at $x = 0.5$, quite a bit lower than the reported value of 328 cal. mole^{-1}. Since it has been noted[26] that values of K calculated from solubility measurements and vapor–liquid equilibrium measurements are sometimes quite different and since the majority of the data used to establish the correlation were solubility data, it is not surprising that the consolute temperature was predicted more accurately than the excess free energy.

Conclusions

Reliable values of the excess free energy of mixing in fluorocarbon–hydrocarbon systems can be calculated from mutual solubility data through the Van Laar equation. Where mutual solubility data are not available, an estimate of the excess free energy of mixing in fluorocarbon–paraffin hydrocarbon systems can be obtained from an empirical correlation if the molal volumes, solubility parameters and ionization potentials of the pure compounds are known.

MANHATTAN, KANSAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Electronic Transitions in Methyl Fluoride and in Fluoroform[1]

BY SUZANNE STOKES[2] AND A. B. F. DUNCAN

RECEIVED MAY 19, 1958

Electronic spectra of CH_3F and of CHF_3 have been obtained in absorption in the vacuum ultraviolet region. The electronic transitions are fitted to series which converge to ionization potentials of the molecules. Vibrational structure associated with two of the transitions is interpreted. A correlation of electronic terms in the series of molecules CH_4, CH_3F, CH_2F_2, CHF_3 and CF_4 is presented.

The electronic energy levels, obtained from a study of vacuum ultraviolet spectra, of a number of halogen derivatives of methane have been reported recently.[3] The present investigation is a continuation of this work, and the vacuum ultraviolet absorption spectra of CH_3F and CHF_3 are presented here.

Experimental Details

The CH_3F was obtained from Dr. W. F. Edgell of Purdue University. He reported that the infrared spectrum of the compound showed that no impurities were present. Another sample of CH_3F was prepared following the procedure given by Edgell.[4] A mass spectrographic analysis indicated that the second sample contained about 0.05% of an impurity which had a mass of 28. This impurity was probably nitrogen or possibly ethylene.

Fluoroform was obtained from the Kinetic Chemicals Division of du Pont de Nemours Company, who stated that the sample showed no impurities by mass spectrographic analysis. This statement was confirmed independently by a mass spectrum determined here.

The spectra were photographed in the first order of a vacuum grating spectrograph.[5] The grating, of one meter radius of curvature, was ruled 30,000 lines per inch on a two inch surface, and was mounted at about normal incidence. The dispersion was equal to about 8.32 Å./mm. The slit was about 0.1 mm. wide. Eastman Kodak Company SWR film was used.

Most of the spectra appeared at very low pressures. In such cases the vapor was introduced directly into the spectrograph through calibrated volumes to a known pressure and was separated from the background source only by the slit. The light source was operated at about 0.5 mm. of He, and while some He diffused through the slit, none of the absorbing gas was lost during an exposure.

The Lyman continuum was used as a background for absorption spectra. It was operated by periodic discharge, once a second, of a one microfarad capacitor, charged to about 15,000 volts. Helium gas at a pressure of about 0.5 mm. was used as a carrier gas. Narrow emission lines of carbon, silicon and atomic oxygen[6] occurring in this source were used as wave length standards. The continuum was satisfactory except in the region 1000 to 840 Å. where the strongest absorption of oxygen occurs. This oxygen probably originated from decomposition of quartz vapor from the capillary where the discharge occurred and could not be eliminated. This region in the methyl fluoride spectrum was investigated in detail with a hollow cathode copper discharge. The numerous well resolved lines of the Cu I[7] spectra in this source allowed a point by point plot of the contours of absorption in this region which was shown to be continuous.

To investigate the possibility of weak absorption at longer wave lengths than about 1300 Å., pressures greater than 0.5 mm. of absorbing gas were required. For this purpose an uncondensed discharge in hydrogen was used, separated from the absorbing gas in the spectrograph by a LiF window. Absorption coefficients in this region were determined at wave lengths of lines in the hydrogen molecular spectrum.

