

## Isotopic Fractionation between Gaseous and Dissolved Carbon Dioxide

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The isotopic fractionation between gaseous carbon dioxide and an equilibrated aqueous solution of the gas has been measured at temperatures between 0° and 60 °C for the carbon isotopes and close to 0 °C for the oxygen isotopes.

$^{13}\text{C}^{16}\text{O}_2$  is slightly less, and  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$  slightly more soluble than  $^{12}\text{C}^{16}\text{O}_2$ , the actual values for the fractionation,  $\epsilon$ , being  $-(1.18 - 0.0041 \cdot t) \text{‰}$  (temperature,  $t$ , in °C) for the carbon isotopes and about  $0.8 \text{‰}$  at 0 °C for the oxygen isotopes.

A theoretical expression is derived for the vapour-solute equilibrium system by treating it in a similar manner as the pure vapour-liquid system. The calculated isotopic fractionation for carbon dioxide, using data on the pure vapour-liquid system, is in satisfactory agreement with the experimental results.

### Introduction

The isotopic fractionation between gaseous and condensed carbon dioxide was discussed in some detail in a recent article<sup>1</sup>. Since the system carbon dioxide-water is of considerable practical importance to environmental isotope studies, we have also investigated the fractionation between gaseous and dissolved carbon dioxide.

Although the differences in vapour pressure between isotopic substances and the isotopic fractionation in equilibrium liquid-vapour systems have received much attention, both theoretically and experimentally (Ref. <sup>1,2</sup>), little consideration has hitherto been given to the system gas-solute. Waldmann<sup>3</sup> drew the general conclusion that the heavy isotopic species should be the more soluble because molecules in the liquid have an extra vibrational degree of freedom — the vibration of the molecules as a whole. This reasoning would also apply to pure liquid-vapour systems and it is well known that in such systems the effect can be outweighed by differences in the binding energy of the molecule<sup>1</sup>.

\* The measurements were performed by PMG under the supervision of WGM; the theoretical section is by JCV.

1 Grootes, P. M., Mook, W. G., Vogel, J. C.: Z. Physik **221**, 257 (1969).

2 Boato, G., Casanova, G.: In: Isotopic and cosmic chemistry, p. 16—33 (ed. Craig, H., Miller, S. L., and Wasserburg, G. J.). Amsterdam, North-Holland 1963.

3 Waldmann, L.: Naturwissenschaften **31**, 205 (1943).

It has, in fact, been shown<sup>4</sup> that, in the case of a solution also, the binding energy of the lighter isotopic species is greater than that of the heavier species and that this effect can lead to the lighter isotopic molecules being more soluble. This reversal of the "normal" fractionation effect has indeed been observed for the carbon isotopes  $C^{13}$  and  $C^{12}$  between gaseous carbon dioxide and carbon dioxide dissolved in water<sup>4-6</sup>.

The theoretical expression which has been developed for the vapour-solute equilibrium system<sup>4</sup>, is based on the assumption that interaction between a solute and solvent molecule can be treated in a similar manner as the interaction between molecules in a pure liquid. Using this expression and the results obtained for the pure carbon dioxide liquid-vapour equilibrium system<sup>1</sup>, the fractionation for the carbon and oxygen isotopic species of carbon dioxide in the vapour-solute equilibrium system can be calculated and compared with the experimental results presented here. The theoretical values show quite good agreement with experiment, thus supporting the validity of the assumption underlying the theory.

### Theory

The equilibrium isotopic fractionation factor,  $\alpha$ , between vapour and solute is by definition:

$$\alpha \equiv \frac{R_s}{R_g},$$

where  $R_s$  is the ratio of the number of heavier isotopic molecules to that of lighter isotopic molecules in the solution and  $R_g$  the same ratio in the gaseous phase when the system is in equilibrium.  $\alpha$  is thus simply the ratio of the solubilities,  $s$ , of the two isotopic species, since by expressing Henry's law for each species in the form

$$x = s p, \quad (1)$$

where  $x$  is the mole fraction of the gas in the liquid and  $p$  the partial pressure, it follows that

$$\alpha = \frac{x'}{x} / \frac{p'}{p} = \frac{s'}{s}, \quad (2)$$

where the prime refers to the heavier molecular type.

