

## The Normal Vibrations of Polyatomic Molecules as Calculated by UreyBradley Field. III. A Table of Force Constants

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# The Normal Vibrations of Polyatomic Molecules as Calculated by Urey-Bradley Field.

## III. A Table of Force Constants

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Assuming the Urey-Bradley field for various chemical structures, stretching, bending and repulsive force constants were determined so as to give the best fit with the observed vibration frequencies. The magnitude of these force constants, especially of repulsive constants, was discussed.

### INTRODUCTION

IN the preceding two papers<sup>1,2</sup> in which consistent normal coordinate treatments were applied to twenty simple polyatomic molecules, it was concluded that the Urey-Bradley field is an adequate type of potential energy in analysing the vibrational spectra. The potential energy of molecules due to this field is expressed as follows:<sup>3</sup>

$$V = \sum_i [K_i' r_{i0} \Delta r_i + \frac{1}{2} K_i (\Delta r_i)^2] + \sum_{i < j} [H_{ij}' r_{ij0}^2 \Delta \alpha_{ij} + \frac{1}{2} H_{ij} (r_{ij0} \Delta \alpha_{ij})^2] + \sum_{i < j} [F_{ij}' q_{ij0} \Delta q_{ij} + \frac{1}{2} F_{ij} (\Delta q_{ij})^2], \quad (1)$$

where  $r_i$  is the bond length C—X<sub>i</sub>,  $\alpha_{ij}$  is the bond angle X<sub>i</sub>—C—X<sub>j</sub>,  $q_{ij}$  is the distance between atoms (X<sub>i</sub> and X<sub>j</sub>) which are not bonded directly,  $r_{ij}$  represents  $(r_i r_j)^{\frac{1}{2}}$ ,  $r_{i0}$ ,  $r_{ij0}$ , and  $q_{ij0}$  denote the equilibrium values of these distances, and  $\Delta$  refers to the change in the following symbol from its equilibrium values.  $K'$  and  $K$  are stretching constants,  $H'$  and  $H$  are bending constants, and  $F'$  and  $F$  are repulsive constants.

The purpose of this paper is to apply this potential to the calculation of frequencies of other polyatomic molecules and to obtain a table of force constants  $K$ ,  $H$ ,  $F'$ ,  $F$ , and intramolecular tensions  $\kappa$ , for various chemical structures.\*

### CALCULATION

Three types of molecules, CX<sub>4</sub>, CX<sub>3</sub>—CX<sub>3</sub>, and —CX<sub>2</sub>—CX<sub>2</sub>—, have been dealt with. Since the technique developed by Wilson<sup>4</sup> is quite straightforward, we have used this procedure. Assuming tetrahedral angles ( $\alpha_0 = 109^\circ 28'$ ), and using the  $G$  and  $F$  matrices, the secular equations for these molecules are found to be

$$|\mathbf{GF} - 3M_C \lambda \mathbf{E}| = 0, \quad (2)$$

<sup>1</sup> T. Simanouti, J. Chem. Phys. 17, 245 (1949).

<sup>2</sup> T. Simanouti, J. Chem. Phys. 17, 734 (1949).

<sup>3</sup> H. C. Urey and C. A. Bradley, Phys. Rev. 38, 1969 (1931).

\* The other constants  $K'$  and  $H'$  are represented in terms of  $F'$  and  $\kappa$  (see reference 1, Eqs. (7) and (8)).

<sup>4</sup> E. B. Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

where  $M_C$  is the mass of C atom,  $\mathbf{E}$  is the unit matrix, and  $\lambda$  is  $4\pi^2 c^2 \nu^2$ ,  $c$  and  $\nu$  being, respectively, the velocity of light and the vibration frequency (cm<sup>-1</sup>).

