Table III. Change of Specific Rate Constant, k, with Temperature

Sarin, Initial Mole Fraction	k, Kg.^{2}/Mole^2/Min.	Temp., ° C.
0.72	$(1.4 \pm 0.1) \times 10^{-5}$	25.0
0.63	$(1.7 \pm 0.1) \times 10^{-5}$	25.0
0.57	$(1.7 \pm 0.1) \times 10^{-5}$	25.0
0.47	$(1.7 \pm 0.1) \times 10^{-5}$	25.0
. . .	8.7×10^{-5} [a]	40.0
. . .	19×10^{-5} [a]	50.0
0.47	$(1.9 \pm 0.4) \times 10^{-3}$	81.5
0.47	$(6.6 \pm 0.7) \times 10^{-3}$	100.0

[a] Calculated from data of Sass *et al.* (*4*).

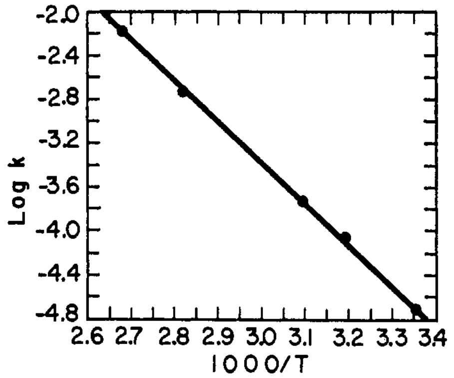

Figure 3. Arrhenius plot for third-order rate constant

$$\frac{dx}{dt} = k\,(a - x)^2\,(b - x) \tag{4}$$

When integrated, Equation 4 becomes

$$k = \frac{1}{t\,(a - b)}\left[\frac{2.303}{(a-b)}\log\frac{b\,(a - x)}{a\,(b - x)} - \frac{x}{a\,(a - x)}\right] \tag{5}$$

The best indication of a third order for the reaction is the constant value of the rate constant, k, both within a given run and between runs having different initial concentrations of reactants when the experimental data are tested with Equation 5. By using a least squares procedure, the rate constant from each experiment was determined (Table III). Values for k at 40° and 50° C. have been calculated, using data from the earlier work of Sass *et al.* (*4*), and are also included. From an Arrhenius plot of these rate constants in Figure 3, the activation energy is 17.8 kcal. per mole. The linearity of the Arrhenius plot and the magnitude of the activation energy indicate that the reaction is homogeneous.

NOMENCLATURE

LD_{50} = lethal dose 50, dose in mg. per kg. of body weight which will kill 50% of a group of animals
x = moles of Sarin or HCl per kg. of solution reacting in time t
t = time
k = specific rate constant, kg.^{2}/mole^2/min.
n = order of reaction
a = initial moles of HCl per kg. of solution
b = initial moles of Sarin per kg. of solution
Δ m.f. Sarin = difference in mole fraction of Sarin when measured at time zero and time t
Δ cps. = difference in position of resonance signal for exchangeable protons at time zero and time t, measured in cycles per second at 60 megacycles per second frequency relative to most upfield line of Sarin spectrum
T = temperature, ° K.

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Sodium Carbonate–Bicarbonate Equilibrium with Monoethanolamine Additive

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CARBON DIOXIDE is absorbed from a gas in many industrial processes. A satisfactory absorbing medium will preferentially absorb the gas and be economical to regenerate. Aqueous solutions of sodium carbonate and sodium bicarbonate are often used as the absorption medium. Additives such as amines are sometimes used industrially to increase the equilibrium constant, to effect separation more easily. The effect of monoethanolamine has not been reported and would have some economic advantages as an additive.

