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9. We thank the Paducah Gaseous Diffusion Plant operated by Union Carbide Nuclear Company for the AEC for making available the facilities and materials; R. W. Levin and V. G. Katzel for assistance with work schedules; and C. R. Beverly and R. E. Simmons for the analyses. This report is abstracted, in part, from a thesis presented by one of us (R.C.S.) in partial fulfillment of the requirements for an M.A. degree from Southern Illinois University.

20 July 1964

## Vapor Pressure of Ice Containing D<sub>2</sub>O

**Abstract.** *The vapor pressures of solid D<sub>2</sub>O and ice containing D<sub>2</sub>O in various amounts were measured with an oil manometer. The result gives the lowest vapor pressure for D<sub>2</sub>O ice ever obtained. The observed value for ice with different proportions of D<sub>2</sub>O and H<sub>2</sub>O agreed well with the values calculated on the assumption that the vapor pressure of HDO is the geometrical mean of those of H<sub>2</sub>O and D<sub>2</sub>O and that the equilibrium constant of isotopic exchange is 4. The fractionation factor of D between ice and vapor phases increases from 1.128 at 0°C to 1.210 at -38°C.*

Vapor pressure of ice consisting of heavy water and light water in various proportions was measured in the temperature range from 0° to -38°C. Water samples of 3 ml each were degassed and frozen at different temperatures in freezing mixtures made of water, ethyl alcohol, carbon tetrachloride, dichloroethane, and dry ice. The vapor pressure was measured with an oil

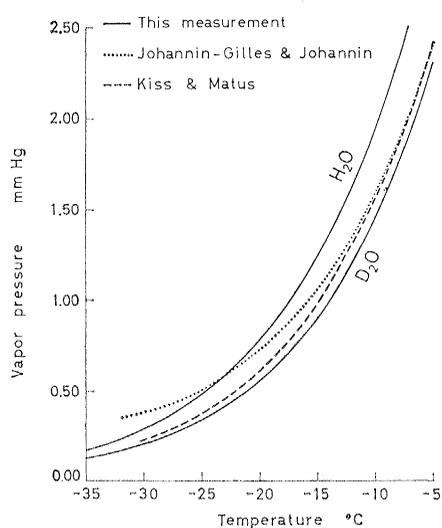


Fig. 1. Vapor pressure of D<sub>2</sub>O and H<sub>2</sub>O ice.

manometer (oil, dioctyl sebacate). The temperature of each freezing mixture was determined with a low-temperature standard thermometer (sensitivity, 0.01°C) (1). The vapor pressure and density of the oil were, respectively,  $5 \times 10^{-8}$  mm-Hg and 0.916 at 25°C; the density of the oil was corrected for the temperature change. The height of the meniscus of the manometer was determined with a cathetometer, which permits the reading of the pressure to 0.001 mm-Hg.

To check the accuracy of the measurement, the vapor pressure of the ice from ordinary water was determined. The results agreed well with previous values (2) within the experimental error of  $\pm 0.01$  mm-Hg.

Then the vapor pressure of ice from pure heavy water (D<sub>2</sub>O) was determined. The sample of heavy water used was of the concentration of 99.65 percent (mole) (manufactured by Showa Denko Co., Tokyo). The results differ from those of Johannin-Gilles and Johannin (3) especially in the lower temperature range (Fig. 1 and Table 1). The results of Kiss and Matus (4) are close to our values though they are still a little higher than ours (2 to 9 percent). Based on the result of our measurement, the relation between the vapor pressure of D<sub>2</sub>O ice and temperature (°K) is expressed by the following empirical equation.

$$\log P = -(2783.66/T) + 10.7478$$

The vapor pressure of the ice containing other proportions of D<sub>2</sub>O was measured in the same way. Five samples which consisted, respectively, of 10, 30, 50, 70, and 90 percent of the heavy water (by volume) were prepared for this purpose (Table 2).

The vapor pressure  $P$  is regarded as a sum of those of H<sub>2</sub>O, HDO, and D<sub>2</sub>O in ice as follows:

$$P = M_{H_2O}P_{H_2O} + M_{D_2O}P_{D_2O} + M_{HDO}P_{HDO}$$

where  $P_{H_2O}$ ,  $P_{HDO}$ , and  $P_{D_2O}$  are vapor pressures of pure ice phase of H<sub>2</sub>O, HDO, and D<sub>2</sub>O, and  $M$  denotes the molar fraction of each component. The vapor pressure  $P_{HDO}$  was estimated under the assumption that it is represented by the assumption that it is represented by the geometric mean of  $P_{D_2O}$  and  $P_{H_2O}$ . This assumption was proved valid (5) for the gas-liquid phases. The mole fraction of HDO was calculated by assuming that the equilibrium constant of isotopic exchange of  $H$  and  $D$  is 4.