For the  $G$  and  $F$  matrices of CX<sub>4</sub> molecule we have

$$\begin{aligned} G_A &= m, \\ F_A &= a + 3c, \\ G_B &= 3m, \\ F_B &= 2b - 4e, \\ G_T &= \begin{pmatrix} 4+m, & -8 \\ -8, & 16+2m \end{pmatrix}, \\ F_T &= \begin{pmatrix} a-c, & 2k \\ 2k, & 2b \end{pmatrix}. \end{aligned} \quad (3)$$

TABLE I. Force constants and intramolecular tensions.

Stretching force constants $K$ ( $10^5$ dynes/cm)					
C—H	4.8~3.9 <sup>a</sup>	Si—H	2.7		
C—C	2.8~2.0 <sup>b</sup>	Si—Si	1.25		
C—F	3.75	Si—F	5.4		
C—CH <sub>3</sub>	3.7	Si—CH <sub>3</sub>	3.05		
C—Cl	1.75	Si—Cl	2.6		
C—Br	1.45	Si—Br	2.0		
Bending force constants $H$ ( $10^5$ dynes/cm)					
H—C—H	0.4	C—C—H	0.15	H—Si—H	0.15
CH <sub>3</sub> —C—CH <sub>3</sub>	0.2	C—C—F	0.15	CH <sub>3</sub> —Si—CH <sub>3</sub>	0.1
F—C—F	0.15	C—C—Cl	0.1	F—Si—F	0.02
Cl—C—Cl	0.1	C—C—Br	0.1	Cl—Si—Cl	0.04
Br—C—Br	0.05	H—C—Cl	0.05	Br—Si—Br	0.04
		Cl—C—Br	0.05		
Repulsive force constants $F'$ ( $10^5$ dynes/cm)					
H...H	0.0	C...H	-0.05	H...H <sup>c</sup>	-0.03
CH <sub>3</sub> ...CH <sub>3</sub>	-0.05	C...F	-0.1	CH <sub>3</sub> ...CH <sub>3</sub> <sup>c</sup>	-0.02
F...F	-0.3	C...Cl	-0.1	F...F <sup>c</sup>	-0.31
Cl...Cl	-0.1	C...Br	-0.1	Cl...Cl <sup>c</sup>	-0.06
Br...Br	-0.1	H...Cl	-0.05	Br...Br <sup>c</sup>	-0.04
		Cl...Br	-0.1		
Repulsive force constants $F$ ( $10^5$ dynes/cm)					
H...H	0.1	C...H	0.4	H...H <sup>c</sup>	0.04
CH <sub>3</sub> ...CH <sub>3</sub>	0.3	C...F	1.3	CH <sub>3</sub> ...CH <sub>3</sub> <sup>c</sup>	0.03
F...F	1.35	C...Cl	0.6	F...F <sup>c</sup>	0.43
Cl...Cl	0.65	C...Br	0.5	Cl...Cl <sup>c</sup>	0.3
Br...Br	0.5	H...Cl	0.8	Br...Br <sup>c</sup>	0.23
		Cl...Br	0.55		
Intramolecular tensions $\kappa$ ( $10^{-11}$ dynes·cm)					
CH <sub>4</sub> ~CD <sub>4</sub>	0	-CH <sub>2</sub> -CH <sub>2</sub> -	0.2	SiH <sub>4</sub>	0.05
C(CH <sub>3</sub> ) <sub>4</sub>	0.1	C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> D <sub>4</sub>	0.05	Si(CH <sub>3</sub> ) <sub>4</sub>	0.05
CF <sub>4</sub>	0.5	-CF <sub>2</sub> -CF <sub>2</sub> -	0.3	SiF <sub>4</sub>	0.7
CCl <sub>4</sub>	0.3	C <sub>2</sub> F <sub>4</sub>	0.3	SiCl <sub>4</sub>	0.25
CBr <sub>4</sub>	0.3	C <sub>2</sub> Cl <sub>4</sub>	0.1	SiBr <sub>4</sub>	0.15
		C <sub>2</sub> Br <sub>4</sub>	0.1		
		CCl <sub>2</sub> Br, CCl <sub>2</sub> Br <sub>2</sub> , CClBr <sub>3</sub>	0.3		

<sup>a</sup> K<sub>CH</sub> = 4.8 (CH<sub>4</sub>), 4.5 (CH<sub>3</sub>-), 4.2 (CH<sub>2</sub>-), 3.9 (CH-).

