25	4.967	5.451	7.745	5.088	23.414	19.127	22.539	23.460	6.199	20.936
30	4.998	5.999	7.043	5.248	24.321	20.167	23.884	24.400	6.680	22.111
35	5.056	6.615	6.633	5.446	25.095	21.138	24.936	25.223	6.974	23.165
40	5.154	7.163	6.423	5.656	25.776	22.059	25.806	25.964	7.111	24.107
50	5.461	7.992	6.393	6.094	26.957	23.737	27.224	27.270	7.141	25.701
75	6.335	7.657	6.657	6.665	29.344	26.831	29.848	29.833	7.023	28.571
100	6.787	7.144	6.876	6.876	31.240	29.004	31.798	31.798	6.987	30.585
125	6.925	7.007	6.945	6.945	32.772	30.580	33.341	33.341	6.977	32.143
150	6.958	6.975	6.963	6.963	34.038	31.854	34.610	34.610	6.974	33.415
175	6.966	6.970	6.967	6.967	35.112	32.929	35.683	35.683	6.973	34.490

T, °K	C_p^o T_2	S^o e-T_2	C_p^o HT	S^o HT
200	6.969	36.614	6.973	35.421
225	6.971	37.435	6.974	36.242
250	6.973	38.169	6.975	36.977
275	6.975	38.834	6.976	37.642
298.1	6.978	39.397	6.978	38.205
300	6.978	39.441	6.978	38.249
400	7.007	41.452	6.986	40.257
500	7.078	43.022	7.002	41.818
600	7.197	44.322	7.037	43.097
700	7.347	45.443	7.097	44.186
800	7.512	46.434	7.182	45.139
900	7.676	47.329	7.286	45.991
1000	7.832	48.146	7.403	46.764
1250	8.168	49.931	7.710	48.449
1500	8.427	51.445	7.995	49.881
2000	8.781	53.921	8.444	52.247
2500	9.013	55.907	8.760	54.166

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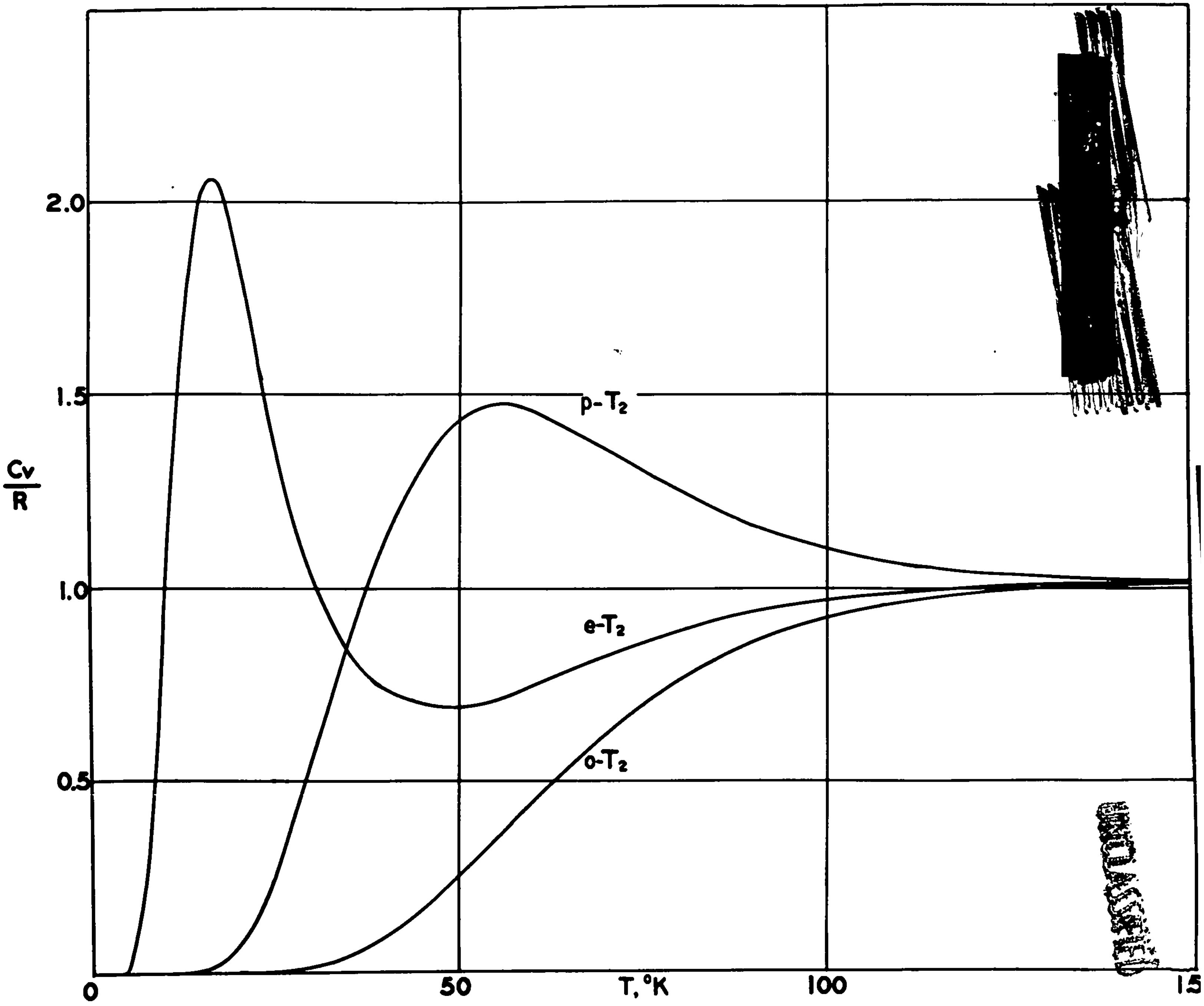

