

Dissociation and Exchange Equilibria of the Tritium Halides

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approximation of the torsional frequency in ethylene to be made.

Note added in proof: The recent paper on the vibrational spectrum of tetrachloroethylene by P. Torkington [Trans. Farad. Soc. 45, 445-7 (1949)] has just come to the attention of the author. On the basis of the early experimental data listed in column 2 of Table I, Torkington suggests the following assignment:

$A_g = 1571, 447, 237$; $A_u = 135$ (estimated from the torsional frequency in ethylene); $B_{1g} = 512, 347$; $B_{1u} = 185$; $B_{2g} = 215$; $B_{2u} = 913, 332$; $B_{3u} = 782, 387$.

ACKNOWLEDGMENT

Thanks are due Dr. E. K. Plyler for permission to use his results on the far infra-red spectrum of C_2Cl_4 and Miss E. Miller for reduction of the spectra.

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Dissociation and Exchange Equilibria of the Tritium Halides*

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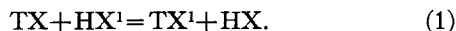
The ratios of the partition functions of the tritium halides to their respective protium halides have been calculated. These are combined with one another to give the exchange equilibria between the six pairs of tritium and protium halides. The exchange equilibria with water are calculated. From the exchange equilibria between the tritium halides and protium and the free energy of dissociation of the protium halides, the dissociation equilibria of the tritium halides have been calculated.

The experimental data on the dissociation of HI are reviewed and it is shown that the data of Taylor and Crist on DI and HI are self-consistent as well as in good agreement with theory. The heat of formation of HI at absolute zero, ΔH_0^0 , is found to be -1007 ± 10 calories per mole.

INTRODUCTION

THE availability of the hydrogen isotope of mass three, tritium, for experimental purposes makes it desirable and important to have available the thermodynamic properties of different chemical compounds of this nuclide. Libby¹ has calculated the exchange equilibria between the isotopic water and the isotopic hydrogen molecules. Urey² has calculated these same equilibria as well as the partition function ratios of the various pairs of isotopic water molecules and the isotopic hydrogen molecules. Jones³ has calculated the thermodynamic functions for tritium and tritium hydride. From these and the free energy function of protium he has calculated the equilibrium between tritium, protium, and tritium hydride. In addition, he has calculated the dissociation of the isotopic hydrogen molecules into atoms.

This paper reports the calculations of the partition function ratios of the tritium to protium halides. The partition function ratios of the four isotopic hydrogen halides are then combined to give the six exchange equilibria between the various tritium and protium halides.



The ratios are also combined with the partition function ratios of the tritium water molecules and the protium water molecules to give the exchange equilibria between

the tritium halides and water. From the calculated exchange equilibria between the tritium halides and protium and the known free energies of formation of the protium halides,⁴ the dissociation equilibria of the tritium halides have been calculated. By means of suitably chosen exchange equilibria, which can be calculated directly from partition function ratios, it is possible to calculate all the thermodynamic equilibrium constants for gaseous tritium compounds from the experimental and theoretical values for the corresponding protium compounds. This is the most rapid procedure for such calculations and the precision and accuracy attained are generally limited by the accuracy of the protium determinations.

PARTITION FUNCTION RATIOS

The formulas and method for the calculation of the partition function ratios have been published previously.⁵ Both chlorine and bromine each have two stable isotopes. The partition function ratios TCl/HCl and TBr/HBr are calculated for the normal isotopic abundance of the halogens. The procedure used was to calculate the spectroscopic properties of the tritium chloride and bromide as though they were each monoisotopic. The mass of the halogen taken was the weighted masses of the isotopes. This simplification over the procedure of calculating the ratios for each of the halogen isotopes and weighting the ratios introduces an error of less than one tenth of one percent for the

* Research done at the Brookhaven National Laboratory under the auspices of the AEC.

¹ W. F. Libby, J. Chem. Phys. 11, 101 (1943).

² H. C. Urey, J. Chem. Soc. 562 (1947).

³ W. M. Jones, J. Chem. Phys. 16, 1077 (1948).

⁴ "Selected values of chemical thermodynamic properties," National Bureau of Standards, June 30, 1948.