Intensity maxima of broad continuous bands were measured from microphotometer tracings. The estimated error in these measurements was about 5 to 8 Å. When hydrogen lines or copper lines served as the background, band envelopes were found by plotting the absorption coefficients against wave lengths. The band maxima were read from these curves to about 5 to 10 Å., depending on the breadth near the maximum. For sharp vibrational bands the error in measurement was about 10 cm.$^{-1}$.

Description of Spectra

The observed electronic transitions in the two molecules are shown in Fig. 1, where relative intensities, derived principally from appearance pressures are plotted against wave number. Further details are reported below concerning the behavior of the transitions with change of pressure.

Methyl Fluoride.—This molecule was studied over the pressure range of 0.003 to 2.6 mm. The spectrum consisted of five electronic transitions, one

---

[1] Part of a dissertation submitted by Suzanne Stokes to the Graduate School of the University of Rochester in partial fulfillment for the requirements of the degree of Doctor of Philosophy. This work was supported in part by the Office of Ordnance Research, U. S. Army, under contract DA-30-115-ORD-728(020) with the University of Rochester. Reproduction in whole or in part is permitted for any use of the U. S. Government.

[2] Eastman Kodak Company Fellow, 1956–1957.

[3] C. R. Zobel and A. B. F. Duncan, THIS JOURNAL, **77**, 2611 (1955). Reference to previous work on related molecules will be found in this reference.

[4] W. F. Edgell and L. Parts, *ibid.*, **77**, 4899 (1955).

[5] G. Moe and A. B. F. Duncan, *ibid.*, **74**, 3136 (1952).

[6] J. C. Boyce and J. T. Moore, "Provisional Wavelength Identification for Vacuum Ultraviolet," Massachusetts Institute of Technology, 1941.

[7] A. G. Shenstone, *Phil. Trans. Roy. Soc.*, **A235**, 195 (1936).

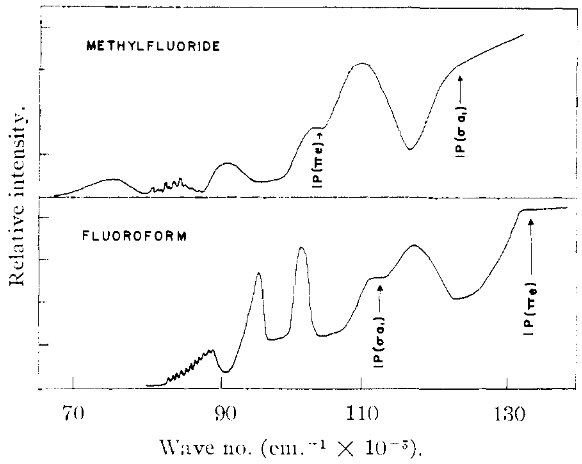

Fig. 1.—Relative intensities of electronic transitions in methyl fluoride and in fluoroform, in arbitrary units, estimated directly from microphotometer tracings at different pressures.

of which showed vibrational structure; the other transitions were regions of continuous absorption.

The low frequency limit of perceptible (continuous) absorption at the lowest pressure (0.003 mm.) was at 115,000 cm.$^{-1}$. The strongest transition occurred at 109,100 cm.$^{-1}$ and was first observed at 0.004 mm. At this pressure a less intense band with maximum absorption at about 103,300 cm.$^{-1}$ appeared. This band overlapped the high frequency transition, and since the absorption was not resolved well, there may be more than one band in this region. At 0.004 mm. the transition at 109,100 cm.$^{-1}$ extended from 105,780 to 116,490 cm.$^{-1}$. The high frequency edge of the 103,300 cm.$^{-1}$ transition was obscured by the 109,100 cm.$^{-1}$ transition, and the low frequency edge was at 100,000 cm.$^{-1}$.

When the pressure was increased to 0.016 mm., the above transitions merged to give continuous absorption, and a band with a maximum at 91,740 cm.$^{-1}$ became apparent. The transition was continuous in nature and at 0.016 mm. extended from 88,650 to 95,370 cm.$^{-1}$. As the pressure was raised to 0.031 mm., a transition with associated vibrational structure was seen. The transition with structure extended from 87,440 to 80,995 cm.$^{-1}$ and had a maximum at about 85,338 cm.$^{-1}$. As the pressure was increased, the low frequency edge of the 91,740 cm.$^{-1}$ transition shifted to lower frequencies and partly overlapped the transition at 85,338 cm.$^{-1}$. As a result the vibrational structure appeared to be superimposed on a continuum. The vibrational bands were sharp and were fully developed at a pressure of 0.050 mm.

