

Infrared Spectrum of Hydrogen Fluoride*

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The infrared vibration-rotation spectrum of HF has been re-examined out through $J=11$ for the fundamental, and through $J=8$ for the first overtone. Five lines of the pure rotational spectrum of HF ($J=10, 11, 12, 14, 15$) have been observed in absorption and emission between 15 and 24 μ . Extension of the measurement to larger J values makes it possible to observe the effect of the term $H_v J^3(J+1)^3$ in the energy, and to obtain H_v . With the new data the molecular constants have been re-evaluated by IBM machine. These constants when used with the energy expression permit accurate prediction of the observed energy levels.

INTRODUCTION

THE vibration-rotation spectrum of the hydrogen fluoride molecule has been the subject of a great many investigations of which the earliest was by Imes¹ who examined the spectra of the hydrogen halides under high dispersion. In 1923 Schaefer and Thomas² observed the overtone with a prism. Considerably later, Kirkpatrick and Salant³ photographed the second and third overtones with a concave grating and gave very precise band centers for these bands. This work, including the first overtone, was repeated by Naudé and Verleger⁴ in 1950. They derived both vibrational and rotational constants. At about the same time the fundamental and first overtone of HF were remeasured and the fundamental and first overtone of DF were measured for the first time by Talley, Kaylor, and Nielsen.⁵ Vibrational and rotational constants were also given in this paper. Quite recently the flame spectrum of hydrogen fluoride, observed with a quartz-equipped prism spectrometer, has been reported by Benedict, Bullock, Silverman, and Grosse.⁶ These authors also give values of several of the molecular constants.

Because the hydrogen fluoride molecule is extremely anharmonic, it is necessary to include terms in $(v+\frac{1}{2})$ and $J(J+1)$ of higher power than the square in the energy in order to represent the data satisfactorily. Such a theoretical treatment was carried out for the diatomic molecule by Dunham⁷ who included terms in the potential energy through q .⁶ The reader is also

referred to Chapter III in Herzberg's⁸ book on diatomic molecules in which the constants used later in this paper are treated in detail. Thus, the constants $z_e\omega_e$ and D_e are sufficiently large to make significant contributions to the line positions for all v and J , and indeed H , the coefficient of the $J^3(J+1)^3$ term, is of the same order of magnitude as D for carbon monoxide and begins to make significant contributions to the line positions at about $J=9$. Because up to the present no lines with $J>8$ have been measured, H has not previously been included. Inclusion of the constant H will, therefore, necessitate revision of the values of the previously given constants.

The present remeasurement of the fundamental and first overtone of HF was undertaken in connection with a study of intensities and line shapes of the vibration-rotation lines (to be published elsewhere), when it became apparent that measurements on lines through $J=11$ were easily attainable. At the same time it became evident that measurements on the pure rotational spectrum of HF from $J=10$ to $J=15$ (15–25 μ region) were also feasible in absorption and emission. The authors concluded that it would be of some value to redetermine the HF constants with the new data which became available.

The pure rotational spectrum of HF was first investigated in 1927 by Czerny⁹ who found three lines for $J=1, 3,$ and 4 between 48 and 125 μ . Pure rotational lines are usually of sufficient intensity to be observed only in the far infrared and microwave region. However, the authors have been able to discover reports of several pure rotation spectra observed at wavelengths shorter than 25 μ . The first of these is that of the troublesome water vapor spectrum¹⁰ which is always present in spectrometers even after assiduous drying of the air in the optical path. The second is the emission spectrum of hydrogen chloride¹¹ which was developed

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¹ E. S. Imes, *Astrophys. J.* **50**, 250 (1919).

² C. Schaefer and M. Thomas, *Z. Physik* **12**, 330 (1923).

³ D. E. Kirkpatrick and E. O. Salant, *Phys. Rev.* **48**, 945 (1935).

⁴ S. M. Naudé and H. Verleger, *Proc. Phys. Soc. (London)* **A63**, 470 (1950).