⁵ J. Bigeleisen and M. G. Mayer, J. Chem. Phys. 15, 261 (1947).

TABLE I.

Nuclide	Mass*
H	1.00813
T	3.01703
F ¹⁹	19.00450
Cl ³⁵	34.97867
Cl ³⁷	36.97750
Br ⁷⁹	78.94438
Br ⁸¹	80.94228
I ¹²⁷	126.95

* The masses for H and T were taken from K. T. Bainbridge, National Research Council Committee on Nuclear Science Report No. 1; those for F and Cl from H. Bethe, *Elementary Nuclear Theory* (John Wiley and Sons, New York, 1947); Br from K. Ogata, *Phys. Rev.* **75**, 200 (1949); I from chemical atomic weight, *J. Am. Chem. Soc.* **70**, 3531 (1948).

TABLE II.*

	ω_e	$x_{e0} \omega_e$	σT
HF	4141.31	90.866	29.527
TF	2511.18	33.410	10.948
HCl	2988.95	51.65	15.0160
TCI	1774.71	18.21	5.3255
HBr	2649.67	45.21	12.023
TBr	1550.54	15.48	4.140
HI	2309.53	39.73	9.292
TI	1345.47	13.48	3.146

* The values for the protium halides were taken from G. Herzberg *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York 1939). The ones for the tritium halides were calculated.

TABLE III.

T°K	TF/HF	f TCI/HCl	TBr/HBr	TI/HI
273.16	40.182	13.736	10.072	7.0768
298.16	28.268	10.556	7.9362	5.7449
300	27.607	10.372	7.8105	5.6660
400	10.630	5.0812	4.0995	3.2295
500	5.9988	3.3225	2.8003	2.3240
600	4.1019	2.5223	2.1868	1.8829
700	3.1325	2.0727	1.8448	1.6326
800	2.5654	1.7998	1.6333	1.4762
900	2.2021	1.6227	1.4930	1.3715
1000	1.9545	1.4980	1.3948	1.2978
1100	1.7770	1.4075	1.3233	1.2443
1200	1.6453	1.3396	1.2694	1.2037
1300	1.5446	1.2889	1.2281	1.1725
1400	1.4659	1.2465	1.1954	1.1479
1500	1.4033	1.2134	1.1695	1.1281
2000	1.2212	1.1175	1.0928	1.0704

tritium to protium chloride ratio at 300°K. The error is smaller at higher temperatures and is smaller at all temperatures for the bromides. The masses of the atoms used in the calculations are given in Table I. The spectroscopic values used are given in Table II. The values of σT were calculated for the ground vibrational state. The conversion factor used, hc/k , was taken as 1.43847 so that the equilibria calculated may be combined directly with those being published by the National Bureau of Standards.⁴

The partition function ratios, f values (Eq. (11), reference 5), corrected for non-classical rotation, Eq. (15), reference 5, for the tritium to protium halides are given in Table III. Interpolations of the values in

TABLE IV.

T°K	TF HI	TF HBr	TF HCl	TCI HI	TCI HBr	TBr HI
	HF TI	HF TBr	HF TCI	HCl TI	HCl TBr	HBr TI
273.16	5.6780	3.9895	2.9253	1.9410	1.3638	1.4232
298.16	4.9205	3.5619	2.6778	1.8375	1.3301	1.3814
300	4.8724	3.5346	2.6617	1.8305	1.3279	1.3785
400	3.2915	2.5930	2.0920	1.5734	1.2395	1.2694
500	2.5812	2.1422	1.8055	1.4296	1.1865	1.2049
600	2.1785	1.8758	1.6263	1.3396	1.1534	1.1614
700	1.9187	1.6980	1.5113	1.2696	1.1235	1.1300
800	1.7378	1.5707	1.4254	1.2192	1.1019	1.1064
900	1.6056	1.4749	1.3571	1.1832	1.0869	1.0886
1000	1.5060	1.4013	1.3047	1.1543	1.0740	1.0747
1100	1.4281	1.3429	1.2625	1.1312	1.0636	1.0635
1200	1.3669	1.2961	1.2282	1.1129	1.0553	1.0546
1300	1.3174	1.2577	1.1984	1.0993	1.0495	1.0474
1400	1.2770	1.2263	1.1760	1.0859	1.0427	1.0414
1500	1.2440	1.1999	1.1565	1.0756	1.0375	1.0367
2000	1.1408	1.1175	1.0928	1.0440	1.0226	1.0209

TABLE V.

