In seeking a possible explanation for the differences between these and earlier results, the heat of solution was found in one instance using water nearly saturated with carbon dioxide. A rapid heat change occurred as in the other runs, and this was followed by a slow evolution of heat, about 30 minutes being required for its completion. The initial and final values thus found for the heat of solution in this run are also shown in Figure 1. Removal of dissolved carbon dioxide from water is known to occur endothermically (*3, 7*). The exothermic effects observed in this case might be connected with displacement of the equilibria present in aqueous carbon dioxide on solution of potassium carbonate. It is known (*4, 5*), for instance, that the reaction

$$CO_2\,(aq.) + OH^- \rightarrow HCO_3^-$$

proceeds at a rate comparable to the slow thermal effect described above.

Small amounts of dissolved carbon dioxide in the water used for solution could therefore explain the lower values of ΔH_s compiled from earlier data (*7*), and this was the reason suggested by Muller (*6*) for the difference between his results and those of Berthelot (*2*) in aqueous potassium carbonate.

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Partition Function Ratios and Equilibrium Constants for Oxygen-18 Exchange Reactions

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KNOWLEDGE of partition functions can be applied in predicting suitable exchange reactions for the enrichment of isotopes. Our present discussion is confined only to the two stable isotopes of oxygen—viz., 16 and 18. The procedure of calculating the equilibrium constants from the spectroscopic data was first given by Urey and Rittenberg (*19*) and later applied to a number of systems by Urey (*18*). Bigeleisen and Mayer (*5*) have further simplified this procedure, and in our calculations we have used their final expression

$$\ln \frac{Q}{Q'} = \sum_i \left(\frac{1}{2} + \frac{1}{e^{u_i} - 1} - \frac{1}{u_i} \right) \Delta u_i \quad \ldots \qquad (1)$$

where

Q = partition function for isotopic molecule
Q' = partition function for normal molecule
u_i = $h\nu_i/kT$
ν_i = vibrational frequency
h = Planck's constant
k = Boltzmann's constant
T = temperature
u_i' = $u_i + \Delta u_i$

In this article Δu_i is $\ll u_i$ for all the systems considered. In deriving Equation 1, anharmonicity is also neglected. Thus, in calculating the partition function ratio, we require the vibrational frequencies of the normal molecule and the frequency shifts. If all this information is experimentally available, extremely reliable values of the equilibrium constants can be determined, as recently shown by Begun and Fletcher (*4*) for isotopic nitrogen exchange. For almost all the molecules in which we are interested, no such experimental data are available. We have, therefore, calculated the vibrational frequencies of the isotopic molecules from known frequencies of normal molecules in conjunction with theoretical formulas for the valence force model (*10*). This particular model is chosen in view of its success for polyatomic molecules, and it has reproduced the measured frequency shifts (*4*) precisely, when proper choice of the force constants is made.

Table I. Vibrational Frequency of Normal and Isotopic Molecules[a]

Molecule	ν_1, Cm.$^{-1}$	ν_2, Cm.$^{-1}$	ν_3, Cm.$^{-1}$	ν_4, Cm.$^{-1}$
$N^{14}O^{16}$	1904.03			
$N^{14}O^{18}$	1854.02			
$N_2^{14}O^{16}$	1300.3	596.5(2)	2276.9	
$N_2^{14}O^{18}$	1257.7	591.8(2)	2269.2(2)	
$N^{14}O_2^{16}$	1357.8	756.8	1665.5	
$N^{14}O_2^{18}$	1309.0	727.5	1633.7	
$C^{12}O_2^{16}$	1351.2	672.2(2)	2396.4	
$C^{12}O_2^{18}$	1273.9	661.9(2)	2359.8	
$N^{14}O^{16}Cl^{35}$	1800.0	604.7	332.4	
$N^{14}O^{18}Cl^{35}$	1754.7	602.6	322.0	
$N^{14}O_3^{16}$-	1049.2	830.9	1375.6(2)	716.8(2)
$N^{14}O_3^{18}$-	989.2	820.4	1361.2(2)	674.3(2)
$N^{14}O_2^{16}$-	1326.0	808.0	1232.0	
$N^{14}O_2^{18}$-	1296.2	766.0	1208.2	
$S^{32}O_2^{16}$	1151.4	517.8	1360.5	
$S^{32}O_2^{18}$	1102.4	495.5	1361.1	
$H_2^1O^{16}$	3825.3	1653.9	3935.6	
$H_2^1O^{18}$	3815.5	1647.8	3919.4	

[a] Number in parentheses indicates multiplicity of degenerate frequency.