<sup>b</sup> K<sub>CC</sub> = 2.8 (C<sub>2</sub>H<sub>4</sub>), 2.0 (C<sub>2</sub>Cl<sub>4</sub>, C<sub>2</sub>Br<sub>4</sub>, C<sub>2</sub>F<sub>4</sub>).

<sup>c</sup> Values for SiX<sub>4</sub>.

In the case of  $CX_3-CX_3$  molecule,<sup>5</sup>

$$\begin{aligned}
 G_{A1g} &= \begin{pmatrix} 36, & -6, & -24 \\ -6, & 1+m, & 4 \\ -24, & 4, & 16+2m \end{pmatrix}, \\
 F_{A1g} &= \begin{pmatrix} a_0/6, & c_1, & k_1 \\ c_1, & a'+2c, & k_2-2k \\ k_1, & k_2-2k, & b_1+b \end{pmatrix}, \\
 G_{A2u} &= \begin{pmatrix} 1+m, & 4 \\ 4, & 16+2m \end{pmatrix}, \\
 F_{A2u} &= \begin{pmatrix} a'+2c, & k_2-2k \\ k_2-2k, & b_1+b \end{pmatrix}, \\
 G_{Eg} &= \begin{pmatrix} 4+m, & -2p, & 8 \\ -2p, & p^2+2m, & -4p+m \\ 8, & -4p+m, & 16+5m \end{pmatrix}, \\
 G_{Eu} &= \begin{pmatrix} 4+m, & -2, & 8 \\ -2, & 1+2m, & -4+m \\ 8, & -4+m, & 16+5m \end{pmatrix}, \\
 F_{Eg} = F_{Eu} &= \begin{pmatrix} a'-c, & k_2, & -k \\ k_2, & b_1-e, & -e \\ -k, & -e, & b-e \end{pmatrix}.
 \end{aligned}$$

And for the infra-red active vibrations of  $-CX_2-CX_2-$  molecule (linear extended form) we have\*\*

$$\begin{aligned}
 G_{A2u} &= 9+3m, \\
 F_{A2u} &= b_1, \\
 G_{A1u} &= \begin{pmatrix} 2+m, & 4 \\ 4, & 8+2m \end{pmatrix}, \\
 F_{A1u} &= \begin{pmatrix} a''+c, & k_2-2k \\ k_2-2k, & (b_1+4b-6e)/2 \end{pmatrix}, \\
 G_{B1u} &= \begin{pmatrix} 4+m, & -4 \\ -4, & 4+2m \end{pmatrix}, \\
 F_{B1u} &= \begin{pmatrix} a''-c, & k_2 \\ k_2, & b_1/2 \end{pmatrix}.
 \end{aligned} \quad (5)$$

<sup>5</sup> These  $G$  matrices are in agreement with those given by E. L. Pace, J. Chem. Phys. 16, 74 (1948).

\*\* These formulas are in agreement with those described in reference 2. Details of the normal coordinate treatment of extended linear polymers and the selection rule for infra-red absorption and Raman effect will be given in near future.