T°K	HT HF	HT HCl	HT HBr	HT HI	f_{HT/H_2}
	H ₂ TF	H ₂ TCI	H ₂ TBr	H ₂ TI	
273.16	0.31135	0.91080	1.2421	1.7678	12.511
298.16	0.37311	0.99912	1.3290	1.8359	10.547
300	0.37767	1.0053	1.3349	1.8402	10.426
400	0.61718	1.2912	1.6003	2.0315	6.5606
500	0.82820	1.4953	1.7742	2.1378	4.9682
600	1.0064	1.6367	1.8878	2.1925	4.1282
700	1.1547	1.7452	1.9608	2.2156	3.6172
800	1.2776	1.8211	2.0067	2.2203	3.2776
900	1.3792	1.8717	2.0343	2.2145	3.0372
1000	1.4633	1.9092	2.0505	2.2037	2.8600
1100	1.5331	1.9356	2.0588	2.1895	2.7244
1200	1.5914	1.9546	2.0627	2.1753	2.6184
1300	1.6404	1.9659	2.0632	2.1610	2.5338
1400	1.6817	1.9777	2.0622	2.1476	2.4652
1500	1.7162	1.9848	2.0593	2.1349	2.4084
2000	1.9031	1.9995	2.0447	2.0874	2.2344

Table III can best be made by a plot of $\log f$ vs. $1/T$, which is linear up to 1000°K and then f approaches unity asymptotically at infinite temperature.

EQUILIBRIUM CONSTANTS

The equilibrium constants for exchange reactions between the tritium and protium halides are given in Table IV.

The equilibrium constants for the exchange of the tritium halides with protium, according to Eqs. (2) and (3)



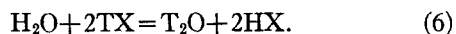
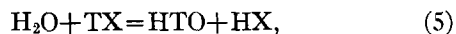
are given in Tables V and VI, respectively. Table V also contains the f values for HT/H₂ necessary for the equilibria, while Table VI contains the f values for T₂/H₂. These f values were calculated with constants given in Table VII. The equilibrium constants for the reaction,



calculated from the f values in Tables V and VI are in

good agreement with those calculated by Jones³ using the free energy functions and ΔH_0^0 from spectroscopic data. The slight discrepancy, less than 0.5 percent at 300°K, results from the fact that Jones uses slightly different spectroscopic values for ω_e and $x_e\omega_e$.

Table VIII lists the partition function ratios HTO/H₂O and T₂O/H₂O from 273.16°K to 2000°K. The vibrational frequencies and anharmonicities used were taken from Libby's calculations.¹ These are combined with those of the halides to give the equilibrium constants for the following reactions



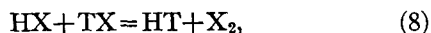
The equilibrium constants are listed in Table VIII.

DISSOCIATION OF THE TRITIUM HALIDES

The exchange equilibria of the tritium halides with protium, Eqs. (2) and (3), can be combined with the dissociation equilibria of the protium halides



to give the dissociation equilibria of the tritium halides in dilute and concentrated tritium mixtures.



$K_8 = K_2K_7$; $K_9 = K_3K_7$. From the dissociation equilibria of the tritium halides (Eq. (9)) their respective free energies of formation are calculated. The equilib-

TABLE VI.