At a pressure of 0.035 mm. a transition at 75,400 cm.$^{-1}$ which was continuous in nature became apparent and at this pressure extended from about 69,100 to 80,500 cm.$^{-1}$.

Fluoroform.—This molecule was investigated throughout the pressure range of 0.002 to 20.0 mm. Five electronic transitions were observed, with some indication of a sixth transition. All except one transition were continuous in nature.

At a pressure of 0.008 mm., the low frequency limit of continuous absorption was about 131,800 cm.$^{-1}$. The transitions at 117,030 and 101,830 cm.$^{-1}$ were the strongest, becoming apparent at a pressure of 0.010 mm. At this pressure, a less intense band with a maximum at about 111,240 cm.$^{-1}$ appeared. This band partly overlapped the 117,030 cm.$^{-1}$ transition. When the pressure was increased to 0.013 mm., the transition with a maximum at 95,490 cm.$^{-1}$ was seen. All four transitions appeared continuous, and at 0.013 mm., the 117,030 cm.$^{-1}$ transition extended from 113,100 to 122,200 cm.$^{-1}$. The low frequency edge of the 111,240 cm.$^{-1}$ transition was 108,600 cm.$^{-1}$ while the high frequency edge was obscured by the 117,030 cm.$^{-1}$ transition. The 101,830 cm.$^{-1}$ transition extended from 100,300 to 103,600 cm.$^{-1}$ and the 95,490 cm.$^{-1}$ from 93,820 to 96,990 cm.$^{-1}$.

These bands merged to give continuous absorption when the pressure was increased to 0.036 mm. At this pressure a transition with a maximum at 89,065 cm.$^{-1}$ appeared. This transition was associated with vibrational structure. The high frequency members became visible at 0.036 mm. The lowest frequency member at 83,015 cm.$^{-1}$ did not appear until the pressure was increased to 0.200 mm. The vibrational bands were sharp and were shaded toward the red.

At 5.0 mm. pressure in the two meter absorbing column, a region of continuous absorption with a maximum at 76,430 cm.$^{-1}$ appeared, which extended from 78,740 to 73,850 cm.$^{-1}$. It is not possible to show this transition in Fig. 1. This absorption region was photographed against the background of the line spectra of the hydrogen molecule, and absorption coefficients were obtained at equally spaced frequencies over the region. The f-number of this transition was estimated to be about 4.5×10^{-5} which is only about 0.008 as large as the next weakest transition at 89,065 cm.$^{-1}$. In addition there may be an extremely weak absorption band with maximum at about 60,000 cm.$^{-1}$ which appeared only when the pressure was increased to 20 mm. in a two meter column. It is possible under these circumstances that these transitions are not due to CHF_3, but to traces of an impurity which we were not able to detect in the mass spectrographic analysis.

Discussion

An attempt will be made here to interpret changes in the electronic spectra which result from substitution of one hydrogen by fluorine in CH_4 and one fluorine by hydrogen in CF_4. This correlation of energy levels will be extended to CH_2F_2.[8]

The ground state electronic configuration of CH_4 may be formulated in the notation of Mulliken[9] as $(1s_C)^2(sa_1)^2(pt_2)^6,{}^1A_1$. The lowest ionization potential corresponds to removal of an electron from the triply degenerate molecular orbital belonging to the representation T_2 in T_d symmetry. The orbitals may be approximated as linear combinations of 2p carbon functions with combinations of 1s hydrogen functions of proper symmetry. The ground state configuration of CF_4 may be formulated in a similar way, with $2p\sigma$ of fluorine instead of 1s of hydrogen.

---

(8) P. Wagner and A. B. F. Duncan, THIS JOURNAL, **77**, 2609 (1955).

