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Jacob Bigeleisen and Maria Goeppert Mayer

Argonne National Laboratory, Chicago, Illinois* and Institute for Nuclear Studies, University of Chicago

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It is pointed out that the possibility of chemical separation of isotopes is a quantum effect. This permits a direct calculation of the difference in the free energies of two isotopic molecules. Tables and approximation methods are given which permit a rapid calculation of equilibrium constants if the frequency shifts on isotopic substitution are known. Several applications are discussed.

INTRODUCTION

THE possibility of calculating equilibrium constants for isotopic exchange reactions from spectroscopic data alone was first pointed out by Urey and Rittenberg.[1] Since then numerous calculations have appeared in the literature. All these calculations can be greatly simplified. The final equilibrium constants can be calculated (except for molecules containing hydrogen) without any knowledge of the moments of inertia of the molecules.

THE METHOD OF CALCULATION

The natural logarithm of the equilibrium constant, K, at any temperature T for any chemical reaction is the difference in the standard free energies of the reactants and products divided by RT. For gaseous substances the free energy is connected to the partition function by the relation

$$F = -RT \ln Q/N, \qquad (1)$$

where Q is the partition function of the molecule. According to the quantum-mechanical treatment the partition function is defined as

$$Q = \sum_n e^{-\epsilon_n/kT}, \qquad (2)$$

where the summation extends over all quantum states (counting a k-fold degenerate level as k states). The energies of the molecular states, ϵ_n, have to be measured from a suitable reference zero. It follows that the equilibrium constant is

$$K = \frac{\Pi Q \text{ products}}{\Pi Q \text{ reactants}}. \qquad (3)$$

[1] H. C. Urey and D. Rittenberg, J. Chem. Phys. 1, 137 (1933).

A calculation of the Q's allows the calculation of equilibrium constants for chemical reactions.

For reactions involving the exchange of isotopes, K is of the order of unity. The free energies of the different isotopic molecules are almost equal and $\ln K$ is the small difference between large numbers. The calculation of $RT \ln K$ as the difference of the total free energies of the reactants and products is likely to lead to, and has in several instances led to, significant errors (even reversing the direction of the reaction). A much simpler and more accurate method is obtained by calculating the differences in the free energies or the ratios of the partition functions directly.

It is well known that the chemical separation of isotopes is a quantum-mechanical effect. The classical partition function is

$$h^f Q = \frac{1}{s} \int \int \int \cdots \int \int e^{-H(p,\,q)/kt} dp \cdots dq, \qquad (4)$$

where s is the symmetry number and H is the Hamiltonian of the momenta p and the coordinates q of the constituent atoms. The momenta occur in the kinetic energy only, in the form $p^2/2m$. The integration over the p's may be performed leading to

$$Q = \frac{1}{s} \Pi_i \left(\frac{2\pi m_i k T}{h^2} \right)^{\frac{3}{2}}$$

$$\times \int \int \int \cdots \int e^{-u/kT} dq_1 \cdots dq_k. \qquad (5)$$

The potential energies for molecules differing only in isotopic constituents are alike. The ratio of the partition functions of two isotopic molecules is, therefore, seen to reduce to the inverse

ratio of the symmetry numbers multiplied by the mass ratio of the different isotopes raised to the three-halves power.

$$\frac{Q}{Q'}=\frac{s'}{s}\left(\frac{m}{m'}\right)^{\frac{3}{2}}. \tag{6}$$

The ratio of the masses of the isotopes will cancel in any chemical reaction. The ratio of the symmetry numbers, no matter what its value, will not lead to isotopic enrichment since it merely represents the relative probabilities of forming symmetrical and unsymmetrical molecules.

In calculating the equilibrium constant of isotopic exchanges the useless classical ratio $(m/m')^{\frac{3}{2}}$ is best omitted. This omission amounts to calculating the ratio of the equilibrium constants for the dissociation of the two isotopic molecules into atoms. We shall accordingly define

$$f=\frac{Q}{Q'}\Pi_i\left(\frac{m_i'}{m_i}\right)^{\frac{3}{2}}. \tag{7}$$

In classical mechanics $(s/s')f$ is equal to one. A value of one for the $(s/s')f$ means no separation of isotopes.

