An Investigation of Absorption-Reaction of Carbon Dioxide in Liquid Diethanolamine by the Direct Chromatographic Perturbation Method

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Physical and chemical equilibrium in the carbon dioxide-diethanolamine system was studied by the direct chromatographic method. The amine was present as a coating on the inside of a capillary tube. Carbon dioxide-helium mixtures were passed through the capillary until equilibrium was attained, at which time a sample of $C^{14}O_2$ was injected into the carrier stream. The retention volumes (carrier volume flowed at peak appearance) of concentration and radioactive perturbations were measured at four temperatures and five carrier gas compositions. Static equilibrium solubility of carbon dioxide in the amine was also measured to verify the dynamic results.

The theory of reactive chromatographic flow was extended to this system. The concentration and isotope retention volumes, which theory predicts to be different functions of carrier composition, were shown to be self-consistent. The static solubility data was also seen to be consistent with theory and with the direct chromatographic data. The liquid phase of the system appeared to be ideal except at infinite dilution of carbon dioxide. The apparent departure from ideality could be explained in terms of weak ionization of reaction products. Electrical conductivity measurements tend to confirm this hypothesis.

Both physical and chemical equilibrium constants for carbon dioxide were obtained at the four temperatures. Gross heat of reaction and apparent ionization heat were also obtained.

The purpose of this investigation (*1*) was to extend the use of direct chromatographic methods to chemically reactive gas-liquid systems. Direct chromatography has been used in vapor-liquid physical equilibrium determinations by Stalkup and Kobayashi (*11*) and Koonce et al. (*5*); in vapor-solid equilibrium studies by Gilmer and Kobayashi (*3*), Peterson et al. (*8*, *9*), and Haydel and Kobayashi (*4*); and most recently for chemically reactive gas-solid systems by Collins and Deans (*2*). The pertinent theory was developed in several of the above papers (*2*, *5*, *8* to *10*). The use of radioactive tracers as a source of independent information was discussed in all of the above work.

In the direct chromatographic technique used earlier and in this paper, the chromatographic column contains the two-phase system whose equilibrium behavior is being studied. After equilibrium conditions are established everywhere in the column by continued flow of the vapor phase, a small perturbation sample is introduced at the column inlet. The retention volumes of the various composition and radioisotope disturbances produced by the sample are detected by monitoring the column output composition. These retention volumes, along with predetermined vapor and column properties, are sufficient to allow calculation of the equilibrium properties of the two-phase system.

The system studied in this work was basically carbon dioxide and diethanolamine (DEA). Helium was added to the vapor phase to allow concentration variation at constant pressure and temperature. The liquid phase consisted of dissolved carbon dioxide (helium solubility is neglected), unreacted DEA, and products of the reaction

$$CO_2 + 2DEA \rightleftharpoons (DEA)_2CO_2 \text{ (carbamide)}$$

There is also evidence that the carbamide product is weakly ionized in the liquid phase.

According to Nunge and Gill (*7*), the pure carbon dioxide-DEA system has not been studied, although voluminous work is available on aqueous solutions. Matsuda (*6*) used glycerol as a solvent, obtaining results which are similar but not quantitatively comparable with the present results. Because of the limitations of the static equilibrium method, Matsuda was unable to separate the solubility constant for carbon dioxide from the chemical equilibrium constant even though he assumed ideal solutions.

In the following section the chromatographic experiments are discussed along with the limited static equilibrium measurements. The necessary theory is then developed for reducing the various retention volumes to usable information. In the final section the solubility constant for carbon dioxide, the chemical equilibrium constant, and an estimate of the dissociation constant for the carbamide product are given.

EXPERIMENTAL

Experimental Systems

The chromatographic data for the carbon dioxide-DEA system were taken at 75°, 85°, 95°, and 105°C. over a range of carbon dioxide partial pressure. The latter variable was controlled by the composition of the helium-carbon dioxide gas mixture employed, since system pressure was held constant at essentially 1 atm. The gases were premixed in pressure cylinders to give approximate compositions of 10, 25, 40, and 62.5% carbon dioxide. Pure helium was used to give 0% carbon dioxide.