T°K	$\frac{T_2}{H_2} \left(\frac{\text{HF}}{\text{TF}} \right)^2$	$\frac{T_2}{H_2} \left(\frac{\text{HCl}}{\text{TCl}} \right)^2$	$\frac{T_2}{H_2} \left(\frac{\text{HBr}}{\text{TBr}} \right)^2$	$\frac{T_2}{H_2} \left(\frac{\text{HI}}{\text{TI}} \right)^2$	$f\text{T}_2/\text{H}_2$
273.16	0.039897	0.34141	0.63496	1.2863	64.417
298.16	0.054294	0.38935	0.68884	1.3145	43.385
300	0.055452	0.39285	0.69279	1.3164	42.263
400	0.12797	0.56009	0.86047	1.3865	14.461
500	0.21122	0.68857	0.96932	1.4074	7.6011
600	0.29460	0.77916	1.0366	1.3982	4.9570
700	0.37282	0.85154	1.0749	1.3725	3.6583
800	0.44377	0.90161	1.0948	1.3402	2.9206
900	0.50693	0.93354	1.1028	1.3069	2.4582
1000	0.56205	0.95682	1.1036	1.2748	2.1471
1100	0.61032	0.97279	1.1006	1.2447	1.9272
1200	0.65223	0.98390	1.0957	1.2186	1.7656
1300	0.68870	0.98904	1.0894	1.1952	1.6431
1400	0.72037	0.99627	1.0833	1.1748	1.5480
1500	0.74773	1.0001	1.0766	1.1571	1.4725
2000	0.91077	1.0054	1.0513	1.0957	1.2555

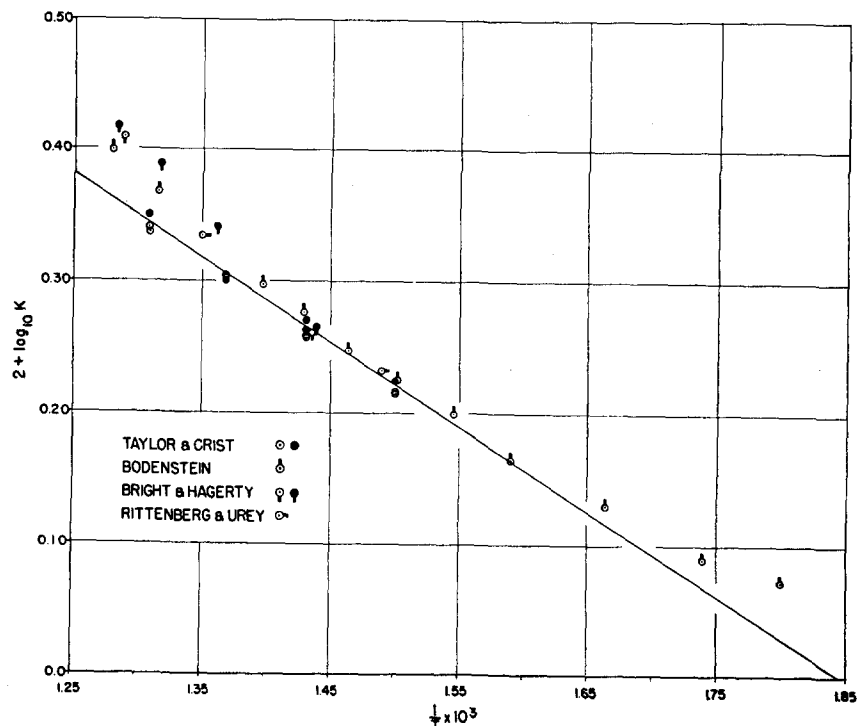
TABLE VII.†

	ω_e	$x_e\omega_e$	σT
H ₂	4405.30	125.325	85.365
HT	3598.01	83.601	57.208
T ₂	2546.49	41.877	28.836

† See reference * in Table II.

rium constants and free energies of formation are listed in Table IX. The values of K_7 used for the respective protium halides were obtained from the following sources: HF from the free energy equation of Murphy and Vance;⁶ HCl and HBr from the National Bureau of

FIG. 1. Equilibrium in the dissociation of HI. $2\text{HI}(g) = \text{H}_2(g) + \text{I}_2(g)$. Open circles HI data; solid circles calculated from DI data.



* G. M. Murphy and J. E. Vance, J. Chem. Phys. 7, 806 (1939).

TABLE VIII.