⁵ Talley, Kaylor, and Nielsen, *Phys. Rev.* **77**, 529 (1950).

⁶ Benedict, Bullock, Silverman, and Grosse, *J. Opt. Soc. Am.* **43**, 1106 (1953).

⁷ J. L. Dunham, *Phys. Rev.* **41**, 721 (1932).

⁸ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1951), second edition, Chap. III.

⁹ M. Czerny, *Z. Physik* **44**, 235 (1927).

¹⁰ Randall, Dennison, Ginsburg, and Weber, *Phys. Rev.* **52**, 160 (1937).

¹¹ J. Strong, *Phys. Rev.* **45**, 877 (1934).

TABLE I. Vacuum wave numbers of the vibration-rotation lines of $0\leftarrow 1$ of HF (band center 3961.64 cm^{-1}).

Assignment	Obs $\bar{\nu}\text{ cm}^{-1}$	Calc $\bar{\nu}\text{ cm}^{-1}$	$\Delta(O-C)$	Assignment	Obs $\bar{\nu}\text{ cm}^{-1}$	Calc $\bar{\nu}\text{ cm}^{-1}$	$\Delta(O-C)$
R(0)	4001.27	4001.196	+0.074	P(1)	3920.45	3920.542	-0.092
R(1)	4039.23	4039.159	+0.071	P(2)	3877.89	3877.952	-0.062
R(2)	4075.51	4075.482	+0.028	P(3)	3833.96	3833.915	+0.045
R(3)	4110.16	4110.110	+0.050	P(4)	3788.47	3788.502	-0.032
R(4)	4143.01	4143.017	-0.007	P(5)	3741.71	3741.748	-0.038
R(5)	4174.11	4174.142	-0.032	P(6)	3693.75	3693.714	+0.036
R(6)	4203.35	4203.442	-0.092	P(7)	3644.44	3644.454	-0.014
R(7)	4230.97	4230.898	+0.072	P(8)	3594.00	3594.024	-0.024
R(8)	4256.45	4256.455	-0.005	P(9)	3542.49	3542.479	+0.011
R(9)	4279.98	4280.085	-0.105	P(10)	3489.97	3489.878	+0.092
R(10)	4301.70	4301.760	-0.060	P(11)	3436.36	3436.277	+0.083
R(11)	4321.48	4321.453	+0.027				

in a low-temperature flame of chlorine in hydrogen. The pure rotational spectrum of hydrogen chloride has not, however, been extended to include these lines in absorption. Recently, several lines of the pure rotation emission spectrum of OH^{12} and of the pressure induced spectrum of H_2^{13} have been reported in the literature at wavelengths between $15\text{--}20$ and $8\text{--}13\ \mu$, respectively.

EXPERIMENTAL DETAILS AND RESULTS

Vibration-Rotation Bands

The difficulties encountered by Talley, Kaylor, and Nielsen in handling HF which were translated into difficulties in observing the spectrum, have largely been overcome with the use of new techniques. They finally resorted to the use of cells and windows made entirely of fluorothene. The transmission properties of fluorothene are, however, not very satisfactory and lines beyond $P(7)$ at 2743.1 cm^{-1} in deuterium fluoride were not observed. Also, it was not found very convenient to heat the cell and windows which further limited the range of the observations.

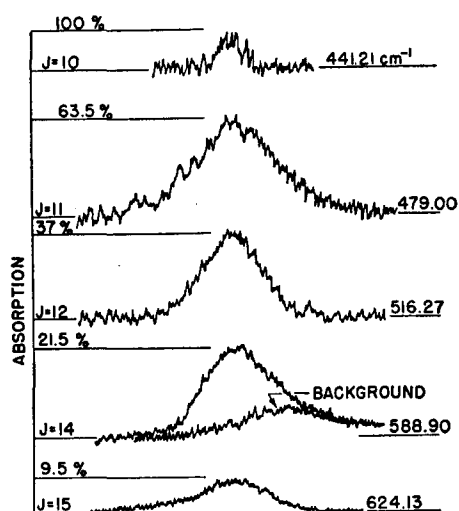


FIG. 1. Pure rotational lines (absorption) of HF.