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The basic flow system for the chromatographic runs is shown in Figure 1. The gas mixture chosen for the given run, (1), flowed through the purification and control section (2); the reference side of a Gow-Mac thermal conductivity cell (3); preheater and presaturator column (4), which was packed with DEA impregnated crushed firebrick; and the main loop of a six-way sample valve (5). A portion of the flow was short circuited through the splitter line (6), while the remainder flowed into the experimental capillary column (7), which contained a known amount of DEA. The rejoined streams then flowed out of the temperature bath into the sample side of the T-C cell (3) and on to the radioactive detector (8). The total flow rate was measured by an in-line bubble flowmeter (9).

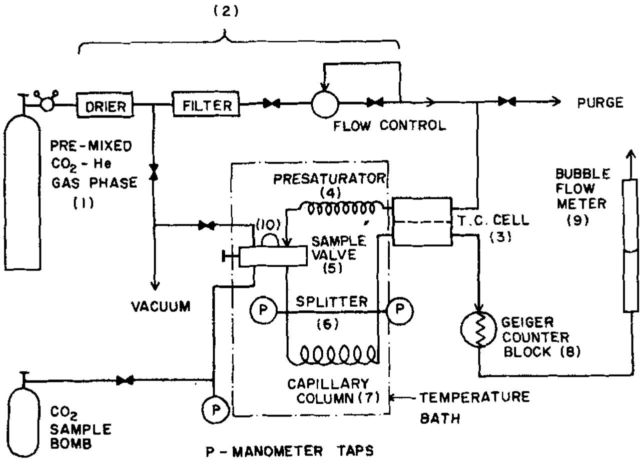

Fig. 1. Flow system for chromatographic runs, carbon dioxide-DEA, 1 atm.

The capillary column (7) was prepared by forcing vacuum distilled DEA through a 0.047 in. I.D. stainless steel capillary approximately 600 cm. long. Filtered helium was used to displace the major part of the DEA from the column, whose internal volume had previously been determined gravimetrically after thorough cleaning. The column was maintained at 100°C. in an air bath during the displacement, which was continued until visible flow of liquid had ceased. Approximately 25 to 30 mg. of DEA were retained on the inside wall of a typical experimental column. Column weight was checked frequently during the course of the runs to check for DEA loss. The low vapor pressure of DEA at experimental conditions along with the presaturator column reduced weight loss to less than 1 mg./run.

The calculated liquid film thickness on the column wall is approximately 2×10^{-4} cm., with uniform distribution assumed. The latter assumption is not essential to the success of the method, provided that the actual distribution allows relatively rapid interphase and intraphase mass transfer. Both absence of pronounced peak tailing and flow rate independence of retention volumes indicate that these conditions were satisfied.

Before each set of runs the splitter line was calibrated at experimental conditions. Flow rate as a function of pressure drop was measured with the bubble flowmeter. The experimental column was replaced by caps during the calibration. For the actual experimental runs, column flow was calculated as the total measured flow minus the bypass flow obtained from this calibration.

Detection of C^{14} beta radiation was by Geiger counter. The details of the Geiger block (8) are shown in Figure 2. The tortuous path was a ⅛ in. groove milled into an aluminum block. This flow path was covered with 2.2 mg./sq. cm. aluminum foil, which was glued to the block. The face of the Geiger tube was placed directly over the foil, as shown by the dotted circle in Figure 2. Counting efficiency and response time were adequate, and pressure drop was negligible.

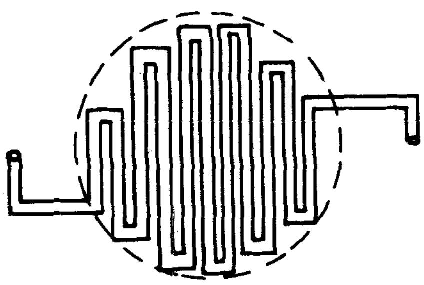

Fig. 2. Geiger channel block.