T°K	$\frac{f}{\text{H}_2\text{O}}$	$\frac{\text{HTO HF}}{\text{H}_2\text{O TF}}$	$\frac{\text{HTO HCl}}{\text{H}_2\text{O TCl}}$	$\frac{\text{HTO HBr}}{\text{H}_2\text{O TBr}}$	$\frac{\text{HTO HI}}{\text{H}_2\text{O TI}}$	$\frac{f}{\text{H}_2\text{O}}$	$\frac{\text{T}_2\text{O}(\text{HF})^2}{\text{H}_2\text{O}(\text{TF})^2}$	$\frac{\text{T}_2\text{O}(\text{HCl})^2}{\text{H}_2\text{O}(\text{TCl})^2}$	$\frac{\text{T}_2\text{O}(\text{HBr})^2}{\text{H}_2\text{O}(\text{TBr})^2}$	$\frac{\text{T}_2\text{O}(\text{HI})^2}{\text{H}_2\text{O}(\text{TI})^2}$
273.16	95.404	2.3743	6.9455	9.4722	13.481	2723.3	1.6867	14.433	26.844	54.377
298.16	65.206	2.3067	6.1772	8.2163	11.350	1243.3	1.5559	11.158	19.740	37.671
300	63.562	2.3024	6.1282	8.1380	11.218	1179.6	1.5477	10.965	19.336	36.743
400	22.678	2.1334	4.4631	5.5319	7.0221	141.79	1.2548	5.4917	8.4369	13.594
500	12.292	2.0491	3.6996	4.3895	5.2892	40.404	1.1228	3.6601	5.1525	7.4808
600	8.2018	1.9995	3.2517	3.7506	4.3559	17.711	1.0526	2.7839	3.7036	4.9956
700	6.1810	1.9732	2.9821	3.3505	3.7860	9.9546	1.0145	2.3171	2.9250	3.7347
800	5.0248	1.9587	2.7919	3.0765	3.4039	6.5335	0.99274	2.0169	2.4491	2.9981
900	4.2970	1.9513	2.6481	2.8781	3.1331	4.7545	0.98047	1.8057	2.1331	2.5276
1000	3.8068	1.9477	2.5413	2.7293	2.9333	3.7183	0.97335	1.6570	1.9112	2.2076
1100	3.4600	1.9471	2.4583	2.6147	2.7807	3.0627	0.96991	1.5460	1.7490	1.9781
1200	3.2042	1.9475	2.3919	2.5242	2.6620	2.6213	0.96834	1.4607	1.6267	1.8092
1300	3.0108	1.9492	2.3359	2.4516	2.5678	2.3098	0.96814	1.3904	1.5315	1.6801
1400	2.8602	1.9512	2.2946	2.3927	2.4917	2.0814	0.96859	1.3396	1.4565	1.5796
1500	2.7408	1.9531	2.2588	2.3436	2.4296	1.9083	0.96902	1.2961	1.3953	1.4995
2000	2.3982	1.9638	2.1460	2.1945	2.2405	1.4553	0.97586	1.1654	1.2186	1.2701

TABLE IX.

T°K	TF			TCl			TBr			TI		
	log ₁₀ K _s	log ₁₀ K ₉	ΔF_f° in kcal.	log ₁₀ K _s	log ₁₀ K ₉	ΔF_f° in kcal.	log ₁₀ K _s	log ₁₀ K ₉	ΔF_f° in kcal.	log ₁₀ K _s	log ₁₀ K ₉	ΔF_f° in kcal.
298.16	-95.593	-96.430	-65.78	-33.3796	-33.7888	-23.049	-19.052	-19.337	-13.19	-2.558	-2.703	-1.84
300	-95.007	-95.841	-65.78	-33.1789	-33.5869	-23.052	-18.943	-19.228	-13.20	-2.545	-2.691	-1.85
400	-71.322	-72.005	-65.89	-25.0202	-25.3829	-23.229	-14.350	-14.619	-13.38	-2.066	-2.232	-2.04
500	-57.109	-57.692	-66.00	-20.1153	-20.4520	-23.395	-11.583	-11.846	-13.55	-1.760	-1.942	-2.22
600	-47.609	-48.142	-66.09	-16.8348	-17.1571	-23.552	-9.7278	-9.9882	-13.71	-1.547	-1.742	-2.39
700	-40.823	-41.324	-66.18	-14.4843	-14.7960	-23.696	-8.3974	-8.6584	-13.87	-1.391	-1.599	-2.56
800	-35.728	-36.188	-66.23	-12.7175	-13.0228	-23.835	-7.3969	-7.6601	-14.02	-1.273	-1.492	-2.73
900	-31.762	-32.197	-66.30	-11.3410	-11.6431	-23.974	-6.6160	-6.8819	-14.17	-1.180	-1.409	-2.90
1000	-28.587	-29.003	-66.35	-10.2373	-10.5374	-24.108	-5.9901	-6.2592	-14.32	-1.104	-1.341	-3.07
1100	-25.987	-26.387	-66.41	-9.3346	-9.6334	-24.244	-5.4784	-5.7504	-14.47	-1.043	-1.288	-3.24
1200	-23.818	-24.205	-66.45	-8.5811	-8.8792	-24.377	-5.0504	-5.3251	-14.62	-0.991	-1.243	-3.41
1300	-21.981	-22.358	-66.50	-7.9430	-8.2414	-24.512	-4.6889	-4.9662	-14.77	-0.948	-1.206	-3.59
1400	-20.406	-20.774	-66.54	-7.3958	-7.6936	-24.642	-4.3797	-4.6592	-14.92	-0.912	-1.174	-3.76
1500	-19.040	-19.400	-66.58	-6.9205	-7.2182	-24.771	-4.1105	-4.3921	-15.07	-0.881	-1.147	-3.94