Here

$$\begin{aligned}
 a &= K_{CX} + F_{XX'} + 2F_{XX}, \\
 a' &= K_{CX} + \frac{2}{3}F_{XX'} + (4/3)F_{XX} + 2t_1^2F_{CX'} + s_1^2F_{CX}, \\
 a'' &= K_{CX} + \frac{1}{3}F_{XX'} + \frac{2}{3}F_{XX} + 4t_1^2F_{CX'} + 2s_1^2F_{CX}, \\
 a_0 &= K_{CC} + 6(2t_0^2F_{CX'} + s_0^2F_{CX}), \\
 b &= (H_{XCX} - \frac{2}{3}F_{XX'} + \frac{1}{3}F_{XX})/2 + (3\kappa/4\sqrt{2}r_1^2), \\
 b_1 &= (H_{CCX} - s_0s_1F_{CX'} + 2t_0t_1F_{CX})(r_0/2r_1) \\
 &\quad + (3\kappa/4\sqrt{2}r_1^2), \\
 c &= -\frac{1}{3}F_{XX'} + \frac{2}{3}F_{XX}, \\
 c_1 &= -2t_0t_1F_{CX'} + s_0s_1F_{CX}, \\
 k &= \frac{1}{3}(F_{XX'} + F_{XX}), \\
 k_1 &= t_0s_1F_{CX'} + t_1s_0F_{CX}, \\
 k_2 &= (t_1s_0F_{CX'} + t_0s_1F_{CX})(r_0/r_1), \\
 e &= (\kappa/2\sqrt{2}r_1^2), \\
 m &= 3M_C/M_X, \\
 p &= (6r_1/r_0) + 1,
 \end{aligned} \quad (6)$$

(4) with the abbreviations

$$\begin{aligned}
 s_0 &= (3r_0+r_1)/3q_{CX}, \\
 s_1 &= (3r_1+r_0)/3q_{CX}, \\
 t_0 &= 2r_1/3q_{CX}, \\
 t_1 &= 2r_0/3q_{CX},
 \end{aligned} \quad (7)$$

$M_X$ ,  $r_0$ , and  $r_1$  being respectively the mass of X atom, C-C bond length, and C-X bond length.

The force constants obtained from these equations are tabulated in Table I,\*\* and the frequencies calculated for various molecules are compared with the observed values in Table II.

## DISCUSSION

In 1941 a table of force constants was given by Crawford and Brinkley.<sup>6</sup> Since that time the table has been extended for various molecules by several authors. These sets of force constants are fairly reliable, being based upon a treatment of sufficient generality and consistency. The table given in the present paper, however, is different from those tables in that it involves *repulsive force constants* ( $F'$  and  $F$ ) and *intramolecular tensions* ( $\kappa$ ) instead of *interaction terms*.

Whether or not this approximation method is more physically significant depends of course upon the molecule discussed. But in the case of heavy atoms such as chlorine and bromine, the approximation of the Urey-Bradley field seems to be more adequate, because it is mainly valency electron that gives too complex potential energy to be expressed by the Urey-Bradley field. In fact the calculated frequencies of  $CCl_3-CCl_3$  and  $CBr_3-CBr_3$  as well as those of  $CClBr_3$ ,  $CCl_2Br_2$ , and  $CCl_3Br$  treated in the preceding paper<sup>1</sup> are in satisfactory agreement with the observed. In the case of molecules which have hydrogen atoms the results also seems better than expected.

The magnitude of stretching force constants ( $K$ ) given in Table I are found to be reasonable when we

\*\* Table I includes force constants obtained in the previous papers.

<sup>6</sup> B. L. Crawford, Jr. and S. R. Brinkley, Jr., J. Chem. Phys. 9, 69 (1941).

TABLE II. Calculated and observed vibration frequencies ( $\text{cm}^{-1}$ ).