4 Vogel, J. C.: Thesis, Heidelberg (1959).

5 Vogel, J. C.: Proc. of the Summer Course on Nuclear Geology, Varenna, 1960, Italian Comm. on Nuclear Energy, Pisa (1961), p. 216.

6 Wendt, I.: Earth and Planetary Sci. Letters 4, 64 (1968).

For ideal solutions, i.e. mixtures of substances with similar internal pressure and polarity,  $s$  is equal to the reciprocal of the vapour pressure,  $p_0$ , and Henry's law becomes

$$p = p_0 x, \quad (3)$$

and

$$\alpha = \frac{p_0}{p_0'}.$$

In this ideal case the isotopic fractionation between gas and solute will be the same as that for a pure liquid-vapour system at a given temperature.

In general, however, gases are considerably less soluble in liquids than this, and it will be necessary to consider the nature of the solution itself. To obtain a theoretical expression for the solubility,  $s$ , it will only be necessary to consider a dilute solution in which each dissolved gas molecule is completely surrounded by solvent molecules as is the case at moderate gas pressures. In essence we shall follow the procedure used by Gurney<sup>7</sup>.

The equilibrium condition for a system in which a gas is partially dissolved in a liquid, is that the free energy shall not change when gas molecules are transferred from one phase to the other, i.e.

$$\left(\frac{\partial F_I}{\partial n}\right)_{VT} = -\left(\frac{\partial F_{II}}{\partial n}\right)_{VT}. \quad (4)$$

Expressing the Helmholtz free energy,  $F$ , in terms of the partition function,  $Z$ , we obtain for the gas in the vapour phase

$$F_I = -n_g k T \left( \ln \frac{Z_g}{n_g} + 1 \right)$$

and

$$\frac{\partial F_I}{\partial n_g} = -k T \ln \frac{Z_g}{n_g}, \quad (5)$$

where the subscript  $g$  refers to the gas molecules in the vapour phase.

The free energy of the solution consists of contributions from different types of particles plus a term due to the mixing. Considering the (dilute) solution to contain three types of molecules:  $n_a$  gas molecules each surrounded by  $z$  solvent molecules, and  $n_b$  solvent molecules of which  $zn_a$  are in contact with a solute molecule and  $(n_b - zn_a)$  are not influenced by

<sup>7</sup> Gurney, R. W.: Introduction to statistical mechanics. New York: McGraw Hill 1949.

the solute, the free energy is

$$F_{II} = -kT [(n_b - z n_a) \ln Z_b + z n_a \ln Z_b^+ + n_a \ln Z_a^+ - n_a \ln x_a]$$

and

$$\frac{\partial F_{II}}{\partial n_a} = -\frac{\partial F_{II}}{\partial n_g} = -kT \left( z \ln \frac{Z_b^+}{Z_b} + \ln Z_a^+ - \ln x_a \right), \quad (6)$$

where  $Z_b$  and  $Z_b^+$  are the partition functions for pure solvent and solvent in contact with solute molecules respectively,  $Z_a^+$  is the partition function for solute molecules and  $x_a$  is the mole fraction of the gas.

By inserting Eqs. (5) and (6) into Eq. (4) we obtain the condition for equilibrium,

$$\ln \frac{Z_g}{n_g} = z \ln \frac{Z_b^+}{Z_b} + \ln Z_a^+ - \ln x_a,$$

or

$$n_g = x_a \left( \frac{Z_b}{Z_b^+} \right)^z \cdot \frac{Z_g}{Z_a^+}. \quad (7)$$

Since  $n_g$ , the number of gas molecules in a given volume, is proportional to the partial pressure of the gas, Eq. (7) is a theoretical expression for Henry's law (Eq. (1)).

Introducing the partition function of the pure liquified gas,  $Z_a$ , Eq. (7) can be written as

$$n_g = x_a \left( \frac{Z_b}{Z_b^+} \right)^z \cdot \frac{Z_a}{Z_a^+} \cdot \frac{Z_g}{Z_a}. \quad (8)$$

Since  $Z_g/Z_a = n_g^0$ , the number of gas molecules in equilibrium with the pure liquified gas (see <sup>1</sup>), Eq. (8) becomes

$$\frac{n_g}{n_g^0} = x_a \left( \frac{Z_b}{Z_b^+} \right)^z \cdot \frac{Z_a}{Z_a^+}. \quad (9)$$

Eq. (9) can be compared with the ideal form of Henry's law, Eq. (3), to which it reduces when the ratios of the partition functions are unity and ideal gas behaviour is assumed, so that  $n_g/n_g^0 = p/p_0$ .