The calculated values for  $P$  are given in Table 2. The fairly good agreement between the calculated and observed

values suggests the validity of the foregoing assumptions for ice too.

From these results the fractionation coefficient  $\alpha$  of deuterium between water vapor and ice phases at different temperature was calculated by

$$\alpha = (D/H)_{\text{sol}} (D/H)_{\text{vap}} = P_{H_2O}/P_{HDO}$$

Table 1. Vapor pressure of D<sub>2</sub>O ice.

T (°C)	P <sub>D<sub>2</sub>O</sub> (mm-Hg)
-0.02	3.59
-2.7	2.86
-4.6	2.42
-11.1	1.34
-14.4	0.98
-19.5	0.59
-24.6	0.35
-28.0	0.25
-38.4	0.08

Table 2. Vapor pressure (P) of ice containing heavy water (mm-Hg) at varying ratios of H<sub>2</sub>O to D<sub>2</sub>O.

Temp. (°C)	P <sub>obs.</sub>	P <sub>calc.</sub>
9H <sub>2</sub> O : 1D <sub>2</sub> O		
0.00	4.49	4.48
-4.2	3.16	3.15
-12.4	1.55	1.53
-14.5	1.25	1.26
-20.7	0.69	0.70
-24.0	.48	.51
-28.4	.33	.33
-37.9	.12	.11
7H <sub>2</sub> O : 3D <sub>2</sub> O		
0.00	4.26	4.28
-3.3	3.22	3.25
-4.4	2.93	2.96
-8.0	2.14	2.15
-10.4	1.68	1.74
-15.1	1.09	1.13
-16.5	0.97	0.99
-27.0	.35	.35
5H <sub>2</sub> O : 5D <sub>2</sub> O		
0.01	4.07	4.07
-4.2	2.87	2.86
-10.9	1.58	1.57
-15.6	1.00	1.02
-19.9	0.66	0.67
-23.3	.47	.48
-28.5	.28	.28
-38.0	.10	.10
3H <sub>2</sub> O : 7D <sub>2</sub> O		
0.03	3.85	3.87
-4.5	2.64	2.65
-10.5	1.56	1.55
-15.1	1.00	1.01
-19.9	0.62	0.63
-23.0	.45	.46
-27.9	.27	.28
-37.9	.09	.10
1H <sub>2</sub> O : 9D <sub>2</sub> O		
0.02	3.68	3.69
-4.3	2.57	2.57
-10.0	1.53	1.52
-15.2	0.93	0.93
-19.2	.62	.63
-23.3	.42	.42
-27.7	.27	.28
-37.9	.09	.09

Table 3. Fractionation factor  $\alpha$  of D and H between ice and vapor.

T °C	$\alpha$
0	1.128
-5	1.137
-10	1.148
-15	1.161
-20	1.174
-25	1.187
-28	1.194
-38	1.210

where,  $P_{\text{HDO}}$  was obtained as described. As given in Table 3, the value for  $\alpha$  gradually increases from 1.128 at 0°C to 1.210 at -38°C. This is substantially different from the calculation made by Miyake and Matsuo (6) based on previous data (3).

SADAO MATSUO  
HIDEKO KUNIYOSHI  
YASUO MIYAKE

Department of Chemistry,  
Tokyo Kyoiku University,  
Ohtsuka, Tokyo, Japan

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### Thermal Reduction of Bicarbonate to Formate

**Abstract.** Thermal decomposition of infrared pellets of sodium or potassium bicarbonates dispersed in KCl, KBr, or KI matrices leads to the production of bicarbonate monomer ions and finally formate ions, as well as other expected products. These products can be identified readily from the infrared spectra of the pressed disks.

In 1950 Garrison *et al.* (1) irradiated aqueous solutions of CO<sub>2</sub> with  $\alpha$ -particles in a cyclotron and showed that the resulting solutions contained appreciable concentrations of formaldehyde and formic acid. These workers suggested that such ionizing radiation might have been one source of reduced carbon compounds in the primeval organic milieu. We wish to report that thermal degradation, under a relatively mild condition, of inorganic bicarbonates dispersed in ionic matrices also produces an appreciable amount of formate.

Our experimental technique was a simple one and was described earlier (2). Potassium or sodium bicarbonates were dispersed in optical grade KCl, KBr, or KI powder by the standard method of grinding or freeze-drying. The powder was transferred to an infrared pellet die, evacuated, and then pressed. The resulting disks were

heated in an oven in air at constant temperatures ranging from about 450° to 600°C for various lengths of time. Chemical changes in the disks were followed by examining the infrared spectra after the disks had been quenched to room temperature.