¹² R. P. Madden and W. S. Benedict, *J. Chem. Phys.* **23**, 408 (1955).

¹³ Ketelaar, Calpa, and Hooge, *J. Chem. Phys.* **23**, 413 (1955).

With continued experience the techniques of handling HF and retaining it in absorption cells without having it etch the windows or become contaminated have improved to the point where it is now possible to conduct experiments on it with about the same ease as with noncorrosive gases. The present gas-handling system and absorption cells were entirely of monel and nickel with all joints silver soldered. Clear polished CaF_2 windows were pressure sealed to the cell with the use of fluorothene or Teflon gaskets. The whole system was carefully cleaned of soldering flux, evacuated, and baked at 120°C . Fluorine gas was admitted at this elevated temperature and permitted to remain in the system for 24 hours for conditioning. The cell was mounted rigidly in the spectrograph beam with a gas line running to the system. Cell and leads were maintained at 120° throughout the runs made. Under these conditions the system has been in service for some months with no trouble, etching of windows, or evidence of polymers.

The spectra were recorded on the University of Tennessee spectrograph equipped with a Bausch and Lomb 15 000 lines-per-inch grating and a lead sulfide detector. Twenty-three lines of the fundamental were observed in first order of the grating, and seventeen lines of the first overtone were measured in second order of the grating. Calibration was carried out using the first overtone lines of carbon monoxide¹⁴ as secondary standards. The vacuum wave numbers of the HF lines are given in Tables I and II.

Pure Rotational Spectrum

The pure rotational spectrum of HF was observed in both emission and absorption. The emission spectrum was taken with a Perkin-Elmer Model 21 double-beam spectrophotometer with the sample cell in the sample position, but with the sample beam shuttered; and with a Perkin-Elmer Model 12C single-beam spectrometer, modified for double pass, with the source shuttered. The cell was of monel, 10-cm long, 2 inches in diameter, equipped with silver chloride windows, $\frac{1}{4}$ inch thick,

¹⁴ Plyler, Benedict, and Silverman, *J. Chem. Phys.* **20**, 180 (1952).

TABLE II. Vacuum wave numbers of the vibration-rotation lines of 0←2 of HF (band center 7751.24 cm⁻¹).

Assignment	Obs $\bar{\nu}$ cm ⁻¹	Calc $\bar{\nu}$ cm ⁻¹	$\Delta(O-C)$	Assignment	Obs $\bar{\nu}$ cm ⁻¹	Calc $\bar{\nu}$ cm ⁻¹	$\Delta(O-C)$
R(0)	7789.18	7789.286	-0.106	P(1)	7710.27	7710.140	+0.130
R(1)	7824.30	7824.234	+0.066	P(2)	7666.11	7666.043	+0.067
R(2)	7856.07	7856.037	+0.033	P(3)	7618.89	7619.004	-0.114
R(3)	7884.47	7884.653	-0.183	P(4)	7569.06	7569.083	-0.023
R(4)	7910.12	7910.044	+0.076	P(5)	7516.48	7516.344	+0.136
R(5)	7932.19	7932.177	+0.013	P(6)	7460.62	7460.853	-0.223
R(6)	7950.95	7951.026	-0.070	P(7)	7402.84	7402.681	+0.159
R(7)	7966.71	7966.546	+0.164	P(8)	7341.87	7341.902	-0.032
R(8)	7978.65	7978.732	-0.082				

and was heated to about 320°C. While at this temperature, a stream of air was blown on the windows in an effort to keep them cooler than the vapor and cell, and to prevent their distortion. The silver chloride windows have usable transparency to about 23 microns wavelength. In the course of the experiments with HF the windows became coated with a yellowish-black deposit, and as the experiments proceeded the transmission from 16–23 μ gradually deteriorated to opacity. The windows, however, appeared opaque to visible light long before the lack of transmission at longer wavelengths rendered them unusable.