Experimental Runs on the Chromatographic System

After the column was connected and the bath positioned, gas flow was begun and continued until all pressure and temperature readings stabilized. A run was begun by injecting a sample with the six-way valve (5). The sample was normally $C^{14}O_2$ diluted with carbon dioxide; sample size was controlled by the pressure in the sample loop (10). Peak retention volumes, the primary data sought, were found to be independent of sample size in the range of sample pressure available (0 to 1 atm.) for the 0.25 cc. sample loop. Sample size could thus be varied to obtain the desired output signal amplitude on the T-C and radioactive detectors.

Approximately 30 to 40% of the total stream bypassed the capillary column by flowing through the splitter, a 7.3 cm. section of 0.014 in. I.D. capillary containing a 28 gauge wire. The splitter assembly is shown in Figure 3. The flow rate and interval volume of the bypass were such that the mean residence time was less than 0.5 sec. Corrections for dead time in sample loops, lines, and detectors were thus unnecessary. The portion of the sample which flowed through the bypass produced true reference peaks on both detectors, since the test column extended between the two ends of the bypass.

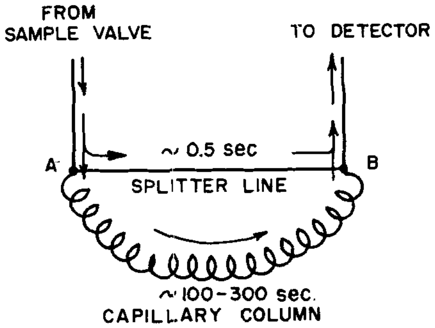

Fig. 3. Flow split across the column.

The data for a given run consisted of the mole fraction of carbon dioxide in the feed mixture, the total flow rate as measured by the bubble meter, the pressure drop across the bypass from which the flow split could be calculated, the bath temperature, and the residence time of the T-C(t_{TC}) and radioactive (t_{RA}) disturbances obtained from the recorder charts for the respective detectors. After a series of runs at a given temperature, the column was flushed with helium, removed from the system, and weighed to verify the constancy of DEA weight. The retention times taken from the recorder charts were reduced by using the gas retention time t_g and the moles of DEA per mole of gas phase $w_B{}^o$ in accordance with the formulas

$$G = \frac{1}{w_B{}^o}\left[\frac{t_{TC}}{t_g} - 1\right] \tag{1}$$

$$G^* = \frac{1}{w_B{}^o}\left[\frac{t_{RA}}{t_g} - 1\right] \tag{2}$$

t_g and $w_B{}^0$ were calculated from column gas volume, total and bypass flow rates, DEA weight, and DEA density corrected for the swelling due to carbon dioxide adsorption (*1*). (The latter was less than 1% at experimental conditions.) The experimental results are shown in Figure 4, (G^*), Table 2 (G_{exp}), and Table 3 (infinite dilution G^*, identical with G).

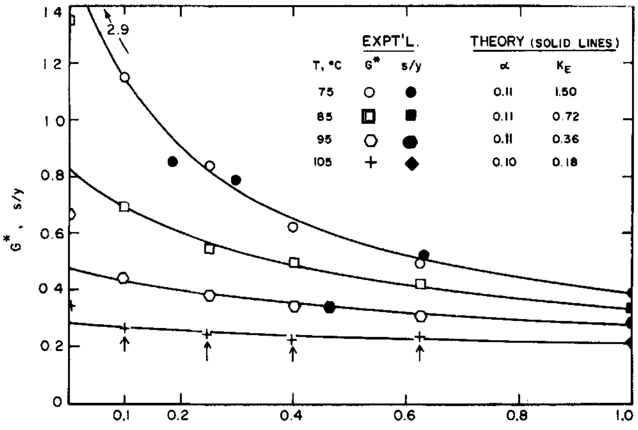

Fig. 4. Experimental G^* and S/y data, theoretical constants for carbon dioxide-DEA, at 1 atm.

Static Equilibrium Data

The equilibrium adsorption of carbon dioxide in pure DEA was determined gravimetrically for the same range of pressure and temperature used in the chromatographic runs. These data were used as a check on the dynamic system results, as described in the data analysis section.