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Table II. Partition Function Ratios and Enrichment Factors for Oxygen Exchange

	$\left(\frac{\mathrm{CO}_2^{18}}{\mathrm{CO}_2^{16}}\right)^{1/2}$	$\left(\frac{\mathrm{N_2O^{18}}}{\mathrm{N_2O^{16}}}\right)$	$\left(\frac{\mathrm{NO^{18}}}{\mathrm{NO^{16}}}\right)$	$\left(\frac{\mathrm{NO^{18}Cl}}{\mathrm{NO^{16}Cl}}\right)$	$\left(\frac{\mathrm{NO}_2^{18}}{\mathrm{NO}_2^{16}}\right)^{1/2}$	$\left(\frac{\mathrm{SO}_2^{18}}{\mathrm{SO}_2^{16}}\right)^{1/2}$	$\left(\frac{\mathrm{NO}_3^{18}\text{-}}{\mathrm{NO}_3^{16}\text{-}}\right)^{1/3}$	$\left(\frac{\mathrm{H_2O^{18}}}{\mathrm{H_2O^{16}}}\right)_l$	$\left(\frac{\mathrm{NO}_2^{18}\text{-}}{\mathrm{NO}_2^{16}\text{-}}\right)^{1/2}$	$\left(\frac{\mathrm{H_2O^{18}}}{\mathrm{H_2O^{16}}}\right)_g$	T, ° K.
$\left(\frac{Q}{Q'}\right)^{1/n}$	1.2077	1.1767	1.1652	1.1587	1.1615	1.1605	1.1608	1.1317	1.1317	1.1108	200.00
	1.1331	1.1127	1.1104	1.1089	1.1030	1.1006	1.0979	1.0888	1.0825	1.0770	273.16
	1.1172	1.0988	1.0982	1.0963	1.0903	1.0878	1.0847	1.0780	1.0719	1.0694	298.16
	1.1042	1.0874	1.0881	1.0858	1.0798	1.0772	1.0740	1.0701	1.0632	1.0630	323.16
	1.0951	1.0796	1.0810	1.0786	1.0727	1.0701	1.0667	1.0642	1.0573	1.0584	343.16
	1.0837	1.0697	1.0720	1.0700	1.0637	1.0611	1.0577	1.0571	1.0498	1.0529	373.16
	1.0688	1.0569	1.0601	1.0575	1.0520	1.0494	1.0462	1.0473	1.0393	1.0452	423.16
$\left(\frac{\mathrm{CO}_2^{18}}{\mathrm{CO}_2^{16}}\right)^{1/2}$	1.0000	1.0263	1.0365	1.0423	1.0398	1.0407	1.0404	1.0672	1.0672	1.0872	200.00
		1.0183	1.0204	1.0218	1.0273	1.0295	1.0321	1.0407	1.0467	1.0521	273.16
		1.0167	1.0173	1.0191	1.0247	1.0270	1.0300	1.0364	1.0423	1.0447	298.16
		1.0154	1.0148	1.0169	1.0226	1.0251	1.0281	1.0319	1.0386	1.0388	323.16
		1.0144	1.0130	1.0153	1.0209	1.0234	1.0266	1.0290	1.0358	1.0347	343.16
		1.0131	1.0109	1.0128	1.0188	1.0213	1.0246	1.0252	1.0323	1.0293	373.16
		1.0113	1.0082	1.0107	1.0160	1.0185	1.0216	1.0205	1.0284	1.0226	423.16
$\left(\frac{\mathrm{N_2O^{18}}}{\mathrm{N_2O^{16}}}\right)$		1.0000	1.0099	1.0155	1.0131	1.0140	1.0137	1.0398	1.0398	1.0593	200.00
			1.0021	1.0034	1.0088	1.0110	1.0135	1.0220	1.0279	1.0332	273.16
			1.0006	1.0023	1.0078	1.0101	1.0130	1.0193	1.0251	1.0275	298.16
			0.9994	1.0015	1.0070	1.0095	1.0125	1.0162	1.0288	1.0230	323.16
			0.9987	1.0009	1.0064	1.0089	1.0121	1.0145	1.0211	1.0200	343.16
			0.9979	0.9997	1.0056	1.0081	1.0114	1.0119	1.0190	1.0160	373.16
			0.9970	0.9994	1.0047	1.0072	1.0102	1.0092	1.0169	1.0112	423.16
$\left(\frac{\mathrm{NO^{18}}}{\mathrm{NO^{16}}}\right)$			1.0000	1.0056	1.0032	1.0040	1.0038	1.0296	1.0296	1.0490	200.00
				1.0013	1.0067	1.0089	1.0114	1.0198	1.0258	1.0310	273.16
				1.0017	1.0072	1.0096	1.0124	1.0187	1.0245	1.0269	298.16
				1.0021	1.0077	1.0101	1.0131	1.0168	1.0234	1.0236	323.16