In quantum mechanics the partition function may in a first approximation be written as a product of translational, rotational, and vibrational partition functions. The translational partition function is equal to the classical one at all temperatures. The rotational partition function in all cases except hydrogen, which we shall treat separately, is classical at room temperature. The form of the vibrational partition function neglecting anharmonicity is

$$Q_{\mathrm{vib}}=\Pi_i\frac{e^{-u_i/2}}{1-e^{-u_i}}, \tag{8}$$

where

$$u_i=\frac{h\nu_i}{kT} \tag{9}$$

and the product is to be taken over the different vibrational frequencies ν_i of the molecule counting an n-fold degenerate frequency n times. We have chosen the zero of the energy scale at the minimum in the potential energy curve which is appropriate since it is the same for the two isotopic molecules.

At high temperatures or low u, Q_{vib} reduces to

$\Pi_i(1/u_i)$, which is identical with the classical expression. In the quantity f these limiting values as well as the rotational and the translational parts cancel, leaving only the ratio of the symmetry numbers.[2]

The value of f depends upon the vibrations only and is of the form

$$\frac{s}{s'}f=\Pi_i\frac{u_i}{u_i'}\frac{e^{-u_i/2}/(1-e^{-u_i})}{e^{-u_i'/2}/(1-e^{-u_i'})}. \tag{10}$$

We shall write $u_i'=u_i+\Delta u_i$, where the primed molecule is the lighter one. Then Δu_i is always positive and

$$\frac{s}{s'}f=\Pi_i\frac{u_i}{u_i+\Delta u_i}e^{\Delta u_i/2}\frac{(1-e^{-(u_i+\Delta u_i)})}{(1-e^{-u_i})}. \tag{11}$$

If we calculate the free energy of formation of two isotopic molecules from their respective gaseous atoms, then the difference in the free energy of formation of the two isotopic molecules will be

$$\frac{\Delta F^0-\Delta F^{0'}}{RT}=\sum_i\left[-\tfrac{1}{2}\Delta u_i+\ln\left(1+\frac{\Delta u_i}{u_i}\right)\right.$$
$$\left.+\ln\frac{(1-e^{-u_i})}{(1-e^{-(u_i+\Delta u_i)})}\right]+\ln\frac{s}{s'}. \tag{11'}$$

If Δu is small which is the case for everything except the isotopes of hydrogen

$$\frac{s}{s'}f=1+\sum_i\left(\frac{1}{2}-\frac{1}{u_i}+\frac{1}{e^{u_i}-1}\right)\Delta u_i, \tag{11a}$$

or

$$\frac{\Delta F^0-\Delta F^{0'}}{RT}=-\sum_i\left(\frac{1}{2}+\frac{1}{e^{u_i}-1}-\frac{1}{u_i}\right)\Delta u_i+\ln\frac{s}{s'}. \tag{11'a}$$

If, in addition, u_i itself is small, then

$$\frac{s}{s'}f=1+\sum_i\frac{\Delta u_i u_i}{12}=1+\sum_i\frac{\Delta(u_i^2)}{24}. \tag{11b}$$

Since Δu_i is positive, $(s/s')f$ will always be greater than 1. The heavy isotope is more stable in the molecule. The lighter isotope favors the

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[2] This could also have been deduced from the product rule which states the invariance under isotopic substitution of the expression $\Pi_i\nu_i^2\Pi_i m_i^3/M^3 I_A I_B I_C$ where the I's are the moments of inertia and M's the molecular weight.

FIG. 1. The separative effect in the free energy per unit shift in u, plotted against $u = hc\omega/kT$.
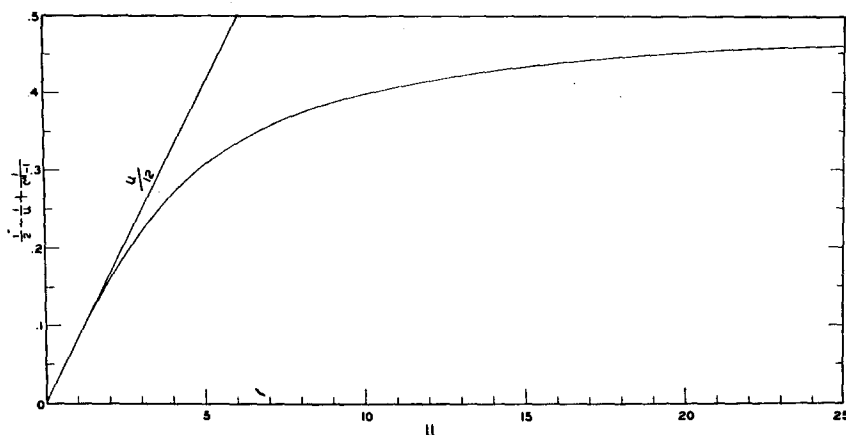
separated atoms. In all isotopic exchange reactions partial cancellation of the separative effect must occur.