		Obs.	Calc.	$\Delta\nu$ Percent			Obs.	Calc.	$\Delta\nu$ Percent
CH <sub>4</sub>	A	2916 <sup>a</sup>	2960	1.5	SiH <sub>4</sub>	A	2187 <sup>b, c, d</sup>	2195	0.4
	E	1499	1480	1.3		E	975	936	4.0
	T	1306	1324	1.4		T	910	885	2.7
		3018	3037	0.6			2183	2189	0.3
C(CH <sub>3</sub> ) <sub>4</sub>	A	734 <sup>e, f</sup>	744	1.4	Si(CH <sub>3</sub> ) <sub>4</sub>	A	598 <sup>g</sup>	598	0.0
	E	336	328	2.4		E	202	199	1.5
	T	415	426	2.6		T	239	240	0.4
		(925)					696		
		(1253)	1133	...			863	782	...
CF <sub>4</sub>	A	904 <sup>h, i, j</sup>	904	0.0	SiF <sub>4</sub>	A	797 <sup>h, i, k</sup>	798	0.1
	E	437	433	0.9		E	268	267	0.4
	T	635	628	1.1		T	463	462	0.2
		1265	1239	2.1			1022	1023	0.1
CCl <sub>4</sub>	A	460 <sup>l, m</sup>	456	0.9	SiCl <sub>4</sub>	A	424 <sup>n</sup>	426	0.5
	E	218	224	2.7		E	150	152	1.3
	T	314	318	1.3		T	221	224	1.4
		761					608	612	0.7
		787	787	...					
CBr <sub>4</sub>	A	269 <sup>l</sup>	271	0.7	SiBr <sub>4</sub>	A	249 <sup>n</sup>	249	0.0
	E	123	126	2.4		E	90	91	1.0
	T	183	188	2.7		T	137	137	0.0
		654					487	487	0.0
		672	696	...					
C <sub>2</sub> Cl <sub>6</sub> (C—C=1.54Å, C—Cl=1.77Å)					C <sub>2</sub> Br <sub>6</sub> (C—C=1.54Å, C—Br=1.92Å)				
A <sub>1g</sub>		170 <sup>o, p</sup>	185	8.8	A <sub>1g</sub>		...	110	...
		431	432	0.2			255 <sup>o</sup>	258	1.2
		975	982	0.7			...	944	...
A <sub>2u</sub>		...	368	...	A <sub>2u</sub>		...	222	...
		...	696	...			...	596	...
E <sub>u</sub>		...	130	...	E <sub>u</sub>		...	80	...
		...	271	...			...	158	...
		...	743	...			...	640	...
E <sub>g</sub>		223	205	8.1	E <sub>g</sub>		139	121	13.0
		340	322	5.3			204	195	4.4
		859	885	2.9			768	828	7.8
C <sub>2</sub> F <sub>6</sub> (C—C=1.54Å, C—F=1.36Å)					—CF <sub>2</sub> —CF <sub>2</sub> — (C—C=1.54Å, C—F=1.36Å)				
A <sub>1g</sub>		349 <sup>q, r, s</sup>	391	12.0	A <sub>1u</sub>		...	573	...
		809	846	4.6			1150 <sup>t</sup>		
		1420	1231	13.3			~1250	1191	...
A <sub>2u</sub>		714	698	2.2	B <sub>1u</sub>		719		
		1117	1154	3.3			~787	665	...
E <sub>u</sub>		216	248	14.8	B <sub>2u</sub>		...	209	...
		523	531	1.5			1150		
		1251	1159	7.3			~1250	1137	...
E <sub>g</sub>		380	376	1.1					
		620	612	1.3					
		1237	1224	1.1					