The heating of the cell serves a twofold purpose: First, at room temperature and at the one-half to one atmosphere pressure used in these experiments, the polymers of HF absorb sufficiently in the 16–23 μ region so that the cell is practically opaque throughout the whole region. Secondly, the intensity of the higher rotational transitions varies directly as N_J , the number of molecules per unit volume in the rotational state from which the transition originates. N_J increases rapidly with temperature for the higher rotational states.

Hydrogen fluoride is sufficiently depolymerized at 120°C to sensibly eliminate the polymer absorptions. At this temperature the lines with $J=10, 11,$ and 12 are observable in absorption. It is however necessary to go to higher temperatures to observe the emission spectrum and the higher J absorption lines. They were readily observable at 325°C.

The absorption spectrum was observed with The University of Tennessee spectrograph equipped with a Michigan 1200 lines-per-inch grating and a thermocouple. The carbon monoxide fundamental observed in fourth order served as a calibration for these measurements. Figures 1 and 2 show the spectra observed, and the vacuum wave numbers are given in Table III.

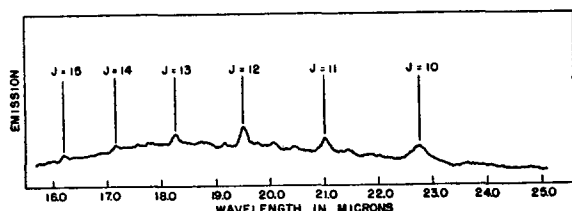


FIG. 2. Pure rotational lines (emission) of HF.

The apparent absorption did not increase with increasing temperature nearly as much as would be expected on the basis of the increased population of the higher rotational states. This is presumably because of the spontaneous emission of radiation. In all three spectrometers the infrared path for absorption measurements was chopped after the beam had passed through the cell so that the emitted radiation was also chopped. Presumably, if the beam could have been chopped before passage through the cell, the apparent absorption would not be decreased by this emission. This point, however, has not been examined. When observed in emission the apparent intensities of the lines did not increase nearly as much with increasing temperature as would be expected from the increase in population of the higher J states because of self-absorption. The emission lines were observed upon a continuous radiation background which probably emanated from the cell windows.

Analysis of the Data

The energy expression which contains sufficient terms to represent the data satisfactorily is given below as Eq. (1).

$$E/hc(\text{cm}^{-1}) = E_0/hc + \{\omega_e - x_e\omega_e(v + \frac{1}{2}) + y_e\omega_e(v + \frac{1}{2})^2 - z_e\omega_e(v + \frac{1}{2})^3\}(v + \frac{1}{2}) + B_e J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 - \{\alpha_e - \gamma_e(v + \frac{1}{2})\}(v + \frac{1}{2})J(J+1). \quad (1)$$

TABLE III. Vacuum wave numbers of the pure rotation lines of hydrogen fluoride.

Assignment	Obs. $\bar{\nu}$ cm ⁻¹	Calc. $\bar{\nu}$ cm ⁻¹	$\Delta(O-C)$
$J=1$	82.56 ^a	82.145	+0.41
$J=2$
$J=3$	163.44 ^a	163.886	-0.45
$J=4$	204.94 ^a	204.477	+0.46
...
$J=10$	441.21	441.090	+0.120
$J=11$	479.00	478.933	+0.067
$J=12$	516.27	516.203	+0.067
$J=13$
$J=14$	588.90	588.865	+0.035
$J=15$	624.13	624.180	-0.050

^a See reference 9.

TABLE IV. Collected constants for HF from present investigation.