Standards tables;⁴ the data used for HI are discussed below.

DISSOCIATION OF HI

The dissociation of protium iodide is one of the most carefully studied gaseous equilibria. Yet, in spite of the considerable amount of careful experimental work and the application of statistical thermodynamics to the problem, there is still a considerable degree of discrepancy between the results of the various workers. Murphy⁷ has reviewed and examined critically the experimental data up to 1936 in his paper on the free energy of formation from spectroscopic data. He concludes that Bodenstein's⁸ data below 600°K and above 700°K are probably in error. Taylor and Crist⁹ have redetermined the dissociation of HI and determined the dissociation of DI. Their results are in good agreement with the calculations of Murphy on HI and those of Blagg and Murphy¹⁰ on DI. Their analysis of their data leads to a change of Murphy's ΔE_0° from 971.83 ± 13.65 cal. mole⁻¹ to 990.40 ± 4 cal. mole⁻¹ and Blagg and Murphy's ΔE_0° from 1014.52 ± 14 cal. mole⁻¹ to

1033.09 ± 4 cal. mole⁻¹. Recently Bright and Hagerty¹¹ have published their data on the dissociation of protium and deuterium iodides. Their data on protium and deuterium iodides are self consistent. They lead to values for the exchange equilibrium



which are in good agreement with the theoretical calculation of Bigeleisen and Mayer.⁵ However, while their data on protium iodide are in good agreement with those of Bodenstein, they are in poor agreement with those of Taylor and Crist and the calculations of Murphy. If we write the equilibrium in the form of Eq. (7) the data of Bright and Hagerty are higher than those of Taylor and Crist.

The free energies of formation of HI(g) given in the National Bureau of Standards tables⁴ are larger than all the previous data. Thus the logK values for Eq. (7) are even lower than those of Murphy. There are no experimental data which are consistently below Murphy's calculations for K₇. This discrepancy was called to the attention of Dr. D. D. Wagman. In reply, Dr. Wagman has informed me that his compilation had unfortunately overlooked the measurements of Taylor and Crist in arriving at a value of $\Delta H_f^\circ_{298.16}$. After

⁷ G. M. Murphy, J. Chem. Phys. 4, 344 (1936).

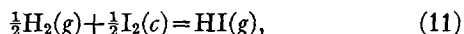
⁸ M. Bodenstein, Zeits. f. physik. Chem. 29, 295 (1899).

⁹ A. H. Taylor and R. H. Crist, J. Am. Chem. Soc. 65, 1377 (1941).

¹⁰ J. C. L. Blagg and G. M. Murphy, J. Chem. Phys. 4, 631 (1936).