A 150-ml. flask equipped with a side entry and a stopcock closure at the top was carefully cleaned and weighed. After evacuation, about 15 cc. of DEA was injected through the stopcock, producing a liquid level above the side arm. The flask plus contents were weighed and placed in a constant temperature bath after a carbon dioxide source and a manometer manifold were connected to the side arm and top tubes, respectively. Carbon dioxide was then bubbled through the liquid for an appropriate time, after which the carbon dioxide source was shut off. The vessel was then agitated until pressure equilibrium was reached. The manometer was read, the temperature verified, and the flask was removed from the bath, dried, and weighed.

The data obtained, expressed as moles carbon dioxide per mole DEA originally present, are shown in Table 1.

TABLE 1. STATIC EQUILIBRIUM DATA
(Moles carbon dioxide absorbed per mole DEA originally present)
$p =$
1 atm.

% carbon dioxide in gas phase	T, °C.	75	85	95	105
18.6		0.159	—	—	—
29.6		0.234	—	—	—
46.5		—	—	0.159	—
63.0		0.324	—	—	—
100.0		0.389	0.346	0.289	0.211

THEORETICAL DEVELOPMENT

The theory of the motion of small disturbances in ideal chromatographic systems has been discussed most recently by Collins and Deans (*2*). The basic assumptions of ideal chromatography are:

1. One-dimensional flow of an ideal gas mixture at constant temperature and pressure.
2. No longitudinal diffusion, local equilibrium between and within phases. Hence no dispersion in the flow direction.

For the system of interest here, the gas phase is assumed to be a binary mixture of helium and carbon dioxide. The single necessary balance for the mole fraction of the latter is

$$\frac{\partial y}{\partial t} + \frac{\partial}{\partial z}(y\overline{V}_z) = R_{\text{CO}_2} \qquad (3)$$

The liquid phase balance for carbon dioxide is given by

$$R_{\text{CO}_2} = -\frac{\partial w_A}{\partial t} - F$$

where the units of w_A are moles carbon dioxide per mole gas phase time.

The stoichiometry for the reaction of carbon dioxide (A) in the liquid phase with DEA (B) to form the carbamide (C) is taken to be

$$A + 2B \rightleftharpoons C \rightleftharpoons D^+ + E^-$$

where D^+ and E^- are the products of the presumed dissociation.

Since DEA, carbamide, and the ionized products are assumed to be nonvolatile, at equilibrium

$$F = -\tfrac{1}{2}\frac{\partial w_B}{\partial t} = \frac{\partial w_C}{\partial t} + \frac{\partial w_{D^+}}{\partial t} \qquad (5)$$

Total continuity is preserved by adding the balance for helium to Equation (3) to obtain

$$\frac{\partial \overline{V}_z}{\partial z} = R_{\text{CO}_2} \qquad (6)$$

which contains the assumption that helium is insoluble. A combination of Equations (3), (4), (5), and (6) produces the overall balance for carbon dioxide:

$$\frac{\partial y}{\partial t} + \overline{V}_z\frac{\partial y}{\partial z} + (1-y)\left[\frac{\partial w_A}{\partial t} + \frac{\partial w_C}{\partial t} + \frac{\partial w_{D^+}}{\partial t}\right] = 0 \qquad (7)$$

The general effect of adding a radioactive isotope of one of the components was also discussed by Collins (*2*). It is assumed that the tagged cimponent ($C^{14}O_2$ in this case) is chemically and physically identical to the untagged isotope within the system but is separately detectable externally because of its radioactivity. Equation (7) can then be used as a continuity relation for the total carbon dioxide component. The independent balance for the tagged isotope is

$$\frac{\partial y^*}{\partial t} + \overline{V}_z\frac{\partial y^*}{\partial z} + \left[\frac{\partial w_A{}^*}{\partial t} + \frac{\partial w_C{}^*}{\partial t} + \frac{\partial w_{D^{+*}}}{\partial t}\right] = 0 \qquad (8)$$

The factor $(1-y^*)$ is missing because $\partial\overline{V}_z/\partial z = 0$ in the neighborhood of a purely isotopic perturbation (*2*).

The reaction implied in Equation (8) is

$$A^* + 2B \rightleftharpoons C^* \rightleftharpoons D^{+*} + E^- \qquad (9)$$

It is irrevelent in which ion the C^{14} atom ends up, since only the stoichiometry matters in Equation (9).