Constant	<i>K, S, and N</i>	Ref.
$\bar{\nu}_0(0\leftarrow 1)$	$3961.641 \pm 0.065 \text{ cm}^{-1}$	a
$\bar{\nu}_0(0\leftarrow 2)$	7751.238 ± 0.136	b
B_0	20.5534 ± 0.0060	a
B_1	19.7819 ± 0.0074	a
B_2	19.0279 ± 0.0146	b
D_0	0.002114 ± 0.000049	a
D_1	0.002069 ± 0.000093	a
D_2	0.002038 ± 0.000151	b
H_0	$(1.757 \pm 1.05) \times 10^{-7}$	a
H_1	$(2.144 \pm 3.75) \times 10^{-7}$	a
ω_e	4137.25_3	c
$x_e\omega_e$	88.72_6	c
$y_e\omega_e$	0.533_4	c
$z_e\omega_e$	-0.021_1	c
B_e	20.945_6	
D_e	0.00213_1	
α_e	0.788_8	
γ_e	0.0087_3	
β_e	-0.00003_8	

* Calculated using 23 lines from fundamental and 5 pure rotational lines. 95% confidence interval.

^b Calculated from first overtone. 95% confidence interval.

^c Calculated from $\bar{\nu}_0(0\leftarrow 1)$, $\bar{\nu}_0(0\leftarrow 2)$ this paper, and $\bar{\nu}_0(0\leftarrow 3)$, $\bar{\nu}_0(0\leftarrow 4)$, reference 3.

E_0 represents a constant term which does not appear in the wave-number relation of the spectral lines. ω_e is the harmonic wave number for infinitesimal amplitudes. $x_e\omega_e$, $y_e\omega_e$, and $z_e\omega_e$ are anharmonic constants involving potential energy constants through q^6 . B_e is the equilibrium rotational constant, $h/8\pi^2 I_e$. D_e is the centrifugal stretching constant and H_e is an additional rotational constant appearing as a result of the higher-powered potential energy terms. α_e and γ_e are equilibrium values of the vibration-rotation constants and depend upon the potential energy constants. v and J are the vibration and rotation quantum numbers, respectively.

The wave number of a spectral line may be determined by application of the Bohr wave-number condition with the selection rules $\Delta v = \pm 1, 2, \dots$, etc., and $\Delta J = \pm 1$. For example, the wave number of any line in the *R* and *P* branch of the fundamental is given by

$$\begin{aligned} \bar{\nu}(R) = & \bar{\nu}_0(\text{band center}) + (B_0 + B_1)(J+1) \\ & + [(B_1 - B_0) - (D_1 - D_0)](J+1)^2 \\ & - [2(D_1 + D_0) - (H_1 + H_0)](J+1)^3 \\ & - [(D_1 - D_0) - 3(H_1 - H_0)](J+1)^4 \\ & + 3(H_1 + H_0)(J+1)^5 + (H_1 - H_0)(J+1)^6 \quad (2) \end{aligned}$$

$$\begin{aligned} \bar{\nu}(P) = & \bar{\nu}_0(\text{band center}) - (B_0 + B_1)J \\ & + [(B_1 - B_0) - (D_1 - D_0)]J^2 \\ & + [2(D_1 + D_0) - (H_1 + H_0)]J^3 \\ & - [(D_1 - D_0) - 3(H_1 - H_0)]J^4 \\ & - 3(H_1 + H_0)J^5 + (H_1 - H_0)J^6. \end{aligned}$$

In Eq. (2) J is the rotational quantum number of the $v=0$ state. Similar expressions may be written for the overtone transitions.

TABLE V. Summary of observed data from all investigations (cm^{-1}).