For low temperatures and high frequencies the bracket in (11a) approaches $\frac{1}{2}$ and the difference in the free energies approaches the difference in zero point energies. For very high temperatures formula (11b) becomes applicable to all molecules and it is seen that $(s/s')f$ approaches one as $1+\overset{\bullet}{k}/T^2$ so that the separative effect disappears.

For most cases the separative effect, $(s/s')f$, can be calculated from the function appearing under the summation sign in (11a) or (11'a)

$$G = \frac{1}{2} - \frac{1}{u} + \frac{1}{e^u - 1}. \tag{12}$$

In Fig. 1 we have plotted G against u. Table I gives values of G from $u = 0$ to $u = 25$.

To test the range of validity of the very simple formula (11b) it may be noted that for $u = 3$, $G(u)$ is 0.218 whereas the approximate expression $u/12$ in (11b) is 0.250. This corresponds to a frequency of 625 cm^{-1} at 300°K. For $u = 4$, the discrepancy between the two expressions is already 25 percent.

The fundamental approximation made was the neglection of interaction between rotation and vibration as well as anharmonicity of the vibrations. Here again we have to consider merely the ratio of the quantum mechanical to classical correction to the partition function for each of the molecules. For diatomic molecules in which the rotation-vibration spectrum is analyzed this can be worked out explicitly.[3] In general, these cor-

[3] See Mayer and Mayer, *Statistical Mechanics* (John Wiley & Sons, New York, 1940), Chapter 7.

rections are very small if the frequency in the ground state and the zero point energy is correctly chosen.

THE ISOTOPES OF HYDROGEN

The frequency shifts for different hydrogen isotopes are so large that as a rule the unexpanded formula (11) for the vibrational contribution to f has to be used. The rotation of hydrogen molecules is not quite classical even at room temperature. The classical expression for Q_{rot} would be σ^{-1} where

$$\sigma = \frac{hcB}{kT} = \frac{h^2}{8\pi^2 IkT}. \tag{13}$$

I is the moment of inertia and B is the rotational constant in cm^{-1}, which is most frequently tabulated in the literature. For small σ the rotational contribution to the quantum-mechanical partition function may be expanded to give

$$\sigma Q_{rot} = \left(1 + \frac{\sigma}{3} + \frac{\sigma^2}{15} + \frac{4\sigma^3}{315} + \cdots\right). \tag{14}$$

Since f is defined such that the classical contribution σ^{-1} is cancelled, Eq. (11a) has to be modified simply by the ratio of the right-hand side of (14) for the two isotopic molecules. For small σ this is

$$1 + \frac{\sigma - \sigma'}{3} + \frac{1}{18}(\sigma - \sigma')^2 + \frac{1}{90}(\sigma^2 - \sigma'^2). \tag{15}$$

The numerical values for the isotopic hydrogen molecules taking into account the interaction

TABLE I.