For non-ideal cases the fractionation factor  $\alpha$  can be deduced from Eq. (8) by evaluating the partition functions for both the isotopic species in the gas. This can be done to a certain extent by applying some approximations. Consider the different terms on the right-hand side of Eq. (8) in turn:

The difference between  $Z_b^+$  and  $Z_b$  is mainly due to a shift in the set of energy levels of the molecule as a whole and only in the second place to a change in the spacing of the levels. The energy shift is the change in

the depth of the potential energy well of a solvent molecule when an adjoining solvent molecule is replaced by a solute molecule. If  $U_{bb}$  is the interaction energy between two solvent molecules and  $U_{ab}$  that between a solvent and solute molecule, the energy change per molecule will be  $\frac{1}{2}(U_{ab} - U_{bb})$ , so that

$$\left(\frac{Z_b}{Z_b^+}\right)^z = e^{-z(U_{ab} - U_{bb})/2kT}.$$

The binding energy for each gas molecule in the solution is  $\frac{z}{2}U_{ab}$  and for a molecule in pure liquified gas it is  $\frac{z}{2}U_{aa}$ , so that

$$\frac{Z_a}{Z_a^+} = e^{-z(U_{ab} - U_{aa})/2kT}.$$

Regarding the partition functions  $Z_g$  and  $Z_a$ , it cannot *a priori* be assumed that the change in the spacing of the levels is small when transferring a molecule from the gaseous to the liquid phase. In fact, a measurable effect arises, as was seen in the discussion of the pure vapour-liquid system<sup>1,4</sup>. The partition functions must, therefore, be retained. In order that they be referred to their normal energy reference level, we write

$$\frac{Z_g}{Z_a} = \frac{Z_g}{Z_l} e^{-zU_{aa}/2kT}.$$

The energy difference between the reference levels is the depth of the potential energy well for the molecules in the liquid phase, which is  $\frac{z}{2}U_{aa}$ , as noted above.

Inserting the foregoing equations into Eq. (8) we obtain the simplified relationship for the solubility of a gas,

$$n_g = x_a \frac{Z_g}{Z_l} \cdot e^{+z(U_{bb} - 2U_{ab})/2kT}. \quad (10)$$

This relationship can be used to deduce an expression for the fractionation factor,  $\alpha$ , since, by definition,

$$\alpha = \frac{x'_a / n'_g}{x_a / n_g}.$$

Thus,

$$\varepsilon \simeq \ln \alpha = \ln \frac{Z_g Z'_l}{Z_l Z'_g} - \frac{z(U_{ab} - U'_{ab})}{kT}, \quad (11)$$

where the fractionation,  $\varepsilon = \alpha - 1$  and the prime refers to the heavier isotopic species.

The factor  $z(U_{ab} - U'_{ab})$  is the difference in binding energy of two isotopic molecules in the solution. Here only the dispersion interaction need be taken into account. Although the dipole and quadrupole interaction of polar molecules contributes significantly to the total binding energy, they are (practically) mass independent and do not contribute to the difference in binding energy of isotopic molecules. The energy difference caused by the dispersion interaction can be calculated from London's dispersion formula on the same lines as followed by Baertschi and Kuhn<sup>8</sup> (see also Ref. <sup>1</sup>). When expressed in terms of the attraction energies in the pure liquified gas, the difference in binding energy in the solution becomes

$$z(U_{ab} - U'_{ab}) = \frac{L - L'}{N} \cdot \frac{\alpha_{b0} r_{aa}^6}{\alpha_{a0} r_{ab}^6}, \quad (12)$$

where  $\alpha_{b0}$  and  $\alpha_{a0}$  are the electron polarizabilities of pure solvent and pure liquified gas respectively,  $r_{aa}$  and  $r_{ab}$  are the intermolecular distance in pure liquified gas and the distance between a solute and solvent molecule respectively,  $L$  is the difference between the reference energy levels of  $Z_l$  and  $Z_g$  per mole, and  $N$  is Avogadro's number.