(9) R. S. Mulliken, *J. Chem. Phys.*, **3**, 517 (1935).

TABLE I

TERM VALUES OF ELECTRONIC TRANSITIONS IN METHANE, FLUOROMETHANES AND CARBON

	CH_4	CH_3F	CH_2F_2	CHF_3	CF_4	C
Ion configuration	$(pt_2)^5$	$(\pi e)^3$	(b_1)	(σa_1)	$(pt_2)^5$	$2s^22p$
First I.P. (cm.$^{-1}$)	105,850[a]	103,300	101,286	111,650	143,680	90,878
Molecular state configuration	$(pt_2)^5 3s$	$(\pi e)^3 3s$	$(b_1)3s$	$(\sigma a_1)3s$	$(pt_2)3s$	$2s^22p3s$
Absorption maximum	82,000[b]	75,400	74,860	89,065	110,500	
Term value of 3s	23,850	27,900	26,426	22,585	33,180	28,870
Molecular state configuration		$(\pi e)^3 4s$		$(\sigma a_1)4s$		$2s^22p4s$
Absorption maximum		91,740		101,830		
Term value of 4s		11,560		9,820		12,540
Ion configuration		(σa_1)	(b_2)	$(\pi e)^3$		
Second I.P.		123,200	107,100	131,800		
Molecular state configuration		$(\sigma a_1)3s$	$(b_2)3s$	$(\pi e)^3 3s$		
Absorption maximum		85,338	80,855	95,490		
Term value of 3s		37,862	26,245	36,310		
Molecular state configuration		$(\sigma a_1)4s$		$(\pi e)^3 4s$		
Absorption maximum		109,100		117,030		
Term value of 4s		14,100		14,770		

[a] C. A. McDowell and J. W. Warren, *Disc. Faraday Soc.*, **16**, 18 (1951). [b] G. Moe and A. B. F. Duncan, THIS JOURNAL, **74**, 3140 (1952). [c] See reference 8. [d] See reference 3.

In CH_3F, the (pt_2) orbital will be split into a totally symmetrical (σa_1) orbital and a doubly degenerate (πe) orbital. Mulliken[10] suggested that these orbitals were associated with lower ionization potentials than the potential of a non-bonding fluorine orbital and that the lowest ionization potential probably was associated with the (πe) orbital. The (πe) orbital is largely localized in the CH_3 group, and the lowest ionization potentials of CH_4 and CH_3F were expected to be roughly the same. Ionization from (σa_1) which is approximately $2p\sigma(C) + 2p\sigma(F)$ is expected to require a somewhat higher energy. The lower excited states of CH_3F are expected to correspond to excitation from these two orbitals.

A proposed correlation of the ionization limits and some related states of CH_4 and CH_3F is shown on the left side of Fig. 2, with the splitting discussed above shown by dashed lines. The excited states are possibly atomic like and may be described as Rydberg states. Possible configurations (omitting closed shells) are shown on the diagram. Correlation with corresponding atomic terms of carbon is shown in Table I. In CH_4, the lowest excited transition is very broad and it is not completely resolved from the strong absorption at the ionization limit. It is quite possible therefore that the higher (σa_1) and (πe) states of CH_3F are correlated with states of CH_4 which cannot be resolved. The observed transitions of CH_3F can be fitted approximately into two Rydberg series: $\nu(\text{cm.}^{-1}) = 103{,}240 - R'(n - 0.05)^2$, $n = 2, 3, \ldots$, for the (πe) states and $\nu = 123{,}200 - R'(n - 0.32)^2$, $n = 2, 3, \ldots$, for the (σa_1) states. The lowest ionization limit is in agreement with the electron impact value.[11] In more recent work, Frost and McDowell[12] found two higher ionization potentials at 14.10 and 16.89 e.v. (113000 and 136260 cm.$^{-1}$). The strong transition centered at about 109000 cm.$^{-1}$ may be associated with the 14.10 e.v. potential, but we prefer our interpretation as a Rydberg series member, particularly since there is evidence for one higher member (not clearly shown in Fig. 1). Our second ionization is thus apparently higher than the electron impact value. But there is some doubt attached to any extrapolation, such as we have made, in which series members close to the limit are not resolved.