¹¹ N. F. H. Bright and R. P. Hagerty, Trans. Faraday Soc. 43, 697 (1947).

consideration of the data of Taylor and Crist, Wagman arrives at the following constants for the reaction



$$\Delta H_f^0_{298.16} = 6.28 \text{ kcal.},$$

$$\Delta F_f^0_{298.16} = 0.39 \text{ kcal.},$$

$$\log_{10} K_f = -0.286.$$

These constants together with the heat of vaporization of iodine, the vapor pressure of iodine and the free energy functions for $\text{H}_2(\text{g})$, $\text{I}_2(\text{g})$, and $\text{HI}(\text{g})$ (all from the National Bureau of Standards tables) yield -1007 ± 10 cal. mole⁻¹ for the heat of formation of $\text{HI}(\text{g})$ at absolute zero. The values of K_7 used for HI were calculated from this ΔH_f^0 and the $(F^0 - H_0^0)$ tables of

the National Bureau of Standards.⁴ A plot of $\log K_7$ vs. $1/T$ is shown in Fig. 1 together with the experimental data of Taylor and Crist,⁹ Bodenstein,⁸ Bright and Hagerty,¹¹ and Rittenberg and Urey.¹² Finally, the equilibrium data of Taylor and Crist and of Bright and Hagerty on DI are combined with the theoretical values⁵ of K_{10} to give K_7 . It is seen that both the data of Taylor and Crist and Bright and Hagerty on DI are consistent with their respective HI data. Furthermore, the data of Taylor and Crist on HI are in good agreement with those calculated from spectroscopic data and the value of $\Delta H_f^0 - 1007$ cal. mole⁻¹.

¹² D. Rittenberg and H. C. Urey, *J. Chem. Phys.* **1**, 137 (1933); *J. Am. Chem. Soc.* **56**, 1885 (1934).

Infra-Red and Raman Spectra of Fluorinated Ethylenes II. 1,1-Difluoro-2,2-Dichloroethylene*

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The infra-red absorption spectrum of gaseous 1,1-difluoro-2,2-dichloroethylene between 2 and 22.6 μ has been investigated with a prism spectrometer of high resolution. The Raman spectrum of $\text{CF}_2:\text{CCl}_2$ in the liquid state has been photographed with a three-prism glass spectrograph of linear dispersion 15A/mm at 4358A. Quantitative polarization measurements have been made. The 12 fundamental vibration frequencies have been assigned, and the observed vibration spectra have been interpreted in detail.

INTRODUCTION

THE Raman spectrum of liquid 1,1-difluoro-2,2-dichloroethylene has been studied by Hatcher and Yost.¹ The infra-red spectrum of the compound in the gaseous state has been investigated by Torkington and Thompson² who made an assignment of ten of the twelve fundamental vibration frequencies. In the present paper more accurate experimental data, a complete assignment of fundamentals and a detailed interpretation of the infra-red and Raman spectra of $\text{CF}_2:\text{CCl}_2$ will be given.

EXPERIMENTAL

The sample of $\text{CF}_2:\text{CCl}_2$ was prepared and purified in the Jackson Laboratory of E. I. du Pont de Nemours and Company. No information was available about its purity. However, the infra-red spectrum showed that it contained certain amounts of carbon dioxide and carbon monoxide as impurities.

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¹ J. B. Hatcher and D. M. Yost, *J. Chem. Phys.* **5**, 992 (1937).

² P. Torkington and H. W. Thompson, *Trans. Faraday Soc.* **41**, 236 (1945).

The infra-red absorption spectrum of gaseous $\text{CF}_2:\text{CCl}_2$ was measured from 2 to 22.6 μ in the manner described in the first paper of this series.³ The Raman spectrum of liquid $\text{CF}_2:\text{CCl}_2$ was photographed by means of a Lane-Wells spectrograph.³ Quantitative measurements of the depolarization ratios of the Raman bands were made with an apparatus similar to that described by Crawford and Horwitz,⁴ except for the use of mercury lamps with internally water-cooled electrodes. The Type H polaroid sheets were given a permanent cylindrical shape by bending them tightly around a glass tube of appropriate diameter, wrapping a string around them along the whole length and heating them in an oven for one to two hours at 75°C.

In order to make the two exposures accurately equivalent, an intensity integrator was used. It consists of a glow tube relaxation circuit in which the resistance in series with the condenser is furnished by a 929 photo-cell and depends on the intensity of the light falling on the cell. The condenser charges at a rate determined by

³ Smith, Nielsen, and Claassen, *J. Chem. Phys.* **18**, 326 (1950).

⁴ B. L. Crawford, Jr. and W. Horwitz, *J. Chem. Phys.* **15**, 882 (1947).