Design of an absorption system requires a knowledge of the equilibrium characteristics of the system. The equilibrium constant of the sodium carbonate–sodium bicarbonate system is a measure of the equilibrium carbon dioxide partial pressure of carbon dioxide above the solution. A higher equilibrium constant corresponds

The equilibrium characteristics of the sodium carbonate–sodium bicarbonate–air carbon dioxide system were determined with and without monoethanolamine as an additive. Equilibrium constants at varying sodium carbonate and sodium bicarbonate concentrations were determined at additive concentrations ranging from 0.05 to 0.50*N*. The equilibrium temperature was 30.0° ± 0.01° C. and the carbonate solution was 1.0*N* with respect to sodium. Addition of monoethanolamine increased the equilibrium constant for the system and reduced the equilibrium carbon dioxide partial pressure. A nonlinear regression analysis was used. The experimental curve is recommended for additive concentrations up to 0.2*N*. The empirical relation for *K* should be used with caution in extending the data over the 0.2 to 0.5 normality range.

to a lower equilibrium partial pressure of carbon dioxide. A lower equilibrium partial pressure for carbon dioxide increases the driving force between the gas and liquid phases, and more carbon dioxide is then absorbed from the gas.

The rate of carbon dioxide absorption and the equilibrium characteristics of this system are controlled by chemical reaction in solution between dissolved molecular carbon dioxide and hydroxyl ions rather than by diffusion (*4*). If the absorption is chemical reaction–controlled, it is possible that an additive exists which would lower the equilibrium carbon dioxide partial pressure and thus increase the rate of carbon dioxide absorption. The determination of the equilibrium constant is the primary objective of this study.

EXPERIMENTAL PROCEDURE

The procedure used is a modification of that employed by McCoy (*5*). The equipment was primarily an apparatus for contacting and separating the gas phase from the liquid phase. This apparatus was submerged in a constant temperature bath and maintained at 30° ± 0.01° C. The separation consisted of using pure, dry mercury to transfer the gas phase from a vessel in which it had been allowed to come to equilibrium with the liquid phase to another vessel where it could be analyzed. Titrimetric analyses similar to those used by McCoy were then made to determine the composition of the liquid and vapor phases.

Since monoethanolamine reacts with hydrochloric acid, the fraction of the sodium in the form of the bicarbonate could not be determined by the method of McCoy. The same analytical procedure was used, but calibration curves were established from which the bicarbonate fraction was determined directly, knowing the volume of 0.1*N* hydrochloric acid used in the titration. Solutions containing 0.0, 25.0, 50.0, 75.0, and 100.0% sodium in bicarbonate form were prepared and adjusted to the desired monoethanolamine normality by adding the necessary volume of monoethanolamine. McCoy's analytical procedure was then applied to a sample of each of the five solutions and the number of milliliters of 0.1*N* hydrochloric acid required for titration was determined. Calibration curves were prepared of volume of hydrochloric acid required *vs.* sodium bicarbonate fraction. The sodium carbonate and sodium bicarbonate concentrations and the equilibrium carbon dioxide partial pressure above the solution were determined.

CALCULATION OF EQUILIBRIUM CONSTANT

The equilibrium constant for the system was calculated from the relationship (*3*, *5*)

$$k = \frac{2X^2C}{(0.0300)\,p\,(1 - X)} \qquad (1)$$

At 30° C., $k = 0.0300$ gram-moles per liter-atm. (*6*).

Table I. Equilibrium Constants

Run	π_S, Total Pressure, Mm. Hg	C, Sodium Concn. (Normality)	C_M, Monoethanolamine Concn. (Normality)	X, Fraction Bicarbonate	$1 - X$, Fraction Carbonate	P, Partial Pressure Carbon Dioxide, Atm.	K
1	753.8	0.10	0.00	0.672	0.328	0.00170	5430
2	750.1	1.00	0.00	0.342	0.658	0.00331	3580
3	748.4	1.00	0.00	0.485	0.515	0.0105	2900
4	746.6	1.00	0.00	0.765	0.235	0.0498	3360
5	749.1	1.00	0.05	0.520	0.480	0.00724	5190
6	744.8	1.00	0.05	0.730	0.270	0.0279	4720
7	753.3	1.00	0.10	0.305	0.695	0.00148	6070
8	747.3	1.00	0.10	0.510	0.490	0.00583	6080
9	746.8	1.00	0.10	0.705	0.295	0.0178	6320
10	752.8	1.00	0.15	0.670	0.330	0.0129	7100
11	748.1	1.00	0.20	0.320	0.680	0.00132	7600
12	750.3	1.00	0.20	0.450	0.550	0.00331	7420
13	747.7	1.00	0.20	0.650	0.350	0.0110	7360
14	756.2	1.00	0.50	0.670	0.330	0.0120	7550

Temperatures (all runs) = 30° C.