				1.0022	1.0077	1.0102	1.0134	1.0158	1.0224	1.0214	343.16
				1.0019	1.0078	1.0103	1.0135	1.0141	1.0211	1.0181	373.16
				1.0025	1.0077	1.0102	1.0133	1.0122	1.0200	1.0143	423.16
$\left(\frac{\mathrm{NO^{18}Cl}}{\mathrm{NO^{16}Cl}}\right)$				1.0000	0.9976	0.9984	0.9982	1.0239	1.0239	1.0431	200.00
					1.0053	1.0075	1.0100	1.0185	1.0244	1.0296	273.16
					1.0055	1.0078	1.0107	1.0170	1.0228	1.0251	298.16
					1.0056	1.0080	1.0110	1.0147	1.0213	1.0214	323.16
					1.0055	1.0079	1.0112	1.0135	1.0201	1.0191	343.16
					1.0059	1.0084	1.0016	1.0122	1.0192	1.0162	373.16
					1.0052	1.0077	1.0108	1.0097	1.0175	1.0118	423.16
$\left(\frac{\mathrm{NO}_2^{18}}{\mathrm{NO}_2^{16}}\right)^{1/2}$					1.0000	1.0009	1.0006	1.0263	1.0263	1.0456	200.00
						1.0022	1.0046	1.0130	1.0189	1.0241	273.16
						1.0023	1.0052	1.0114	1.0172	1.0195	298.16
						1.0024	1.0054	1.0091	1.0156	1.0158	323.16
						1.0024	1.0056	1.0080	1.0146	1.0135	343.16
						1.0025	1.0057	1.0062	1.0132	1.0103	373.16
						1.0025	1.0055	1.0045	1.0122	1.0065	423.16
$\left(\frac{\mathrm{SO}_2^{18}}{\mathrm{SO}_2^{16}}\right)^{1/2}$						1.0000	0.9997	1.0254	1.0254	1.0447	200.00
							1.0025	1.0108	1.0167	1.0219	273.16
							1.0029	1.0091	1.0148	1.0172	298.16
							1.0030	1.0066	1.0132	1.0134	323.16
							1.0032	1.0055	1.0121	1.0111	343.16
							1.0032	1.0038	1.0108	1.0078	373.16
							1.0031	1.0020	1.0097	1.0040	423.16
$\left(\frac{\mathrm{NO}_3^{18}\text{-}}{\mathrm{NO}_3^{16}\text{-}}\right)^{1/3}$							1.0000	1.0257	1.0257	1.0450	200.00
								1.0084	1.0142	1.0194	273.16
								1.0062	1.0119	1.0143	298.16
								1.0036	1.0102	1.0103	323.16
								1.0023	1.0089	1.0078	343.16
								1.0006	1.0075	1.0046	373.16
								0.9989	1.0066	1.0010	423.16
$\left(\frac{\mathrm{H_2O^{18}}}{\mathrm{H_2O^{16}}}\right)_l$								1.0000	1.0000	1.0188	200.00
									1.0058	1.0110	273.16
									1.0057	1.0080	298.16
									1.0065	1.0067	323.16
									1.0065	1.0055	343.16
									1.0070	1.0040	373.16
									1.0077	1.0020	423.16
$\left(\frac{\mathrm{NO}_2^{18}\text{-}}{\mathrm{NO}_2^{16}\text{-}}\right)^{1/2}$									1.0000	1.0188	200.00
										1.0051	273.16
										1.0023	298.16
										1.0002	323.16
										0.9990	343.16
										0.9971	373.16
										0.9953	423.16

Calculations of the equilibrium constants for oxygen exchange have been reported earlier by Urey (*18*), Taylor and Clarke (*17*), Saxena and Taylor (*16*), and Monse (*13*). Since then new and more accurate frequency assignments have appeared. In this article the partition function ratios were calculated as a function of temperature, and a few systems are discussed which have favorable equilibrium constants and show promise for setting up counter-current exchange columns for the enrichment and production of oxygen-18.