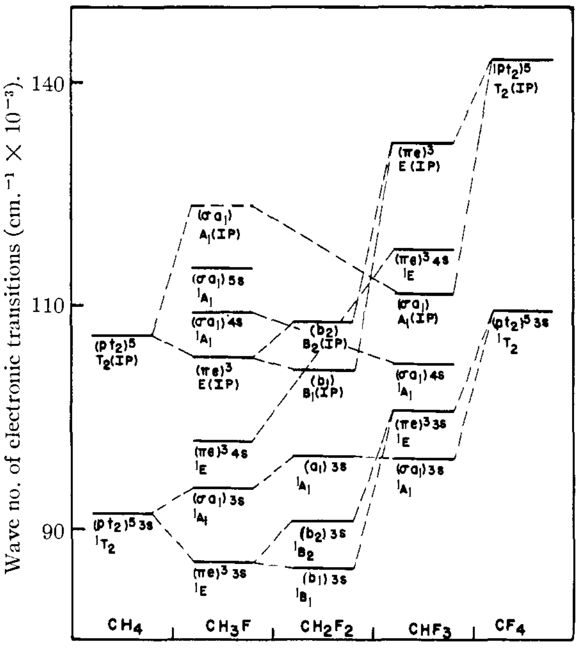

Fig. 2.—Electronic energy levels of methane and of fluoromethanes.

Transitions to the excited (πe) states are all continuous, as is to be expected from the Jahn–Teller principle. The single transition with vibrational structure is to the lowest (σa_1) state. Transitions to the higher (σa_1) states are relatively narrow and vibrational transitions, if they exist, may be unresolved at the high frequencies of transition.

Correlation between states of CF_4 and CHF_3 might be expected on the same basis, but with an

---

(10) R. S. Mulliken, *Phys. Rev.*, **47**, 413 (1935).

(11) C. A. McDowell and B. C. Cox, *J. Chem. Phys.*, **22**, 946 (1954).

(12) D. C. Frost and C. A. McDowell, *Proc. Roy. Soc.* (*London*), **A241**, 194 (1957).

important difference. The (σa_1) orbital in CHF_3 is partly localized in the C–H bond and is believed to be associated with a lower ionization potential than (πe) which is here principally concerned in C–F bonding. It might be expected that the ionization potential from a (σa_1) orbital, approximately described as $2p\sigma(C) + 1s\ (H)$, may not be very different from the lowest ionization potential of methane. The lowest ionization limit is difficult to locate precisely because of interfering absorption of traces of oxygen and the low frequency end of a broader more intense (πe) transition which has a maximum at slightly higher frequencies. But there is definite evidence that such a limit occurs in the expected region. Furthermore the transition at 89,065 cm.$^{-1}$, which shows resolved vibrational structure can be fitted with the relatively narrow transition at 101,830 cm.$^{-1}$ to a series which converges at about 111,650 cm.$^{-1}$. The formula is $\nu(\text{cm.}^{-1}) = 111{,}650 - R/(n + 0.15)^2$ with $n = 2{,}3$. The (σa_1 states connected with this ionization potential are expected to resemble atomic states. There is qualitative correlation here also between the 3s and 4s term value of carbon (Table I) and correlation also with the lower Rydberg series in CH_3F.

The (πe) ionization limit in CHF_3 should correspond roughly however to the (σa_1) ionization limit in CH_3F, and this hypothesis is supported by the qualitative fit of the transitions at 95,490 and 117,030 cm.$^{-1}$ into a series $\nu = 130{,}500 - R/(n - 0.26)^2$ with $n = 2{,}3$. The correspondence between (σa_1) ns terms of CH_3F and $(\pi e)^3$ ns terms of CHF_3 shown in Table I, is believed to be significant and lends confidence to the general qualitative interpretation of the states of both molecules. It is believed that the electronic spectrum of CHF_3 is complete as described here, although it is possible that the two very weak transitions at 76,430 and 60,000 cm.$^{-1}$ may be real and that other electronic levels may be found at higher pressures and at higher resolution.