The equilibrium flow system is determined by the statement of physical and chemical equilibrium relationships. If the liquid phase is ideal

$$\frac{x_A}{y} = \frac{x_A{}^*}{y^*} = \alpha \tag{10}$$

and

$$\frac{x_C}{y\, x_B{}^2} = \frac{x_C{}^*}{y^*\, x_B{}^2} = K_E \tag{11}$$

$$\frac{x_D{}^+\, x_E{}^-}{x_C} = \frac{x_D{}^{+*}\, x_E{}^-}{x_C{}^*} = K_D \tag{12}$$

where α, K_E, and K_D depend only on temperature for the constant pressure experiments discussed here. The first of each pair of equations is the appropriate condition of isotopic identity.

The molar concentrations are related to the mole fractions in the liquid phase by

$$x_i = \frac{w_i}{\Sigma\, w_j} \tag{13}$$

When one assumes that the gas phase volume remains constant, stoichiometry requires that $w_B{}^o = w_B + 2w_C + w_{D^+} + w_{E^-}$, so that

$$\Sigma w_j = w_B{}^o + w_A - w_C \tag{14}$$

where the units of the w_i are moles i per mole gas phase. Equations (13) and (14) may be inverted to give

$$w_i = w_B{}^o \frac{x_i}{1 + x_C - x_A} \tag{15}$$

which holds for all components (including tagged ones) if x_C and x_A in the denominator are taken to be sums of the mole fractions of all isotopes of the type C and A, respectively (2).

Equation (10) is used to eliminate x_A in Equation (15), which then substituted into Equations (7) and (8) to give

$$\frac{\partial y}{\partial t} + \overline{V}_z \frac{\partial y}{\partial z} + w_B{}^o (1 - y) \frac{\partial}{\partial t} \left[\frac{\alpha y + x_C + x_D{}^+}{1 + x_C - \alpha y} \right] = 0 \tag{16}$$

and

$$\frac{\partial y^*}{\partial t} + \overline{V}_z \frac{\partial y^*}{\partial z} + w_B{}^o \frac{\partial}{\partial t} \left[\frac{\alpha y^* + x_C{}^* + x_D{}^{+*}}{1 + x_C - \alpha y} \right] = 0 \tag{17}$$

Since the total isotope mole fractions are constant in the neighborhood of a purely isotopic disturbance, the term $1 + x_C - \alpha y$ may be treated as a constant in Equation (17).

The characteristics of these two first-order hyperbolic equations are just the propagation velocities of infinitesimal concentration and isotopic dsturbances, respectively [see Collins and Deans (2)]. They are

$$(V_C)_{\text{conc}} = \left(\frac{\partial z}{\partial t} \right)_y = \frac{\overline{V}_z}{1 + w_B{}^o (1 - y) \dfrac{d}{dy} \left(\dfrac{\alpha y + x_C + x_D{}^+}{1 + x_C - \alpha y} \right)} \tag{18}$$

and

$$(V_C)_{\text{isotopic}} = \left(\frac{\partial z}{\partial t} \right)_{y^*} = \frac{\overline{V}_z}{1 + \dfrac{w_B{}^o}{1 + x_C - \alpha y} \dfrac{d}{dy^*} (\alpha y^* + x_C{}^* + x_D{}^{+*})} \tag{19}$$

The characteristics take on this simple form because the quantities in brackets to be differentiated in Equations (16) and (17) are functions only of y and y^*, respectively.