Inserting Eq. (12) into Eq. (11) the fractionation,  $\varepsilon$ , becomes

$$\begin{aligned} \varepsilon &\simeq \ln \alpha = \ln \frac{Z_g Z'_l}{Z'_g Z_l} - \frac{L - L'}{RT} \cdot \left( \frac{\alpha_{b0} r_{aa}^6}{\alpha_{a0} r_{ab}^6} \right) \\ &= \varepsilon_Z + \varepsilon_L. \end{aligned} \quad (13)$$

In cases where the factor in brackets is equal to unity, the expression becomes identical with that for the pure vapour-liquid equilibrium system (Eq. (4) in Ref. <sup>1</sup>). As has been discussed previously<sup>1</sup>,  $\varepsilon_L$  is always negative and at moderately high temperatures it may outweigh  $\varepsilon_Z$ , thus causing  $\varepsilon$  to be negative and the heavier isotopic species to be concentrated in the vapour phase.

If data on the pure vapour-liquid system are available the fractionation of a solute can thus be deduced directly from Eq. (13). Although in most cases it may be difficult to evaluate the ratio  $r_{aa}/r_{ab}$  accurately, it can be estimated from the densities of the solvent and the liquified gas.

The fractionation for an aqueous carbon dioxide solution, i.e. the fractionation between  $^{12}\text{C}^{16}\text{O}_2$  and  $^{13}\text{C}^{16}\text{O}_2$  on the one hand ( $\varepsilon^{13}$ ) and  $^{12}\text{C}^{16}\text{O}_2$  and  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$  on the other ( $\varepsilon^{18}$ ), will be calculated here, using the experimental data for the pure vapour-liquid system<sup>1</sup> shown in Fig. 1. Since the latter system is highly non-ideal at temperatures above 0°C, the measured fractionation is smaller than it would be at normal pressures, ultimately becoming zero at the critical temperature. For evaluating the

<sup>8</sup> Baertschi, P., Kuhn, W.: *Helv. Chim. Acta* **40**, 1084 (1957).

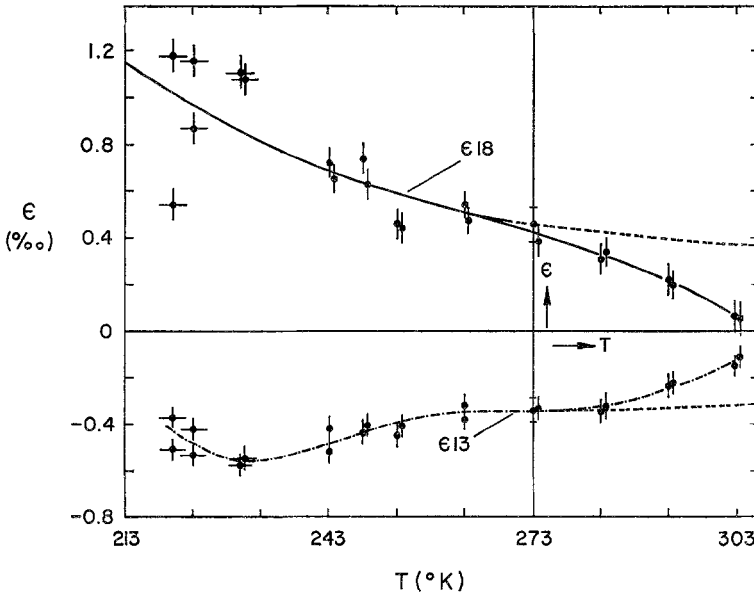


Fig. 1. Isotopic fractionation,  $\epsilon_{vl}$ , of the carbon ( $\epsilon^{13}$ ) and oxygen ( $\epsilon^{18}$ ) isotopic species of carbon dioxide in the pure vapour-liquid equilibrium system. The dashed lines give the extrapolated low temperature values

Table 1. Calculated values for the equilibrium fractionation,  $\epsilon$ , of the carbon dioxide isotopic species between the gaseous phase and an aqueous solution;  $\epsilon_{vl}$  is the extrapolated fractionation for the pure vapour-liquid system obtained from Fig. 1, and  $\epsilon_Z$  and  $\epsilon_L$  are the terms in Eq. (13). Positive values indicate that the lighter isotopic species is concentrated in the gaseous phase