The correlation between levels of CH_4 and CH_3F and CF_4 and CHF_3 may be extended to the electronic levels of CH_2F_2 observed by Wagner and Duncan. The principal change in electronic configuration will result from splitting of the E states of CH_3F and CHF_3 into B_1 and B_2 states which will probably not differ greatly in energy. At the same time the differences in significance of (πe) and (σa_1) orbitals in CH_3F and CHF_3 will disappear, and the energies of the orbitals b_1, b_2 (from πe) and a_1 (from (σa_1)) will be rather close together. Reconsideration of the spectrum of CH_2F_2[8] leads to the suggestion that strong absorption maxima at 107,000 and 101,290 cm.$^{-1}$ might actually correspond to two ionization limits which may be correlated with the lowest ionization potential of CH_3F (and the higher ionization potential of CHF_3). One limit in CH_2F_2 could be associated with ionization from a b_1 orbital and the other from b_2. The two lowest excited states of CH_2F_2 appear to be correlated in the same way with the lowest state of CH_3F and could correspond thus to 3s terms of the B_1 and B_2 states of $CH_2F_2^+$. The similarity in numerical values of 3s terms based on this assumption, to similar terms throughout the series of molecules considered here and to terms of the carbon atom, is shown in Table I. We may assume further that the next higher state in CH_2F_2 is of type A_1, from its similarity in vibrational structure to the lowest (σa_1) states of CH_3F and CF_3H and that it is the 3s term based on the lowest A_1 state of $CH_2F_2^+$. Taking this term as 26,300 cm.$^{-1}$ we obtain 115,331 cm.$^{-1}$ as the energy of ionization from the a_1 orbital of CH_2F_2. This value is approximately halfway between the ionization potentials of (σa_1) in CH_3F and CHF_3. The proposed correlations between excited states of all the molecules discussed above is shown in Fig. 2, where the analogous states are joined by dashed lines.

Tentative analyses of the vibrational structure of the lowest (σa_1) transitions in CH_3F and CF_3H are shown in Tables II and III. These tables require little comment. In Table II, the frequency ν_2 is believed to be a symmetrical CH_3 deformation vibration with a value 1278 cm.$^{-1}$ corresponding to the normal state value 1464 cm.$^{-1}$ for this mode. The frequency ν_3 is possibly a C–F stretching mode with an excited state value 975 cm.$^{-1}$ and a ground

TABLE II

VIBRATIONAL STRUCTURE IN THE 82,338 CM.$^{-1}$ TRANSITION IN CH_3F

Frequency (in cm.$^{-1}$)	Assignment
80,995	ν_0
81,972	$\nu_0 + \nu_3$
82,260	$\nu_0 + \nu_2$
82,941	$\nu_0 + 2\nu_3$
83,221	$\nu_0 + \nu_2 + \nu_3$
83,474	$\nu_0 + 2\nu_2$
84,187	$\nu_0 + \nu_2 + 2\nu_3$
84,438	$\nu_0 + 2\nu_2 + \nu_3$
84,669	$\nu_0 + 3\nu_2$
85,179	$\nu_0 + \nu_2 + 3\nu_3$
85,338	$\nu_0 + 2\nu_2 + 2\nu_3$
85,783	$\nu_0 + 4\nu_2$
86,276	$\nu_0 + 2\nu_2 + 3\nu_3$
86,919	$\nu_0 + 5\nu_2$
87,438	$\nu_0 + 3\nu_2 + 3\nu_3$

TABLE III

VIBRATIONAL STRUCTURE IN THE 89,065 CM.$^{-1}$ TRANSITION IN CHF_3

Frequency (in cm.$^{-1}$)	Assignment
83,015	ν_0
83,455	$\nu_0 + \nu_3$
83,821	$\nu_0 + 2\nu_3$
84,229	$\nu_0 + \nu_2$
84,630	$\nu_0 + \nu_2 + \nu_3$
85,002	$\nu_0 + \nu_2 + 2\nu_3$
85,416	$\nu_0 + 2\nu_2$
85,829	$\nu_0 + 2\nu_2 + \nu_3$
86,206	$\nu_0 + 2\nu_2 + 2\nu_3$
86,606	$\nu_0 + 3\nu_2$
87,010	$\nu_0 + 3\nu_2 + \nu_3$
87,387	$\nu_0 + 3\nu_2 + 2\nu_3$
87,823	$\nu_0 + 4\nu_2$
88,202	$\nu_0 + 4\nu_2 + \nu_3$
88,572	$\nu_0 + 4\nu_2 + 2\nu_3$
89,065	$\nu_0 + 5\nu_2$