u	G	$\Delta G/\Delta u$	u	G	$\Delta G/\Delta u$	u	G	$\Delta G/\Delta u$	u	G	$\Delta G/\Delta u$
0.00	.00000		2.50	.18943	.0630	5.00	.30679	.0334	9.00	.38901	.0123
.05	.004165		2.55	.19253	.0620	5.05	.30844	.0330	9.10	.39022	.0121
.10	.008415		2.60	.19561	.0616	5.10	.31007	.0326	9.20	.39140	.0118
.15	.01265		2.65	.19866	.0610	5.15	.31168	.0322	9.30	.39256	.0116
.20	.01671		2.70	.20168	.0604	5.20	.31327	.0318	9.40	.39370	.0114
.25	.02075		2.75	.20465	.0594	5.25	.31484	.0314	9.50	.39481	.0111
.30	.02496		2.80	.20761	.0592	5.30	.31638	.0308	9.60	.39590	.0109
.35	.02910	.0832	2.85	.21051	.0580	5.35	.31790	.0304	9.70	.39697	.0107
.40	.03326	.0824	2.90	.21339	.0576	5.40	.31940	.0300	9.80	.39802	.0105
.45	.03738	.0824	2.95	.21625	.0572	5.45	.32088	.0296	9.90	.39904	.0102
.50	.04150	.0822	3.00	.21906	.0562	5.50	.32234	.0292	10.00	.40005	.0101
.55	.04561	.0818	3.05	.22184	.0556	5.55	.32378	.0288	10.10	.40103	.0098
.60	.04970	.0818	3.10	.22459	.0550	5.60	.32520	.0284	10.20	.40200	.0097
.65	.05379	.0816	3.15	.22731	.0544	5.65	.32660	.0280	10.30	.40294	.0094
.70	.05787	.0812	3.20	.22999	.0536	5.70	.32798	.0276	10.40	.40388	.0094
.75	.06193	.0808	3.25	.23264	.0530	5.75	.32934	.0272	10.50	.40479	.0091
.80	.06597	.0804	3.30	.23526	.0524	5.80	.33068	.0268	10.60	.40568	.0089
.85	.06999	.0804	3.35	.23785	.0518	5.85	.33200	.0264	10.70	.40656	.0088
.90	.07401	.0798	3.40	.24041	.0512	5.90	.33330	.0260	10.80	.40743	.0087
.95	.07800	.0796	3.45	.24294	.0506	5.95	.33458	.0256	10.90	.40828	.0085
1.00	.08198	.0790	3.50	.24544	.0500	6.00	.33583	.0250	11.00	.40911	.0083
1.05	.08593	.0788	3.55	.24790	.0492	6.10	.33831	.0252	11.10	.40993	.0082
1.10	.08987	.0782	3.60	.25032	.0484	6.20	.34075	.0244	11.20	.41072	.0079
1.15	.09378	.0780	3.65	.25271	.0478	6.30	.34311	.0236	11.30	.41151	.0079
1.20	.09768	.0774	3.70	.25508	.0474	6.40	.34541	.0230	11.40	.41229	.0078
1.25	.10155	.0770	3.75	.25741	.0466	6.50	.34766	.0225	11.50	.41305	.0076
1.30	.10540	.0764	3.80	.25972	.0462	6.60	.34984	.0218	11.60	.41380	.0075
1.35	.10922	.0760	3.85	.26200	.0456	6.70	.35198	.0214	11.70	.41454	.0074
1.40	.11302	.0756	3.90	.26425	.0450	6.80	.35406	.0208	11.80	.41526	.0072
1.45	.11680	.0750	3.95	.26647	.0444	6.90	.35608	.0202	11.90	.41598	.0072
1.50	.12055	.0746	4.00	.26866	.0438	7.00	.35805	.0197	12.00	.41668	.0070
1.55	.12428	.0738	4.05	.27082	.0432	7.10	.35998	.0193	12.10	.41736	.0068
1.60	.12797	.0734	4.10	.27295	.0426	7.20	.36186	.0188	12.20	.41803	.0067
1.65	.13164	.0728	4.15	.27505	.0420	7.30	.36369	.0183	12.30	.41870	.0067
1.70	.13528	.0722	4.20	.27712	.0414	7.40	.36547	.0178	12.40	.41935	.0065
1.75	.13889	.0716	4.25	.27919	.0408	7.50	.36722	.0175	12.50	.42000	.0065
1.80	.14247	.0712	4.30	.28119	.0402	7.60	.36892	.0170	12.60	.42063	.0063
1.85	.14603	.0704	4.35	.28318	.0398	7.70	.37058	.0166	12.70	.42126	.0063
1.90	.14955	.0700	4.40	.28515	.0394	7.80	.37220	.0162	12.80	.42187	.0061
1.95	.15305	.0694	4.45	.28709	.0388	7.90	.37379	.0159	12.90	.42248	.0061
2.00	.15652	.0688	4.50	.28901	.0384	8.00	.37534	.0155	13.00	.42308	.0060
2.05	.15996	.0678	4.55	.29090	.0378	8.10	.37684	.0150	13.10	.42366	.0058
2.10	.16335	.0674	4.60	.29276	.0372	8.20	.37832	.0148	13.20	.42424	.0058
2.15	.16672	.0668	4.65	.29460	.0368	8.30	.37977	.0145	13.30	.42481	.0057
2.20	.17006	.0662	4.70	.29641	.0362	8.40	.38117	.0140	13.40	.42537	.0056
2.25	.17337	.0654	4.75	.29820	.0358	8.50	.38255	.0138	13.50	.42593	.0056
2.30	.17665	.0648	4.80	.29997	.0354	8.60	.38390	.0135	13.60	.42647	.0054
2.35	.17989	.0642	4.85	.30172	.0350	8.70	.38523	.0133	13.70	.42701	.0054
2.40	.18310	.0636	4.90	.30343	.0342	8.80	.38651	.0128	13.80	.42754	.0053
2.45	.18628		4.95	.30512	.0338	8.90	.38778	.0127	13.90	.42806	.0052