T (°C)	$^{12}\text{C}^{16}\text{O}_2 - ^{13}\text{C}^{16}\text{O}_2 (\text{‰})$				$^{12}\text{C}^{16}\text{O}_2 - ^{12}\text{C}^{16}\text{O}^{18}\text{O} (\text{‰})$			
	$\epsilon_{vl}$	$\epsilon_Z$	$\epsilon_L$	$\epsilon^{13}$	$\epsilon_{vl}$	$\epsilon_Z$	$\epsilon_L$	$\epsilon^{18}$
0	-0.34	+1.69	-2.64	-0.95	+0.46	+0.99	-0.69	+0.30
10	-0.34	+1.62	-2.55	-0.93	+0.43	+0.94	-0.66	+0.28
20	-0.33	+1.57	-2.47	-0.90	+0.40	+0.90	-0.65	+0.25
30	-0.32	+1.51	-2.38	-0.87	+0.38	+0.86	-0.62	+0.24

first term in Eq. (13),  $\epsilon_Z$ , we therefore do not use the actual measured values, but rather the extrapolated low temperature data (dashed line in Fig. 1). The second term  $\epsilon_L$ , is obtained by multiplying the values for  $(L-L')/RT$  calculated previously (Ref. <sup>1</sup> Table 2) by 1.3. The factor 1.3 is calculated from the density of water and liquid carbon dioxide and the appropriate electron polarizabilities. The results are given in Table 1. The calculated values will be compared with the experimental results given below.

It should be noted that, in contrast to the molecular species  $^{12}\text{C}^{16}\text{O}_2$  and  $^{13}\text{C}^{16}\text{O}_2$ , the molecule  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$  has a small, but real, dipole moment which would contribute to its binding energy in water (orientation effect). This effect has not been taken into account in the calculations since it is thought to be small.

### Experiment and Results

When measuring isotopic fractionation in two-phase equilibrium systems, the main problem is to sample the two phases for measurement without disturbing the isotopic equilibrium. The recovery of the sample must also be quantitative to ensure that kinetic fractionation does not change its isotopic composition. In the experiment on hand carbon dioxide is allowed to equilibrate with water at the prescribed temperature and a sample of carbon dioxide is then extracted from both the gaseous and liquid phases. We decided that the most practical procedure to obtain the samples was to separate the phases completely and then to extract the carbon dioxide from each phase quantitatively.

In principle, the fractionation of the carbon isotopes  $^{12}\text{C}$  and  $^{13}\text{C}$  and of the oxygen isotopes  $^{16}\text{O}$  and  $^{18}\text{O}$  can then be determined. It is, however, obvious that the extraction of  $\text{CO}_2$  from the aqueous solution poses difficulties as far as the oxygen isotopes are concerned since any change in the chemical equilibrium between the carbon dioxide and the water during the extraction of the dissolved carbon dioxide can cause a change in the distribution of the oxygen isotopes.

The reaction of the dissolved carbon dioxide with the water does not pose any problems as far as the carbon isotopes are concerned. Theoretically the isotope ratio of the extracted carbon dioxide must be corrected for the presence of  $\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-$  in the solution, but under normal conditions, less than 1% of the carbon dioxide is present in these forms and, using the known fractionation factor for the isotopic equilibrium<sup>9</sup>, the correction to  $\epsilon$  is found to be less than 0.06‰. For our purposes the solution can thus be treated as a purely molecular solution.

Since the fractionation factors are independent of the relative concentrations of the isotopic species, natural carbon dioxide was used in the experiments.

Once carbon dioxide samples of each phase were obtained, both the carbon and oxygen isotope ratios,  $\text{C}^{13}/\text{C}^{12}$  and  $\text{O}^{18}/\text{O}^{16}$ , were measured on an "Atlas M 86" mass spectrometer relative to a standard sample. All samples were measured twice and corresponding samples of the

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<sup>9</sup> Emrich, K., Ehhalt, D. H., Vogel, J. C.: *Earth and Planetary Sci. Letters* (in print).



gaseous and liquid phases analysed consecutively. The relative difference in isotopic composition between sample and standard gas is given by

$$\delta = \frac{R - R_{st}}{R_{st}},$$

where  $R$  and  $R_{st}$  are the isotopic ratios of sample and standard gas respectively. Thus the fractionation,  $\epsilon$ , is given by

$$\epsilon \equiv \alpha - 1 = \frac{R_s - R_g}{R_g} = \frac{\delta_s - \delta_g}{1 + \delta_g},$$

where  $s$  and  $g$  refer to the solution and gaseous phase respectively. The standard deviations of the  $\delta$ -values, introduced by the mass spectrometer, were 0.05 and 0.12 or 0.07‰ for the carbon and oxygen isotopes respectively.