state value 1046 cm.$^{-1}$.[13] The observed transitions fit the following formula, derived by a least squares fit.

$$\nu = 80{,}995 + 1278v_2 - 19.0v_2^2 + 975v_3 + 3.8v_3^2 - 21.2v_2v_3$$
$$v_2 = 1..5,\ v_3 = 1..3$$

Analysis of the vibrational structure of the corresponding (σa_1) state of CF_3H, shown in Table III, utilizes ν_2 = 1191 cm.$^{-1}$ and ν_3 = 446 cm.$^{-1}$. The former is interpreted as a symmetrical C–F stretching mode with normal state value of 1209 cm.$^{-1}$, while ν_3 is interpreted as a CF_3 symmetrical deformation mode with normal state value 699 cm.$^{-1}$.[14] The frequencies of Table III fit a formula, derived by least squares fit

$$\nu = 83.015 + 1191v_2 + 3.4v_2^2 + 446v_3 - 18.2v_3^2 - 9.8v_2v_3$$
$$v_2 = 1..5,\ v_3 = 1,2$$

---

[13] F. Andersen, B. Bak and S. Brodersen, *J. Chem. Phys.*, **24**, 989 (1956).

[14] H. D. Rix, *ibid.*, **21**, 1077 (1953).

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Thermodynamics of Aqueous Hydrogen Chromate and Dichromate Ions. Heats of Formation of Chromates and Dichromates

BY LOREN G. HEPLER[1]

RECEIVED JULY 11, 1958

New thermodynamic calculations based on results of earlier calorimetric investigations have been carried out and heats of the reactions $HCrO_4^-(aq) = H^+(aq) + CrO_4^{=}(aq)$ and $Cr_2O_7^{=}(aq) + H_2O = 2HCrO_4^-(aq)$ have been obtained from these calculations. These reaction heats have been combined with entropies and free energies from the literature to obtain new values for the entropies of $Cr_2O_7^{=}(aq)$ and $HCrO_4^-(aq)$. Also, from the heats of the above reactions, the heat of solution of $(NH_4)_2Cr_2O_7(c)$ and the heat of reaction of $CrO_3(c)$ with $OH^-(aq)$, it has been shown that the heats of formation of $CrO_3(c)$ and $(NH_4)_2Cr_2O_7(c)$ are consistent. Heats of formation of $HCrO_4^-(aq)$, $Cr_2O_7^{=}(aq)$, $CrO_4^{=}(aq)$, $K_2Cr_2O_7(c)$ and $K_2CrO_4(c)$ and free energies of formation of $HCrO_4^-(aq)$, $Cr_2O_7^{=}(aq)$ and $CrO_4^{=}(aq)$ have been calculated. The relation between calorimetric and equilibrium investigations of various Cr(IV) species in aqueous solution has been discussed.

As a result of calculations made to determine the optimum conditions for a reasonably direct calorimetric investigation of the aqueous hydrogen chromate ion, $HCrO_4^-$, it became apparent that results of heat of solution and reaction experiments already reported[2] from this Laboratory were sufficient to give the desired information about $HCrO_4^-(aq)$. Some of the calculations of heats of formation and entropies given in the earlier paper[2] are incorrect because of the unjustified neglect of $HCrO_4^-(aq)$. Results of correct and more complete calculations, reported in this paper, yield directly the desired information about $HCrO_4^-(aq)$ and also bring the heats of formation of $CrO_3(c)$ and $(NH_4)_2Cr_2O_7$ into accord,[3] thus making possible reliable calculations of a number of heats and free energies of formation.