Fig. 2: Internal portion of the low temperature

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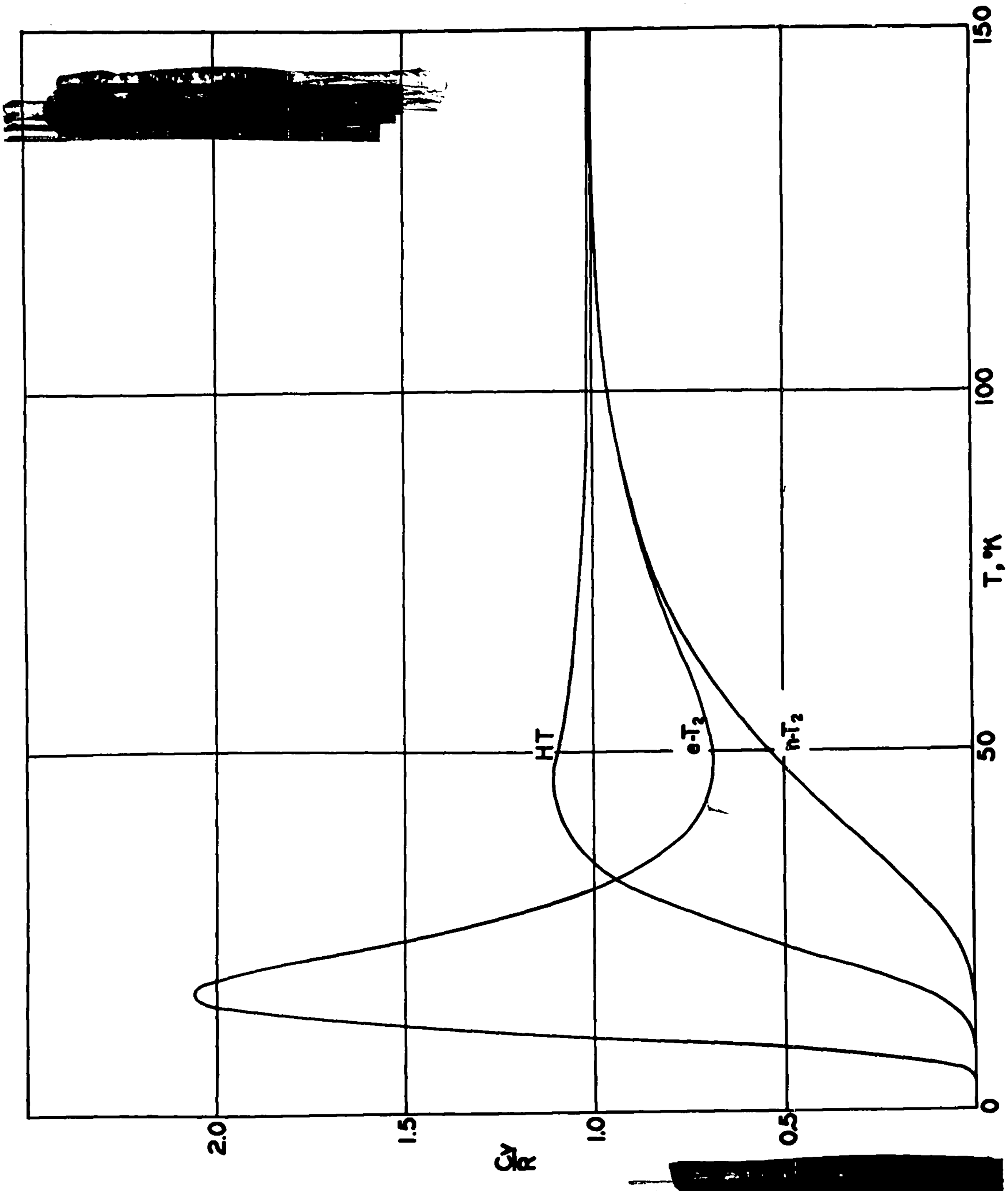