#### *Comparison of Different Sampling Procedures*

To find a reliable method for sampling the carbon dioxide in the two phases, three different procedures were tried at the same equilibrium temperature (25 °C). The time necessary for attaining equilibrium without shaking the solution was measured with isotopically enriched carbon dioxide and found to be less than 22 hours at 25 °C. In experiments conducted at 25 °C and higher, the system was therefore left at the temperature for at least 20 hours to ensure that equilibrium was reached before sampling the phases. At lower temperatures (0°–20 °C) times between 70 and 40 hours were allowed to elapse before sampling.

Equilibrium was established in the following manner: 25 ml of demineralized water was inserted into a 300 ml round-bottomed flask which was then freed of air by freezing the water and evacuating the flask several times. Subsequently carbon dioxide was filled into the flask to a pressure of about 50 cm mercury and the flask then placed in a waterbath at 25 °C for 22 hours.

After equilibration the phases were separated in three different ways:

(a) The aqueous solution was allowed to escape into an evacuated 30 ml flask through a jet and then closed off from the gas phase. The carbon dioxide was collected quantitatively in an attached container cooled with liquid air. Before measurement on the mass spectrometer the gas was dried by passing it through a dry-ice trap. Finally a sample of the gas phase remaining in the 300 ml flask was tapped off and similarly dried. Here the volume of the system is increased during sampling and this could cause a small amount of carbon dioxide to escape from the solution into the gaseous phase.

Table 2. Results for different methods of sampling at 25 °C

Method	Carbon (‰)			Oxygen (‰)		
	$\delta_g$	$\delta_s$	$\epsilon^{13}$	$\delta_g$	$\delta_s$	$\epsilon^{18}$
a (av.)	-2.10	-3.20	-1.07	-6.75	-5.40	+1.17
b	-1.90	-2.85	-0.93	-6.88	-5.02	+1.89
	-1.89	-2.92	-1.01	-6.80	-5.16	+1.75
	-1.90	-2.95	-1.03	-6.85	-4.28	+2.59
	-1.93	-2.98	-1.03	-6.78	-5.18	+1.63
c	-2.10	-3.17	-1.05	-6.86	-6.18	+0.72

(b) The aqueous solution (here in a 100 ml flask) was rapidly frozen in dry ice and the gas phase removed, dried and filled into a container, ready for analysis. The dissolved carbon dioxide which evolved after thawing was collected in a similar manner.

(c) All the aqueous solution was shaken through an open stop-cock into a 25 ml flask which had been attached previously. After closing the stop-cock the gas from the two phases was extracted separately and dried as in (b).

The results of the three procedures are given in Table 2. The values for the fractionation of the carbon isotopic species,  $\epsilon^{13}$ , are in good agreement with each other. Since the nature of the deviations from ideal circumstances during sampling differs in the three methods, it is concluded that the error introduced in each case is negligible. Furthermore, since the spread in the results is not larger than the estimated standard deviation in the mass spectrometric measurement, the error introduced during sampling and treatment is small in comparison. Notably, any kinetic isotopic fractionation caused by the volume increase in method (a) is obviously within the limits of accuracy of measurement.

The values for  $\epsilon^{18}$ , the fractionation for the oxygen isotopic species, show variations which are well outside the accuracy of measurement. The same water and gas was used for all experiments so that the isotopic ratios of the individual samples are comparable. Since  $\delta_g^{18}$  was always constant and  $\delta_s^{18}$  erratic, it is obvious that the error is to be ascribed to the extraction procedure of the dissolved gas. As pointed out before, difficulties are to be expected in this respect because the oxygen isotopic equilibrium between the dissolved carbon dioxide and the water is seriously disturbed during extraction of the gas.

The separation of carbon dioxide and water is effected by allowing the gas to evolve into a vacuum and trapping it in a liquid air trap.