The important species in a weakly acidic aqueous solution of Cr(VI) can be deduced from the equilibrium constants[4–6] for equilibria 1, 2, 3 and 4, all at 25°

$$HCrO_4^-(aq) = CrO_4^{=}(aq) + H^+(aq) \quad (1)$$
$$H_2CrO_4(aq) = H^+(aq) + HCrO_4^-(aq) \quad (2)$$
$$Cr_2O_7^{=}(aq) + H_2O = 2HCrO_4^-(aq) \quad (3)$$
$$HCr_2O_7^-(aq) = H^+(aq) + Cr_2O_7^{=}(aq) \quad (4)$$

In solutions in which the total Cr(VI) concentration is between about 10^{-3} and 5×10^{-2} M and the pH is about 3, the important Cr(VI) species are $HCrO_4^-(aq)$ and $Cr_2O_7^{=}(aq)$. These conditions of Cr(VI) and H^+ concentration are pertinent to the calculations that follow.

The heat of solution of $K_2Cr_2O_7(c)$ in dilute $HClO_4$ has been measured at a number of total Cr(VI) concentrations[2] denoted by $\Sigma(Cr)$. The two important reactions that occur in this process are given by equations 5 and 6 and equation 7 gives the

$$K_2Cr_2O_7(c) + H_2O = 2K^+(aq) + 2HCrO_4^-(aq) \quad \Delta H_5 \quad (5)$$
$$K_2Cr_2O_7(c) = 2K^+(aq) + Cr_2O_7^{=}(aq) \quad \Delta H_6 \quad (6)$$
$$(x + y)K_2Cr_2O_7(c) + xH_2O = 2(x + y)K^+(aq) + 2xHCrO_4^-(aq) + yCr_2O_7^{=}(aq) \quad (x + y)\Delta H_7 \quad (7)$$

total calorimetric reaction where x and y represent the number of moles of $K_2Cr_2O_7(c)$ that dissolve to give $HCrO_4^-(aq)$ and $Cr_2O_7^{=}(aq)$, respectively. ΔH_7 represents the calorimetrically determined heat content change per mole of $K_2Cr_2O_7$ and ΔH_5 and ΔH_6 represent the heat content changes of reactions 5 and 6 per mole of $K_2Cr_2O_7(c)$. Equation 8 gives ΔH_7 in terms of x, y, ΔH_5 and ΔH_6. This equation has been rearranged to equation 9 where

$$x\Delta H_5 + y\Delta H_6 = (x + y)\Delta H_7 \quad (8)$$
$$(X/\Delta H_7) = -(Y/\Delta H_7) \quad (\Delta H_6/\Delta H_5) + (1/\Delta H_5) \quad (9)$$

X and Y represent $x/(x + y)$ and $y/(x + y)$, respectively.

From the equilibrium constant (at zero ionic strength) for reaction 3 given by Tong and King[5] and a known value of $\Sigma(Cr)$, a first approximation was made to the concentrations of $HCrO_4^-(aq)$ and $Cr_2O_7^{=}(aq)$. These calculations were based on relations 10 and 11. The $(HCrO_4^-)$ and $(Cr_2O_7^{=})$

$$\Sigma(Cr) = 2(Cr_2O_7^{=}) + (HCrO_4^-) \quad (10)$$
$$\Sigma(Cr) = 2(HCrO_4^-)/K_3 + (HCrO_4^-) \quad (11)$$

so obtained were used to calculate to a first approximation the ionic strength of the solution under con-

---

[1] Alfred P. Sloan Research Fellow.

[2] C. N. Muldrow, Jr., and L. G. Hepler, THIS JOURNAL, **79**, 4045 (1957).

[3] C. A. Neugebauer and J. L. Margrave, *J. Phys. Chem.*, **61**, 1429 (1957).

[4] J. D. Neuss and W. Rieman, THIS JOURNAL, **56**, 2238 (1934).

[5] J. Y. Tong and E. L. King, *ibid.*, **75**, 6180 (1953).

[6] W. G. Davies and J. E. Prue, *Trans. Faraday Soc.*, **51**, 1045 (1955).