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Fig. 3: Internal portion of the low temperature heat capacities at constant volume of equilibrium tritium, normal tritium, and tritium hydride.

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THE INTERNAL ENERGY AND THE FREE ENERGY

The internal energy and the free energy, both given with reference to the state in which $\nu = J = 0$ are given in Tables IV and V. Table IV does not include the contribution $(E - E^\circ_0)_{translation} = 3/2\ RT$. The entries of Table V include the nuclear spin contribution of Rln4 for T_2 and HT and of Rln4 for atomic T, arising from the half units of nuclear and electron spin.

THE EQUILIBRIUM OF HYDROGEN AND TRITIUM WITH TRITIUM HYDRIDE

Values of $\left(\frac{F^\circ - E^\circ_0}{T}\right)$ for H_2, T_2 and HT may be employed to calculate the equilibrium constant, K, for the reaction $H_2 + T_2 = 2HT$ from the relationship:

$$-R\ln K = \Delta\left(\frac{F^\circ - E^\circ_0}{T}\right) \quad \frac{\Delta E^\circ_0}{T} . \qquad (2)$$

The values of $-\left(\frac{F^\circ - E^\circ_0}{T}\right)$ for H_2 were taken from the tables of Giauque[1] at 298.1° K. and at higher temperature, while the values of Urey and Rittenberg[11], corrected to $R = 1.9869$ cal. deg.$^{-1}$ mole^{-1}, were used below this temperature. The quantity ΔE°_0 is obtained from the zero point energies 6184.3, 3597.9, and 5065.0 cal. mole^{-1} for H_2, T_2 and HT, and it has the value 347.8 cal. mole^{-1}. The possibility of isotopic electronic shifts[2,5,6] has not been considered in this and the following section. Table VI gives values of K at several temperatures.

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TABLE IV

$E - E_o^o$ IN CAL. DEG.$^{-1}$ MOLE^{-1} FOR T_2 AND HT

(EXCLUDING TRANSLATION)

T, °K	o-T_2	p-T_2	e-T_2	n-T_2	HT
0	113.79	0.00	0.00	85.34	0.00
10	113.79	0.00	3.24	85.34	0.01
15	113.79	0.02	18.80	85.35	0.35
20	113.79	0.32	38.80	85.42	2.29
25	113.84	1.77	55.02	85.82	6.98
30	113.89	5.50	67.02	86.80	14.42
35	114.17	12.20	76.27	88.68	23.79
40	114.84	21.86	84.01	91.60	34.22
50	118.14	47.51	97.87	100.49	55.97
75	141.90	113.02	135.74	134.69	108.67
100	182.68	176.66	181.17	181.18	159.52
125	230.27	228.98	229.95	229.95	209.87
150	279.73	279.48	279.67	279.67	260.07
175	329.63	329.58	329.62	329.62	310.22
200	379.65	379.64	379.65	379.65	360.36