During this procedure the water is cooled considerably, and since isotopic exchange between the carbon dioxide and water is relatively rapid at normal temperatures, a re-distribution of the oxygen isotopes can easily take place. The rate of oxygen isotopic exchange is determined by the hydration rate of carbon dioxide. (The rate of dehydration is three orders of magnitude greater.) From the rate constants<sup>10</sup> the average lifetime,  $\tau$ , of a carbon dioxide molecule in water is calculated to be 27 sec at 25 °C, and since the extraction requires a few seconds, a marked isotopic exchange towards the equilibrium value at lower temperatures can take place. At higher temperatures the reaction is faster ( $\tau = 7$  sec at 38 °C) and the solution also cools faster so that the effect will be even more serious. At 0 °C, where  $\tau = 500$  sec, it may be possible to obtain reliable results for the fractionation  $\epsilon^{18}$ , but above 15 °C, where  $\tau = 70$  sec, the results become dubious.

The second method of extraction, (b), where the liquid phase is frozen, is, for this reason, bound to give incorrect results for the oxygen isotopes at all temperatures.

#### *Temperature Dependence of the Fractionation*

As seen in the previous section the fractionation of the carbon isotopes can conveniently be determined by any of the described methods, while methods (a) and (c) may be applicable at temperatures close to 0 °C for <sup>18</sup>O. Method (a) was adopted for measurements at varying temperatures.

In all, 27 sets of samples representing 12 different temperatures ranging from 0° to 60 °C were analysed. The values obtained for the fractionation of the carbon isotopes,  $\epsilon^{13}$ , are plotted in Fig. 2. The standard deviations attributed to the points (0.05‰) are calculated from the spread in the  $\delta$  values and are equal in magnitude to the error introduced by the mass spectrometer. The experimental errors are therefore small in comparison.

The low-temperature values of  $\epsilon^{18}$  are listed in Table 3. Above 10 °C the measured  $\epsilon^{18}$  values increase up to +2.8‰ at 60 °C, but as these figures are probably meaningless, they are omitted.

On the other hand, the oxygen isotope measurements on the gaseous CO<sub>2</sub> are reliable and these can be used to calculate the temperature dependence of the oxygen isotope fractionation between water and carbon dioxide. After applying a small correction for the finite amount of water,

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10 Edsall, J. T., Wyman, J.: *Biophysical chemistry*. New York: Academic Press 1958.

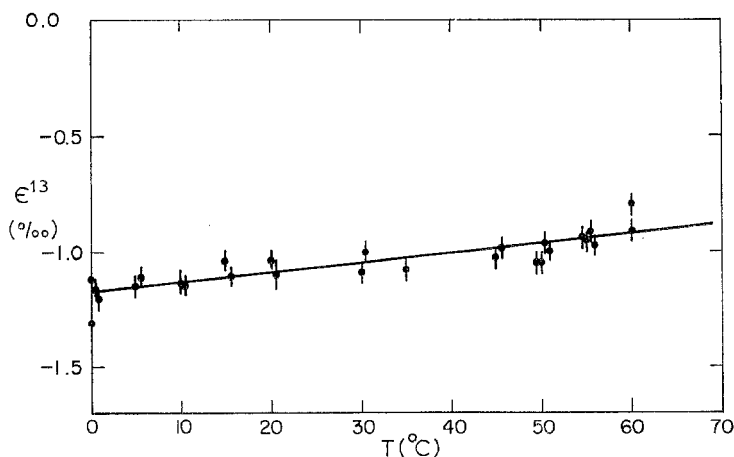


Fig. 2. Measured isotopic fractionation,  $\epsilon^{13}$ , of the carbon isotopic species between gaseous carbon dioxide and an equilibrated aqueous solution of the gas at varying temperatures

Table 3. Experimental  $\delta$ -values and fractionation,  $\epsilon^{18}$ , for the oxygen isotopes in gaseous and dissolved carbon dioxide

$T$ (°C)	$\delta_g^{18}$ (‰)	$\delta_s^{18}$ (‰)	$\epsilon^{18}$ (‰)
0	-1.97	-1.02	$+0.92 \pm 0.12$
	-1.83	-0.96	$+0.84 \pm 0.12$
0.5	-2.04	-1.77	$+0.25 \pm 0.12$
	-2.11	-1.07	$+1.01 \pm 0.12$
5.0	-3.14	-2.43	$+0.70 \pm 0.17$
	-3.25	-2.47	$+0.77 \pm 0.17$
10.0	-4.00	-3.12	$+0.85 \pm 0.12$
	-3.97	-3.14	$+0.80 \pm 0.12$

the result is

$$\frac{d\alpha_{wg}}{dT} = -\frac{17.15}{T^2}$$

over the temperature range 0° to 60 °C, or  $-(0.193 \pm 0.002)^{\circ}/_{00}/^{\circ}\text{C}$  at 25 °C.