<sup>a</sup> D. M. Dennison, *Rev. Mod. Phys.* **12**, 208 (1940).<sup>b</sup> W. B. Steward and H. H. Nielsen, *Phys. Rev.* **47**, 828 (1935).<sup>c</sup> F. Stitt and D. M. Yost, *J. Chem. Phys.* **4**, 82 (1936).<sup>d</sup> Straley, Tindal, and Nielsen, *Phys. Rev.* **58**, 1002 (1940).<sup>e</sup> K. W. F. Kohlrausch and F. Köppl, *Zeits. f. physik. Chemie* **B26**, 209 (1934).<sup>f</sup> D. H. Rank, *J. Chem. Phys.* **1**, 572 (1933).<sup>g</sup> F. T. Wall and C. R. Eddy, *J. Chem. Phys.* **6**, 107 (1938).<sup>h</sup> Yost, Lassetre, and Gross, *J. Chem. Phys.* **4**, 325 (1936).<sup>i</sup> A. Eucken and A. Betram, *Zeits. f. physik. Chemie* **B31**, 361 (1936).<sup>j</sup> Bailey, Hale, and Thompson, *Proc. Roy. Soc. (London)* **A167**, 555 (1938).<sup>k</sup> D. M. Yost, *Proc. Ind. Acad. Sci.* **8A**, 333 (1938).<sup>l</sup> A. Langseth, *Zeits. f. Physik* **72**, 350 (1931).<sup>m</sup> Morino, Watanabe, and Mizushima, *Sci. Pap. I.P.C.R. (Tokyo)* **39**, 348 (1938).<sup>n</sup> K. W. F. Kohlrausch, *Der Smekal-Raman-Effect, Ergänzungsband 1931-1937* (Verlag, Julius Springer, Berlin, 1938).<sup>o</sup> D. T. Hamilton and F. F. Cleveland, *J. Chem. Phys.* **12**, 249 (1944).<sup>p</sup> See also references in this article.<sup>q</sup> S. Mizushima and co-workers, unpublished.<sup>r</sup> P. Torkington and H. W. Thompson, *Trans. Faraday Soc.* **41**, 236 (1945).<sup>s</sup> D. H. Rank and E. L. Pace, *J. Chem. Phys.* **15**, 39 (1947).<sup>t</sup> Nielsen, Richards, and McMurry, *J. Chem. Phys.* **16**, 67 (1948).<sup>u</sup> W. E. Hanford and R. M. Joyce, *J. Am. Chem. Soc.* **68**, 2082 (1946).

compare them with the corresponding values calculated by Badger's rule<sup>7</sup> which was proposed to give force constants for diatomic molecules. The details will be discussed in the following paper in which we shall treat various oxide molecules.

The bending force constants ( $H$ ) are small (0.1~0.05) in the case of Cl—C—Cl and Br—C—Br, and large

<sup>7</sup> R. M. Badger, *J. Chem. Phys.* **2**, 128 (1934).

(0.4) in the case of H—C—H. This fact gives some suggestions as to the density distribution of valency electron clouds for these molecules. We wish that these values may be extended and be compared with theoretical values which will in future be obtained by the theory of chemical bond.

From the magnitude of repulsive force constants ( $F'$  and  $F$ ) we may justify the present assumption. The

TABLE III. Constants for interatomic potential energy.

	Neon <sup>a</sup>	Argon <sup>a</sup>	Krypton <sup>b</sup>
$r_0$ (Å)	3.08	3.83	4.06
$\phi_0$ (10 <sup>16</sup> erg)	4.89	16.5	22.6

<sup>a</sup> R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1939), p. 285.

<sup>b</sup> T. Kihara and M. Kotani, *Proc. Phys. Math. Soc. Japan* **25**, 602 (1943).

exact magnitude of those repulsive forces, when atoms are so close together, has not yet been published so far as we know. But it seems likely that the corresponding extrapolation of interatomic forces of neon, argon, and krypton empirically obtained from interatomic distances, heats of sublimation, second virial coefficients and other methods gives the right order of magnitude as the values of  $F_{FF'}$ ,  $F_{FF}$ ,  $F_{ClCl'}$ ,  $F_{ClCl}$ ,  $F_{BrBr'}$ , and  $F_{BrBr}$ .

The interatomic potential energy of neon etc., is expressed by Lennard-Jones as

$$U(q) = \phi_0 \left[ \left( \frac{r_0}{q} \right)^{12} - 2 \left( \frac{r_0}{q} \right)^6 \right], \quad (8)$$

where  $r_0$  is the value of interatomic distance  $q$  at which  $U(q)$  has a minimum value equal to  $-\phi_0$ . The values of  $\phi_0$  and  $r_0$  used are tabulated in Table III. From this equation  $F'$  and  $F$  defined in Eq. (1) are expressed by

$$F' = \left( -\frac{1}{q} \frac{dU}{dq} \right)_{q=q_0} = \frac{12\phi_0}{q_0^2} \left[ -\left( \frac{r_0}{q_0} \right)^{12} + \left( \frac{r_0}{q_0} \right)^6 \right], \quad (9)$$

$$F = \left( \frac{d^2U}{dq^2} \right)_{q=q_0} = \frac{12\phi_0}{q_0^2} \left[ 13 \left( \frac{r_0}{q_0} \right)^{12} - 7 \left( \frac{r_0}{q_0} \right)^6 \right]. \quad (10)$$

TABLE IV. Force constants,  $F'$  and  $F$ , and interatomic forces (10<sup>6</sup> dynes/cm).