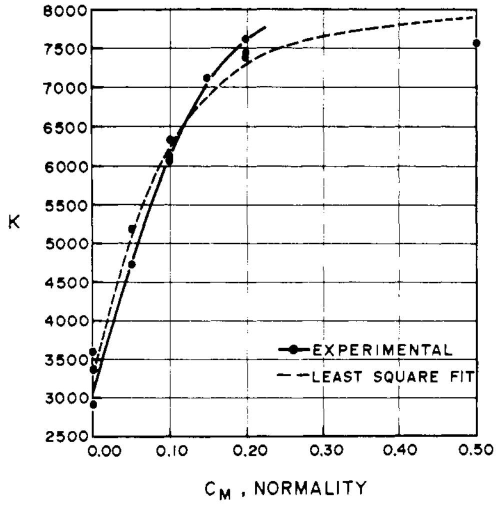

Figure 1. Effect of additive concentration on equilibrium constant

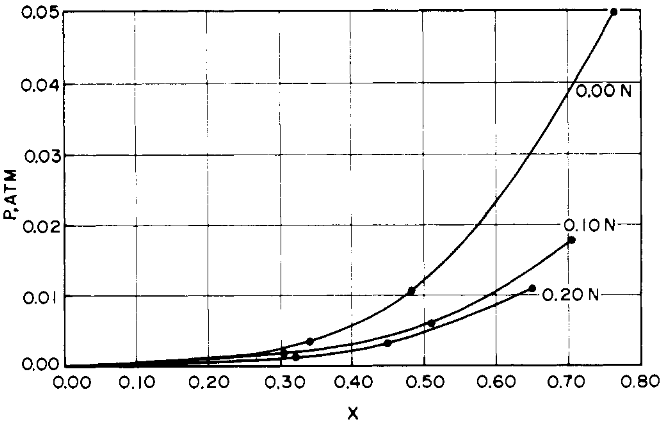

Figure 2. Effect of fraction of bicarbonate on carbon dioxide partial pressure

Additive concentration as a parameter

RESULTS AND CONCLUSIONS

The equilibrium constant for the system was first determined for a solution of 0.1*N* strength with respect to sodium at 30° C. with no additive. The equilibrium constant was found to be 5430. McCoy (*5*) calculated the equilibrium constant for 0.1*N* sodium solution at 25° C. and found values which ranged from 4900 to 5700, with a mean value of 5290. Equilibrium constants were then determined at 30°C. for a sodium concentration of 1.0*N* for each of three solutions and found to be 3580, 2900, and 3360, with a mean value of 3280. McCoy calculated values of the equilibrium constant ranging from 2920 to 3280 with a mean value of 3120 for 1.0*N* solutions at 25° C. An equilibrium constant of 3100 was calculated from the equation of Harte *et al.* (*2*) for a solution of 1.0*N* sodium strength at 30° C.

The results with and without additive are summarized in Table I. The equilibrium constant at 30° C. as a function of additive concentration was fitted to the following empirical equation:

$$K = 3280 + 4610\,[(1 - \exp(-10.2\,C_M)] \qquad (2)$$

This fit was determined by a nonlinear least squares regression analysis (*1*) and has a standard error of estimate of 235. Equation 2 is plotted in Figure 1 with the experimentally determined equilibrium constants. The variation of the equilibrium carbon dioxide partial pressure with fraction bicarbonate for the 0.00, 0.10, and 0.20*N* monoethanolamine solutions is shown in Figure 2.

NOMENCLATURE

C = sodium concentration, normality
C_M = monoethanolamine concentration, normality
K = equilibrium constant
k = solubility of carbon dioxide in water under a pressure of 1 atm. at a fixed temperature, gram-moles/liter-atm.
p = partial pressure of carbon dioxide, atm.
X = fraction of sodium in form of bicarbonate

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