of rotation and vibration are given in Table II. It is seen from these figures that at room temperature the rotational correction is small.

For non-linear polyatomic molecules containing hydrogen the moments of inertia are generally high enough so that no rotational correction need be made.

As an example we have calculated the equilibrium constants for the reaction

$$H_2 + 2DI = D_2 + 2HI \qquad (16)$$
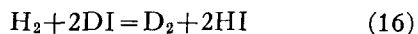
at various temperatures. The constants used in the calculations are given in Table III. The results of the calculations, which include a correction for the non-classical rotation, are given in Table IV and Fig. 2.

This equilibrium has been calculated previously.[4] Our results are in good agreement with those of Urey and Rittenberg at the four temperatures for which they have made the calculation considering the fact that we have used a slightly

[4] H. C. Urey and D. Rittenberg, J. Chem. Phys. 1, 137 (1933). J. C. L. Blagg and G. M. Murphy, J. Chem. Phys. 4, 631 (1936).

TABLE I.—*Continued.*

u	G	ΔG/Δu	u	G	ΔG/Δu	u	G	ΔG/Δu	u	G	ΔG/Δu
14.00	.42857	.0051	16.80	.44048	.0036	19.60	.44898	.0026	22.40	.45536	.0020
14.10	.42908	.0051	16.90	.44083	.0035	19.70	.44924	.0026	22.50	.45556	.0020
14.20	.42958	.0050	17.00	.44118	.0035	19.80	.44949	.0025	22.60	.45575	.0019
14.30	.43007	.0049	17.10	.44152	.0034	19.90	.44975	.0026	22.70	.45595	.0020
14.40	.43056	.0049	17.20	.44186	.0034	20.00	.45000	.0025	22.80	.45614	.0019
14.50	.43103	.0047	17.30	.44220	.0034	20.10	.45025	.0025	22.90	.45633	.0019
14.60	.43151	.0048	17.40	.44253	.0033	20.20	.45050	.0025	23.00	.45652	.0019
14.70	.43197	.0046	17.50	.44286	.0033	20.30	.45074	.0024	23.10	.45671	.0019
14.80	.43243	.0046	17.60	.44318	.0032	20.40	.45098	.0024	23.20	.45690	.0019
14.90	.43289	.0046	17.70	.44350	.0032	20.50	.45122	.0024	23.30	.45708	.0018
15.00	.43333	.0044	17.80	.44382	.0032	20.60	.45146	.0024	23.40	.45726	.0018
15.10	.43377	.0044	17.90	.44413	.0031	20.70	.45169	.0023	23.50	.45745	.0019
15.20	.43421	.0044	18.00	.44444	.0031	20.80	.45192	.0023	23.60	.45763	.0018
15.30	.43464	.0043	18.10	.44475	.0031	20.90	.45215	.0023	23.70	.45781	.0018
15.40	.43506	.0042	18.20	.44505	.0030	21.00	.45238	.0023	23.80	.45798	.0017
15.50	.43548	.0042	18.30	.44536	.0031	21.10	.45261	.0023	23.90	.45816	.0018
15.60	.43590	.0042	18.40	.44565	.0029	21.20	.45283	.0022	24.00	.45833	.0017
15.70	.43631	.0041	18.50	.44595	.0030	21.30	.45305	.0022	24.10	.45851	.0018
15.80	.43671	.0040	18.60	.44624	.0029	21.40	.45327	.0022	24.20	.45868	.0017
15.90	.43711	.0040	18.70	.44652	.0028	21.50	.45349	.0021	24.30	.45885	.0017
16.00	.43750	.0039	18.80	.44681	.0029	21.60	.45370	.0022	24.40	.45902	.0017
16.10	.43789	.0039	18.90	.44709	.0028	21.70	.45392	.0021	24.50	.45918	.0016
16.20	.43827	.0038	19.00	.44737	.0028	21.80	.45413	.0021	24.60	.45935	.0017
16.30	.43865	.0038	19.10	.44764	.0027	21.90	.45434	.0021	24.70	.45951	.0016
16.40	.43902	.0037	19.20	.44792	.0028	22.00	.45455	.0021	24.80	.45968	.0017
16.50	.43939	.0037	19.30	.44819	.0027	22.10	.45475	.0020	24.90	.45984	.0016
16.60	.43976	.0037	19.40	.44845	.0026	22.20	.45494	.0020	25.00	.46000	.0016
16.70	.44012	.0036	19.50	.44872	.0027	22.30	.45516	.0021			