Constant	<i>K and S</i> ^a	<i>N and V</i> ^b	<i>T, K, and N</i> ^c	<i>B, B, S, and G</i> ^d	<i>K, S, and N</i> ^e
$\bar{\nu}_0(0\leftarrow 1)$	3961.42	3961.31	3961.64
$\bar{\nu}_0(0\leftarrow 2)$...	7751.766	7750.81	7751.84	7751.24
$\bar{\nu}_0(0\leftarrow 3)$	11372.88	11372.574
$\bar{\nu}_0(0\leftarrow 4)$	14831.68	14831.550
B_0	(20.544, 20.540)	20.5352	20.555	20.569	20.553
B_1	...	19.7870	19.795	19.814	19.782
B_2	...	19.0249	19.035	...	19.028
B_3	...	18.2876	18.303
B_4	...	17.5609	17.573
B_e	(20.920, 20.913)	20.9093	20.939	...	20.945 ₆
D_0	0.0022	0.00242	0.00211 ₄
D_1	0.001 ₉	0.00234	0.00206 ₉
D_2	0.003 ₂	0.00226	0.00204
D_3	0.002 ₂
D_4	0.001 ₆
D_e	-0.00215, -0.00215	0.00108	0.002 ₂	...	0.00213 ₁
H_0	1.76×10^{-7}
H_1	2.1×10^{-7}
α_e	0.7523, 0.745	0.7482	0.7705	0.751	0.788 ₈
γ_e	0.005 ₉	...	0.0087 ₃
β_e	0.00025 ₆ , 0.000314	0.0002	-0.00003 ₈

^a See reference 3.

^b See reference 4.

^c See reference 5.

^d See reference 6.

^e Present investigation.

The best data obtained in this investigation were considered to be the wave numbers of the twenty-three lines observed in the fundamental, and the five lines observed in the pure rotational spectrum. Computation of the constants from the data was carried out by the Numerical Analysis Department of the Operations Analysis Division, Oak Ridge Gaseous Diffusion Plant, by means of an IBM calculator. The fundamental and pure rotation data were treated as a separate problem from the first overtone data. The constants obtained are listed in Table IV and are, for the most part, given with a 95% confidence interval. These constants have been used to calculate the wave numbers of the lines in the fundamental, first overtone and the rotational lines and the differences between them and the observed wave numbers appear as columns 3 and 6 in Tables I, II, and III. Theoretical expressions for the constants D_e and β_e , which occur in $D_v = D_e + \beta_e(v + \frac{1}{2})$, and for H_e , are given in reference (8). The calculated values of these constants are 0.002146 cm^{-1} , $-5.7 \times 10^{-5} \text{ cm}^{-1}$ and $1.8 \times 10^{-7} \text{ cm}^{-1}$, respectively, in good agreement with the observed values 0.00213_1 , -3.8×10^{-5} , and $1.76 \times 10^{-7} \text{ cm}^{-1}$ found in Table IV.

The constants ω_e , $x_e\omega_e$, $y_e\omega_e$, and $z_e\omega_e$ may now be calculated from the new band centers $\bar{\nu}_0(0\leftarrow 1)$ and $\bar{\nu}_0(0\leftarrow 2)$ combined with $\bar{\nu}_0(0\leftarrow 3)$ and $\bar{\nu}_0(0\leftarrow 4)$. Calculations were made both with the data of Naudé and Verlerger (reference 4) and those of Kirkpatrick and Salant (reference 3). When the new $\bar{\nu}_0(0\leftarrow 1)$ and $\bar{\nu}_0(0\leftarrow 2)$ were combined with $\bar{\nu}_0(0\leftarrow 3)$ and $\bar{\nu}_0(0\leftarrow 4)$ of reference 4, $y_e\omega_e$ and $z_e\omega_e$ were obtained as -0.1317 cm^{-1} and -0.094 cm^{-1} , respectively. The sign of $y_e\omega_e$ is wrong and the constants are of the same order of magnitude,

which they should not be. When $\tilde{\nu}_0(0\leftarrow 1)$ was combined with $\tilde{\nu}_0(0\leftarrow 2)$, $\tilde{\nu}_0(0\leftarrow 3)$, and $\tilde{\nu}_0(0\leftarrow 4)$ from reference 4, $\gamma_e\omega_e$ and $z_e\omega_e$ were found to be -2.24 cm^{-1} and -0.31 cm^{-1} , respectively. Again, the sign of $\gamma_e\omega_e$ is wrong and both constants would appear to be unreasonably large numerically. On the other hand, when the new $\tilde{\nu}_0(0\leftarrow 1)$ and $\tilde{\nu}_0(0\leftarrow 2)$ were combined with $\tilde{\nu}_0(0\leftarrow 3)$ and $\tilde{\nu}_0(0\leftarrow 4)$ of reference 3, $\gamma_e\omega_e$ and $z_e\omega_e$ became 0.533_4 cm^{-1} and -0.02_1 cm^{-1} , respectively. These constants appear to be of the right orders of magnitude and have the right sign. The values of these constants given in Table IV are, therefore, the ones calculated using reference 3. New values of α_e and γ_e , obtained by plotting the relation $[(B_0 - B_v)/v] = \alpha_e - (v+1)\gamma_e$