Figure 1 shows the changes observed in the spectrum of a typical KBr disk in the characteristic CO-bond stretch region for carbonates. Initially, the spectrum was that of a hydrogen-bonded cyclic dimer of the bicarbonate ion (lower spectrum, C), but on heating for a short time the dimers were destroyed. The products in the matrix were the expected carbonate ion (absorption bands X, spectrum B), some trapped CO<sub>2</sub> gas, and the bicarbonate monomer ion (absorption bands Y, spectrum B). These products were not due to any contaminants in the disks; other disks prepared in the same manner but without the solute gave none of these absorption bands after they were heated. The identification of the carbonate bands was made by comparing the spectrum to that of a heated disk which contained only potassium carbonate as a solute. The assignments of the bicarbonate monomer absorption bands were made by using the isotopic molecules (deuterium and carbon-13) and by comparing the spectrum to that of the isoelectronic nitric acid molecule. Vibrational frequencies and normal coordinate analysis of the bicarbonate monomer will be reported elsewhere (3).

On further heating of the disks, new bands appeared (Fig. 1, absorption band X, spectrum B), and they were identified as belonging to the formate ion. Spectrum A in Fig. 1 is from a heated disk containing potassium formate as a solute. Band Z is the anti-symmetric stretch mode in the -CO<sub>2</sub> group of the formate ion. Other formate bands observed but not shown in Fig. 1 were the CH stretch mode and the angle deformation mode in the -CO<sub>2</sub> group. These assignments were confirmed by the use of deuterium and carbon-13 isotopic substitutions. The frequencies of the formate ion in different alkali halide matrices, the changes of the spectra on heating, and the quantitative kinetic study of the thermal decomposition of the formate ion will be reported elsewhere (4).

Figure 2 shows the changes in optical densities of a formate ion band and two bicarbonate monomer bands with heating time in a typical KBr

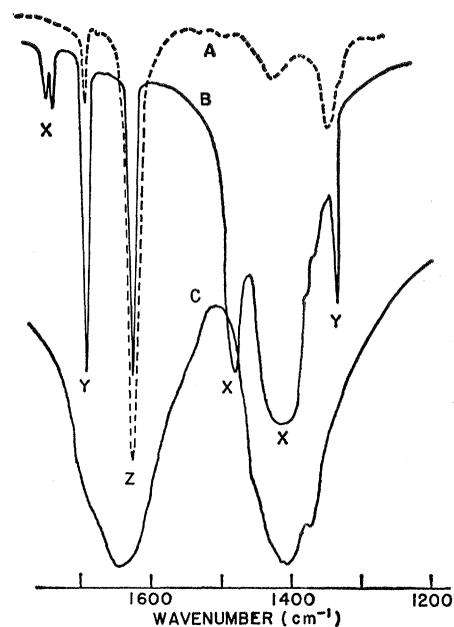


Fig. 1. Infrared spectra of formate and bicarbonate in the region of wave number 1500 cm<sup>-1</sup>. Spectrum A, 0.12 mg formate in 0.5 g KBr heated at 534°C for 5 minutes. Spectrum B, 3 mg KHCO<sub>3</sub> in 0.5 g KBr heated at 500°C for 200 minutes. Carbonate bands, X; bicarbonate monomer bands, Y; and formate bands, Z. Spectrum C, same disk as that used for spectrum B, before heating. All spectra were recorded at room temperature. The disks were 1 mm thick by 15 mm diameter.

disk. Optimum concentrations for the formation of a bicarbonate monomer was found to be approximately 3 mg of solute dispersed in 0.5 g of matrix salt. The yield of formate ions in such disks was about 5 percent based on initial solute concentrations.

The formate ions resulting from the thermal decomposition of bicarbonate appeared to be well isolated from each other and may have been in solid solution with the matrix salt. Not only were the absorption bands exceedingly sharp, but the ions showed unusual stability toward further decomposition.

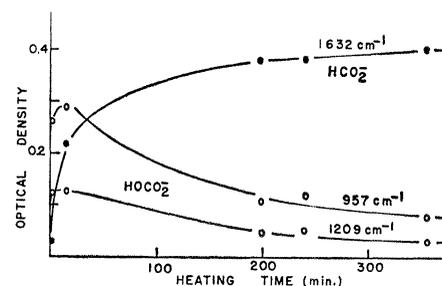


Fig. 2. Changes in the optical density of the absorption bands of formate and bicarbonate monomer with heating time. Data obtained from the sample described for spectrum B, Fig. 1. The temperature was 500°C.