different spectroscopic assignment. It will be seen from Fig. 2 that at high temperatures $K=1 +k/T^2$. At low temperatures, the calculation can only be made by summing the rotational states, giving each state its proper statistical weight taking into account the nuclear spin. These methods are well known and need not be elaborated further.

ISOTOPES OF THE HEAVY ELEMENTS

In considering exchange reactions of two polyatomic molecules containing isotopes of a heavy element, it may be possible to calculate the equilibrium constant sufficiently accurately by means of Eq. (11b). If these conditions are fulfilled then it is possible to make an approximate calculation without a complete knowledge of the vibrational frequencies of the molecules. The sum of the squares of all the frequencies of a

molecule has the form

$$4\pi^2 \sum_i \nu_i^2 = \sum_{n=1}^{N} \frac{A_n}{m_n}, \qquad (17)$$

where the summation on the right-hand side extends over all atoms in the molecule and the A's depend on force constants only. Then

$$\Delta \sum_i \nu_i^2 = \frac{\Delta m}{mm'} \frac{1}{4\pi^2} A, \qquad (18)$$

where A is to be computed in the following manner. Let all the atoms in the molecule except the one which is to be isotopically substituted be fixed in position. A is then the sum of the three

TABLE II.*

	σT in °K
H₂	85.387
D₂	43.032

* Taken from Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939).

TABLE III.*

	ωₑ	Xₑωₑ	B₀	σT
H₂	4405.30	125.325	59.338	85.387
D₂	3117.05	63.034	29.904	43.032
HI	2309.53	39.73	6.459	9.295
DI	1640.18	20.04	3.258	4.688

* The vibrational frequencies for H₂ and D₂ are those reported by G. K. Teal and G. E. MacWood, J. Chem. Phys. 3, 760 (1935). The B₀ values are calculated from the tables in Herzberg (footnote to Table II). The vibration frequency for HI is taken from Herzberg also and was used to calculate the frequency for DI.
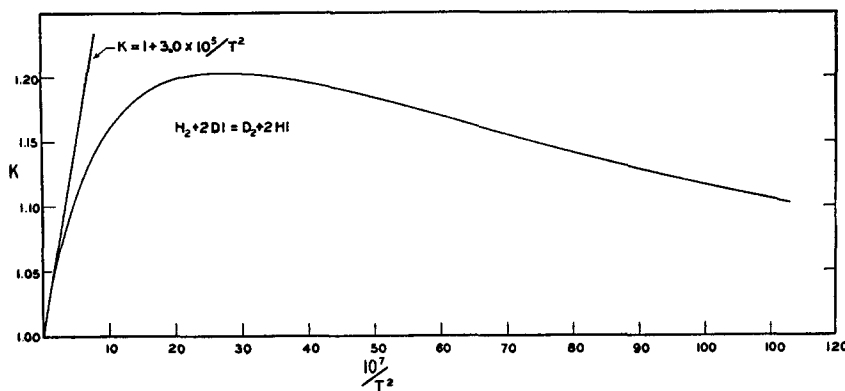
FIG. 2. The equilibrium constant for the reaction $H_2+2DI=D_2+2HI$ as a function of temperature.

restoring force constants corresponding to the displacement of the isotopic atom in three mutually perpendicular directions.