T, °K	T_2	HT	T, °K	T_2	HT
225	429.72	410.52	700	1436.6	1379.9
250	479.84	460.70	800	1682.8	1596.9
275	530.01	510.91	900	1945.5	1823.5
298.1	576.43	557.33	1000	2224.3	2061.1
300	580.25	561.15	1250	2984	2708
400	782.49	762.56	1500	3818	3431
500	989.6	965.1	2000	5644	5063
600	1206.3	1170.1	2500	7612	6885

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TABLE V

$-\left(\frac{F^o - E^o_o}{T}\right)$ FOR o-T_2, HT, and T IN CAL. DEG.$^{-1}$ MOLE^{-1}

(SPIN EFFECTS INCLUDED)

T, °K	o-T_2	HT	T, °K	o-T_2	HT	T
10	9.585	11.075	250	31.283	30.167	26.205
15	11.900	13.092	275	31.940	30.817	26.679
20	13.795	14.539	298.1	32.496	31.368	27.080
25	15.371	15.689	300	32.540	31.411	27.111
30	16.683	16.663	400	34.528	33.384	28.540
35	17.789	17.518	500	36.076	34.921	29.649
40	18.739	18.284	600	37.344	36.179	30.554
50	20.299	19.614	700	38.423	37.248	31.320
75	23.071	22.155	800	39.364	38.175	31.983
100	25.019	24.023	900	40.200	38.997	32.563
125	26.535	25.497	1000	40.955	39.736	33.092
150	27.778	26.714	1250	42.576	41.315	34.195
175	28.833	27.750	1500	43.932	42.627	35.106
200	29.748	28.652	2000	46.132	44.748	36.535
225	30.558	29.451	2500	47.895	46.445	37.643

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TABLE VI

EQUILIBRIUM CONSTANT FOR $H_2 + T_2 = 2HT$

T, °K	K, [redacted]	T, °K	K, [redacted]
50	0.243	700	3.59
100	0.947	800	3.69
200	1.953	900	3.76
298.1	2.58	1000	3.82
300	2.59	1250	3.91
400	2.99	1500	3.95
500	3.26	2000	3.99
600	3.45	2500	4.00

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THE DISSOCIATION OF ISOTOPIC HYDROGEN MOLECULES

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The dissociation constants of T_2 and HT have been calculated from a relationship of the form of Eq. (2). The value of ΔE° is found from $D_o(H_2)$ and the difference in the zero point energies of H_2 and the isotopic molecule. The work of Beutler and Jünger[12] provides the accurate value of 103,222 ± 17 cal. mole^{-1} for $D_o(H_2)$. The values for the dissociation constants of H_2, HD and D_2[1,2] have been corrected using the present value of $D_o(H_2)$. Dissociation constants are presented in Table. VII. The corresponding percentages of dissociation for a total pressure of one atmosphere are given in Table VIII.

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

[12] Beutler and Jünger, Z. Physik 101, 304 (1936)

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TABLE VII

DISSOCIATION CONSTANTS OF ISOTOPIC HYDROGEN MOLECULES IN ATMOSPHERES

T, °K	1000	1500	2000	2500
H_2	5.22×10^{-18}	3.13×10^{-10}	2.66×10^{-6}	6.35×10^{-4}
HD	2.00	1.36	1.23	3.01
D_2	3.00	2.34	2.24	5.67
HT	1.82	1.30	1.19	2.94
T_2	2.44	2.12	2.11	5.44

TABLE VIII

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

T, °K	1000	1500	2000	2500
H_2	11×10^{-8}	8.8×10^{-4}	8.2×10^{-2}	1.26
HD	7.1	5.8	5.5	0.87
D_2	8.7	7.7	7.5	1.19
HT	6.8	5.7	5.4	0.86
T_2	7.6	7.3	7.3	1.17

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