using B_0, B_1, B_2 from the present investigation and B_3 and B_4 from the data of reference 3, are given in Table IV. The abnormally large value of α_e given by Talley, Kaylor, and Nielsen from the graph in their Fig. 7 was apparently caused by the fact that their B_1 and B_2 were not sufficiently accurate. The present α_e agrees much better with their preferred value given in their Fig. 4. The D_e and β_e given in Table V were obtained by plotting the present D_0, D_1 , and D_e versus $(v + \frac{1}{2})$.

In conclusion, it is believed that the set of constants from the present investigation given in Table IV form a consistent set and represent the observed data as well as possible at the present time.

Periodic Precipitation*

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The phenomenon of periodic precipitation has been subjected to calculations based on the diffusion-plus-supersaturation model first proposed by Ostwald. The mathematical difficulty caused by an infinite density of Liesegang rings at the original junction between the two solutions is avoided by the introduction of a thin "clear" zone which is supposed to be initially free of reactants. A further simplification results from assuming that one of the reactants is present in considerable excess, so that its diffusion remains essentially unaffected by the precipitation. Calculations show that the ratio between the distances from the initial boundary of two successive rings rapidly approaches a constant value, in agreement with experiment. Results have been obtained for the case where both reactants have the same diffusion coefficient.

INTRODUCTION

WHEN a solution of silver nitrate is poured on top of a column of jelled (to prevent convection) potassium dichromate solution in a test tube, the resulting formation of silver dichromate precipitate does not proceed uniformly as the silver ions diffuse into the gel, but seems rather to occur in bands, with clear spaces inbetween. This phenomenon was discovered by Liesegang¹ over fifty years ago, and is named after him. Shortly afterwards Ostwald² proposed an explanation which, in spite of many objections raised by various authors,³ seems to be essentially correct.

Ostwald suggested that the precipitation is not an equilibrium process, but occurs only when a certain critical value K_c of the concentration product $K = [\text{Ag}^+]^2[\text{Cr}_2\text{O}_7^{2-}]$ has been attained, at which point silver dichromate precipitates until K reaches its equilibrium value. This is certainly a very idealized

picture of supersaturation, but, since the Liesegang phenomenon is probably not seriously dependent on the detailed mechanism of nucleation and growth, we may feel justified in using it as a basis for our calculations.

One may wonder at this point whether the introduction of supersaturation is really necessary in order to account for Liesegang rings, and whether the interaction of the diffusion and precipitation processes is not sufficient for this purpose. Wagner⁴ has shown that if the equilibrium value of K is assumed to be zero, no rings are formed unless supersaturation is present. I have recently been able to extend this conclusion to include cases where the equilibrium K does not vanish, so that supersaturation would seem to play an essential part in periodic precipitation.

THEORY AND CALCULATIONS

Calculations based on Ostwald's model have already been performed by Wagner,⁴ but proved too cumbersome to be carried very far. Nevertheless, with two important exceptions discussed below, our mathematical formulation of the problem will essentially follow Wagner's development. Let $a(x,t)$ and $b(x,t)$ represent the

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² W. Ostwald, *Lehrbuch der Allgemeinen Chemie* (Engelman, Leipzig, 1897).

³ K. H. Stern, *Chem. Revs.* **54**, 79 (1954).

⁴ C. Wagner, *J. Colloid Sci.* **5**, 85 (1950).