The following consideration will show that the above definition will give A. Let the atoms in the molecule be numbered from 1 to N; the isotopic atom will be 1. The force constants are denoted by $a_{i,j}^{x,y}(i, j=1\cdots N)$; the masses of the atoms by m_i and m_j; m_1 is written as M. The frequencies are determined by the equation

$$0 = \begin{vmatrix} \dfrac{a_{11}^{xx}}{M}-4\pi^2\nu^2 & \dfrac{a_{11}^{xy}}{M} & \dfrac{a_{11}^{xz}}{M} & \dfrac{a_{12}^{xx}}{(Mm_2)^{\frac{1}{2}}} & \dfrac{a_{12}^{xy}}{(Mm_2)^{\frac{1}{2}}} & \dfrac{a_{12}^{xz}}{(Mm_2)^{\frac{1}{2}}} & \cdots & \dfrac{a_{1N}^{xz}}{(Mm_N)^{\frac{1}{2}}} \\[2ex] \dfrac{a_{11}^{yx}}{M} & \dfrac{a_{11}^{yy}}{M}-4\pi^2\nu^2 & \dfrac{a_{11}^{yz}}{M} & \dfrac{a_{12}^{yx}}{(Mm_2)^{\frac{1}{2}}} & \dfrac{a_{12}^{yy}}{(Mm_2)^{\frac{1}{2}}} & \dfrac{a_{12}^{yz}}{(Mm_2)^{\frac{1}{2}}} & \cdots & \dfrac{a_{1N}^{yz}}{(Mm_N)^{\frac{1}{2}}} \\[2ex] \dfrac{a_{11}^{zx}}{M} & \dfrac{a_{11}^{zy}}{M} & \dfrac{a_{11}^{zz}}{M}-4\pi^2\nu^2 & \dfrac{a_{12}^{zx}}{(Mm_2)^{\frac{1}{2}}} & \dfrac{a_{12}^{zy}}{(Mm_2)^{\frac{1}{2}}} & \dfrac{a_{12}^{zz}}{(Mm_2)^{\frac{1}{2}}} & \cdots & \dfrac{a_{1N}^{zz}}{(Mm_N)^{\frac{1}{2}}} \\[2ex] \dfrac{a_{21}^{xx}}{(Mm_2)^{\frac{1}{2}}} & \dfrac{a_{21}^{xy}}{(Mm_2)^{\frac{1}{2}}} & \dfrac{a_{21}^{xz}}{(Mm_2)^{\frac{1}{2}}} & \dfrac{a_{22}^{xx}}{m_2}-4\pi^2\nu^2 & \dfrac{a_{22}^{xy}}{m_2} & \dfrac{a_{22}^{xz}}{m_2} & \cdots & \dfrac{a_{2N}^{xz}}{(m_2m_N)^{\frac{1}{2}}} \\[2ex] \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \cdot \\[1ex] \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \cdot \\[1ex] \dfrac{a_{N1}^{zz}}{(Mm_N)^{\frac{1}{2}}} & \cdot & \cdot & \cdot & \cdot & \cdot & & \dfrac{a_{NN}^{zz}}{m_N}-4\pi^2\nu^2 \end{vmatrix}. \quad (19)$$