This can be compared with earlier measurements of Emrich *et al.*<sup>9</sup> who found a value of  $-0.16^{\circ}/_{00}/^{\circ}\text{C}$  at 25 °C, and with the calculated value<sup>11</sup> of  $-0.18^{\circ}/_{00}/^{\circ}\text{C}$  at 25 °C.

<sup>11</sup> Urey, H. C.: J. Chem. Soc., 562 (1947).

### Discussion

The measurements show that, under equilibrium conditions, a small but distinct fractionation of both the carbon and oxygen isotopes occurs between gaseous carbon dioxide and an aqueous solution of the gas. As has previously been found<sup>4-6</sup>, the lighter isotopic species,  $^{12}\text{C}^{16}\text{O}_2$ , is

Table 4. *Calculated and measured fractionation for carbon dioxide between the gaseous phase and an aqueous solution*

$T$ (°C)	$\epsilon^{13}$ (‰)		$\epsilon^{18}$ (‰)	
	exper. ( $\pm 0.04$ )	theor.	exper. ( $\pm 0.12$ )	theor. <sup>a</sup>
0	-1.17	-0.95	+0.8	+0.30
10	-1.13	-0.93		+0.28
20	-1.09	-0.90		+0.25
30	-1.05	-0.87		+0.24
40	-1.01			
50	-0.97			
60	-0.92			

<sup>a</sup> No account has been taken of the orientation interaction of the  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$  dipole.

concentrated in the solution with respect to  $^{13}\text{C}^{16}\text{O}_2$ , although the enrichment we measure is somewhat larger. On the other hand, the heavier isotopic species  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$  is more soluble than  $^{12}\text{C}^{16}\text{O}_2$ . The actual values obtained are

$$\epsilon^{13} = -(1.18 \pm 0.01) + (0.0041 \pm 0.0005)t \text{ ‰},$$

$$\epsilon^{18} \simeq +0.8 \text{ ‰ at } 0^\circ\text{C},$$

where  $t$  is the temperature in °C. The result for the oxygen isotope fractionation is uncertain, since a change in the isotopic composition of the dissolved carbon dioxide during extraction from the water cannot be excluded.

The experimental results for the carbon isotopes are in good agreement with the calculated values (Table 4). For the oxygen isotopes the agreement is less good, but quite satisfactory if one considers the uncertainty of the measured value and the fact that the extra binding energy, caused by the permanent dipole moment of  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$  in the dipole field of the water, has not been taken into account. The latter effect would tend to increase the calculated figures and bring them into closer agreement with experiment.

The general agreement between theory and experiment and the fact that the fractionations in this system are similar in magnitude and sign to those in the pure vapour-liquid system, suggest that the assumptions underlying the theoretical treatment are justified.

### Conclusion

A theoretical expression for the fractionation of the isotopes in a gas between the vapour phase and a solution under equilibrium conditions, can be deduced by treating the molecular interactions in the solution in a similar way as those in a pure liquid. To test the theory the system carbon dioxide-water was investigated.

By using the measured fractionation factors for the pure carbon dioxide vapour-liquid system the fractionation for both the carbon and oxygen isotopes in the vapour-solute system can be calculated and compared with experiment.

The fractionation factors were measured by equilibrating carbon dioxide of natural isotopic composition with water at temperatures between 0° and 60 °C, separating the phases quantitatively and extracting the gas from each phase for mass spectrometric analysis. Different methods of separating the phases were compared at 25 °C and the most suitable method adopted for measurements at the other temperatures.

Both theory and experiment show  $^{13}\text{C}^{16}\text{O}_2$  to be less, and  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$  slightly more soluble in water than  $^{12}\text{C}^{16}\text{O}_2$ . The calculated value for the fractionation of the carbon isotopes and its temperature dependence agree quantitatively with the measurements. The results for the oxygen isotopes are less accurate, but show qualitative agreement. It is, therefore, concluded that vapour-solution systems are not essentially different to the pure vapour-liquid systems as far as isotopic fractionation is concerned even though the solutions are not ideal.

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