	$F$	$F'$		$F$	$F'$
F...F (CF <sub>4</sub> )	1.35	-0.30	F...F (SiF <sub>4</sub> )	0.43	-0.31
Ne...Ne (2.22Å)	0.75	-0.05	Ne...Ne (2.51Å)	0.12	-0.01
Cl...Cl (CCl <sub>4</sub> )	0.65	-0.10	Cl...Cl (SiCl <sub>4</sub> )	0.30	-0.06
Ar...Ar (2.87Å)	0.91	-0.06	Ar...Ar (3.30Å)	0.11	-0.01
Br...Br (CBr <sub>4</sub> )	0.50	-0.10	Br...Br (SiBr <sub>4</sub> )	0.23	-0.04
Kr...Kr (3.12Å)	0.75	-0.05	Kr...Kr (3.50Å)	0.13	-0.01

We can calculate from these equations the values of  $F'$  and  $F$  when the two neon (argon, krypton) atoms are so close together as the two fluorine (chlorine, bromine) atoms are in CF<sub>4</sub> (CCl<sub>4</sub>, CBr<sub>4</sub>) and in SiF<sub>4</sub> (SiCl<sub>4</sub>, SiBr<sub>4</sub>). The calculated values are compared with the repulsive force constants obtained from normal coordinate treatment in Table IV. The agreement of these two kinds of values seems to be of significant. That the repulsive force constants for CF<sub>4</sub> molecule are large as compared with those of others is to be attributed partly to the shortness of the CF bond length and partly to the ionic nature of CF bond. In view of these facts it is not a good approximation to neglect interactions between two CF<sub>3</sub>- groups in the normal coordinate treatment of CF<sub>3</sub>-CF<sub>3</sub> molecule.

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*Note added in proof.*—Since some revisions have been made in proof, the calculated frequencies of C<sub>2</sub>Cl<sub>6</sub> molecule given in Table II are somewhat different from those reported in the article by Mizushima, Morino, Simanouti, and Kuratani, *J. Chem. Phys.* **17**, 838 (1949). The conclusion of our previous paper, however, is not affected by this revision.

## The Kinetics of Membrane Processes. I. The Mechanism and the Kinetic Laws for Diffusion through Membranes\*

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The equations for diffusion in binary systems are extended to the case of diffusion through a membrane. Three elementary rate processes are considered at a solution-membrane interface: (1) adsorption of the diffusing species, (2) desorption back into the solution, and (3) diffusion into the membrane, and an expression for the rate constant of the over-all process of surface penetration is developed in terms of three specific rate constants. Various special cases are considered and discussed with reference to the experimental data. A general expression for the rate of diffusion of a species through a membrane under steady-state conditions is derived, the rate being expressed as a function of activities. It is shown that the application of this expression to the case of a solvent passing through a membrane which is impermeable to the solute leads to the thermodynamically exact equation for the osmotic pressure. Expressions are given for the rate of flow of solvent and solute through a membrane as a function of the osmotic and hydrostatic pressures across the membrane.

### INTRODUCTION

IN a paper on the diffusion laws in liquid systems<sup>1</sup> it has been shown on both statistical and thermo-

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<sup>1</sup> K. E. Shuler and K. J. Laidler (to be published).

dynamical grounds that the proper composition unit to be used is the mole fraction activity  $N_i$ , and that more constant diffusion coefficients are found if the equations are formulated on this basis. In the present paper this treatment is extended to the case in which phase boundary processes occur in addition to diffusion, i.e., to the permeation of a solid by molecules in solution. The kinetic laws for the penetration of membranes, in the steady state of flow, are derived, and