The sum of all roots of this equation is the trace, or sum of all diagonal elements, of the matrix of force constants. Consequently

$$4\pi^2 \sum_i \Delta(\nu_i)^2 = \frac{\Delta M}{MM'}(a_{11}^{xx}+a_{11}^{yy}+a_{11}^{zz})$$

$$\simeq \frac{\Delta M}{M^2}(a_{11}^{xx}+a_{11}^{yy}+a_{11}^{zz}). \quad (20)$$

If the central atom of mass M or $M+\Delta M$ is symmetrically surrounded by n identical atoms of mass m, a useful approximation may be derived. In the first approximation, all force constants except those arising from the stretching of the bonds with the central atom, a, may be neglected. In that case, A in Eq. (18) becomes na. The force constant may be estimated from the totally symmetric frequency, ν_1, which is usually known from Raman spectra and which obeys the equation $4\pi^2\nu_1^2=a/m$. One obtains
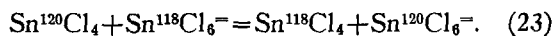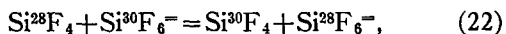
TABLE IV.

$T°K$	fD_2/H_2	$f(DI)/(HI)$	$K = \dfrac{D_2}{H_2}\left(\dfrac{HI}{DI}\right)^2$
0			0.0
300	13.744	3.5207	1.109
400	6.5481	2.3654	1.170
500	4.1972	1.8709	1.199
600	3.1214	1.6079	1.207
700	2.5285	1.4497	1.203
800	2.1616	1.3465	1.192
900	1.9160	1.2753	1.178
1000	1.7425	1.2238	1.164
1100	1.6147	1.1854	1.149
1200	1.5126	1.1564	1.135
1300	1.4422	1.1333	1.123
1400	1.3815	1.1150	1.112
1500	1.3327	1.0999	1.102
2000	1.1867	1.0555	1.066

TABLE V.

Molecule	ω_1	f	K
SiF_4	800[a]	1.111	
SiF_6^-	600[b]	1.109	1.002
$SnCl_4$	367[c]	1.00256	
$SnCl_6^-$	314[b]	1.00281	1.00025

[a] Yost, Lassettre, and Gross, J. Chem. Phys. 4, 325 (1936).
[b] Redlich, Kurz, and Rosenfeld, Zeits. f. physik. Chemie B 19,231 (1932).
[c] Daure, Comptes rendus 187, 940 (1928).

then the rough approximation

$$\frac{s}{s'}f = 1 + \frac{\Delta M_m}{24 M^2} u_1^2 n. \tag{21}$$

Of course, the force constants arising from the bending of bonds and interaction between outer atoms are not actually negligible. The values of ν_1^2 and $\sum_i \Delta(\nu_i)^2$ are both greater than computed by this rough estimate. Equation (21) which merely equates the sum of the force constants of the center atom with ν_1^2 is somewhat more accurate than the neglections indicate.

We are now in a position to make a rough estimate of the enrichment factor to be expected for two typical exchange reactions of the heavy elements. The reactions chosen are

$$Si^{28}F_4 + Si^{30}F_6^- = Si^{30}F_4 + Si^{28}F_6^-, \tag{22}$$

$$Sn^{120}Cl_4 + Sn^{118}Cl_6^- = Sn^{118}Cl_4 + Sn^{120}Cl_6^-. \tag{23}$$

The results for 300°K are tabulated in Table V.

In both of these exchange reactions the cancellation of the separative effect is over ninety percent. This large cancellation is caused by the fact that although there are more bonds in the octahedral ions contributing to the restoring force constant for the central atom, the bonds have become weaker than those in the tetrahedral molecules and the total restoring force is approximately unchanged. This is usually the case of acid-base exchange equilibria. To get a large separative effect it is necessary to equilibrate one compound which has high frequencies and large frequency shifts on isotopic substitution with another compound (preferably the gaseous atom) with low frequencies and small frequency shifts.

Addendum: After this paper had been completed, Professor W. F. Libby kindly called a paper by L. Waldmann[5] to our attention. In this paper, Waldmann discusses briefly the fact that the chemical separation of isotopes is a quantum effect. He gives formulae which are equivalent to our (11′) and (11a) and discusses qualitatively their application to two acid base exchange equilibria. These are the exchange between NH_3 and NH_4^+ and HCN and CN^- studies by Urey[6] and co-workers.

[5] L. Waldmann, Naturwiss. 31, 205 (1943).
[6] H. G. Thode and H. C. Urey, J. Chem. Phys. 7, 34 (1939). C. A. Hutchison, D. W. Stewart, and H. C. Urey, J. Chem. Phys. 8, 532 (1940).