RESULTS

The spectroscopic data used for molecules and ions containing oxygen-16 are listed in Table I. Zero-order frequencies were used for NO, N_2O, and NO_2 molecules, and the force constants of Begun and Fletcher (*3*) and Arakawa and Nielsen (*1*) for N_2O and NO_2, respectively. These force constants successfully reproduce the frequencies of the nitrogen-15 substituted molecules for which experimental data are available (*1, 3*). The frequency assignment for CO_2^{16} as given by Dennison (*8*) and calculated values of Urey (*18*) for CO_2^{18} were directly used. These values, however, receive some confirmation from the recent measurements of Eggers and Arends (*9*). The experimental and calculated vibrational frequencies for $NO^{16}Cl$ and $NO^{18}Cl$, respectively, are given by Landau and Fletcher (*12*), and seem to be reliable as similarly computed values of $N^{15}OCl$ from $N^{14}OCl$ agree very well with the observed frequencies (*12*). For NO_2^- and NO_3^- observed fundamental frequencies have recently been published (*4*). The force constants for NO_2^- are given by Weston and Brodsky (*20*) and for NO_3^- by Herzberg (*10*). These force constants successfully predict for both cases the measured values (*4*) of nitrogen-15 substituted ions, and we have, therefore, used these very force constants for computing frequencies of oxygen-18 substituted ions. For SO_2 the frequency assignment recommended by Polo and Wilson (*14*) has been used along with their force constants, as these are successful in correlating the available observed vibrational frequencies of normal and isotopic molecules. For H_2O^{16} and H_2O^{18} the frequencies are given by Urey (*18*).

Partition function ratios are calculated, according to Equation 1 and utilizing the data of Table I, as a function of temperature and are reported in Table II. The partition functions for liquid water were generated from those of gaseous water by multiplying the partition functions for the latter with the ratio of the vapor pressures of H_2O^{16} and H_2O^{18}. The vapor pressure ratio at each temperature was calculated according to the formula given by Urey (*18*). The equilibrium constants for all possible exchanges are also given in this table.

DISCUSSION OF RESULTS

Carbon dioxide has most favorable equilibrium constants with almost all the molecules and ions listed in Table II. Except for water, it is extremely difficult to use these exchanges for operating countercurrent cascades to enrich oxygen-18. The difficulty arises mostly either in getting the countercurrent streams of gaseous and liquid phases or in designing the proper refluxer. Even the water and carbon dioxide system has not proved very successful (*7*). Some possibilities have been suggested recently for the proper catalysis of this exchange (*15*).

Nitrous oxide has the next preferable values for equilibrium constants for several exchanges; the exchange with water, in particular, seems to be interesting. Friedman and Bigeleisen (*11*) found the exchange rate to be negligible in the neutral medium. Bonner and Bigeleisen (*6*) also investigated this exchange in an alkaline and acid medium, but found very long half-times. We think that the use of nitric acid instead of sulfuric acid might lead to satisfactory exchange rate. Our view stems from the fact that nitrogen compounds and ions have good equilibrium constants against nitrous oxide, and nitric acid has been successful (*16, 17*) in catalyzing the exchange between water and nitric oxide, probably by forming suitable intermediate compounds. It will be interesting to test this view.

The exchange between nitric oxide and water has been tried (*17*) and developed (*16*) with completely satisfactory results. The design of the product refluxer as well as the optimum operating conditions have been determined (*16*). Nitrosyl chloride is almost as good as nitric oxide in values of equilibrium constants. In actual practice nitrosyl chloride will be much harder to work with (*2*). Liquid NOCl and NO exchange has been studied by Yeatts (*21*). He found the enrichment of oxygen-18 in the NOCl phase, the values of the equilibrium constant being 1.012 at −50° C. Our calculations for NOCl gas with NO suggest much less enrichment in the NO phase, which, however, one would expect also.

On the whole, the two exchanges which are important and show promise for the production of oxygen-18 by adopting chemical exchange method are the exchange of carbon dioxide and water and the exchange of nitric oxide and water. On both exchanges much still remains to be done, and attempts are being made in this laboratory to evaluate these exchanges further.

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