ANALYSIS OF EXPERIMENTAL DATA

Comparison of Theory with Experiment

The theoretically predicted values of the residence times required in Equations (1) and (2) are inversely proportional to the characteristic velocities of Equations (18) and (19). The equations for G and G^* produced by the theory are thus

$$G = \frac{1}{w_B{}^o} \left[\frac{\overline{V}_z}{(V_C)_{\text{conc}}} - 1 \right] = (1 - y) \frac{d}{dy} \left[\frac{\alpha y + x_C + x_D{}^+}{1 + x_C - \alpha y} \right] \tag{20}$$

and

$$G^* = \frac{1}{w_B{}^o} \left[\frac{\overline{V}_z}{(V_C)_{\text{isotopic}}} - 1 \right] = \frac{1}{1 + x_C - \alpha y} \frac{d}{dy^*} [\alpha y^* + x_C{}^* + x_D{}^{+*}] \tag{21}$$

It is readily seen that these two functions are not independent. x_B and x_E are constant in an isotopic perturbation, so that

$$\frac{dx_C{}^*}{dy^*} = K_E\, x_B{}^2 \tag{22}$$

and

$$\frac{dx_D{}^{+*}}{dy^*} = \frac{K_D}{K_E} \frac{dx_C{}^*}{dy^*} = \frac{K_D\, K_E\, x_B{}^2}{x_E} \tag{23}$$

Hence

$$\frac{d}{dy^*} [\alpha y^* + x_C{}^* + x_D{}^{+*}] = \alpha + K_E\, x_B{}^2 \left(1 + \frac{K_D}{x_E} \right) \tag{24}$$

and, from Equation (21)

$$G^* = \frac{\alpha + K_E\, x_B{}^2 \left(1 + \dfrac{K_D}{x_E} \right)}{1 + x_C - \alpha y} \tag{25}$$

It is seen from Equations (10), (11), (12), and (25) that

$$yG^* = \frac{\alpha y + x_C + x_D{}^+}{1 + x_C - \alpha y} \tag{26}$$

It follows from this and Equation (20) that

$$G = (1 - y) \frac{d}{dy} (yG^*) \tag{27}$$

$$= (1 - y)\, G^* + (1 - y) y \frac{dG^*}{dy} \tag{27a}$$

The behavior of G as the active mole fraction y approaches its limits is to be noted. As y → 1, G → 0 as would be expected, since the system becomes invariant (no concentration perturbation possible, so that $V_C \rightarrow V$). As $y \rightarrow 0$, G will approach G^* as long as $(y(dG^*)/(dy))$ has zero limit, which it should for any physically reasonable equilibrium function.

Equation (27) provides a means of testing both the internal consistency of the experimental data and the validity of the theory which produced the equation. The experimental G^* data of Table 1 are shown in Figure 4 with smooth curves drawn through the points. The curves were graphically differentiated to obtain values of dG^*/dy at $y = 0.1$, 0.25, 0.40, and 0.625. The results of putting these data into Equation (27*a*) are shown in Table 2. The agreement between G_{calc} from Equation (27*a*), and G_{exp} is seen to be within experimental scatter.

TABLE 2. COMPARISON OF EXPERIMENTALLY MEASURED G WITH THEORETICALLY CALCULATED G

T, °C.	y	$\frac{dG^*}{dy}$	G_{calc} [Equation (27*a*)]	G_{exp}
75	0.1	—3.1	0.71	0.75
	0.25	—1.51	0.33	0.34
	0.40	—0.92	0.17	0.18
	0.625	—0.44	0.09	0.08
85	0.1	—1.16	0.52	0.48
	0.25	—0.63	0.30	0.29
	0.40	—0.43	0.19	0.21
	0.625	—0.27	0.09	0.09
95	0.1	—0.389	0.35	0.35
	0.25	—0.250	0.24	0.23
	0.40	—0.190	0.16	0.18
	0.625	—0.141	0.09	0.09
105	0.1	—0.119	0.23	0.22
	0.25	—0.089	0.17	0.16
	0.40	—0.064	0.13	0.13
	0.625	—0.045	0.07	0.08

Another test of theory and data is provided by the static equilibrium measurements. The equilibrium solubility, listed in Table 1 as total moles carbon dioxide in solution per mole DEA originally present, would have the theoretical value

$$S = \frac{\alpha y + x_C + x_D{}^+}{1 + x_C - \alpha y} \tag{28}$$

which follows from the stoichiometry assumed and Equation (15) for *A*, *C*, and *D*. From Equation (26) it follows that

$$G^* = \frac{S}{y} \tag{29}$$

The data of Table 1 are plotted in this fashion in Figure 4. Again the general agreement is good, although poorer at smaller values of y. It is clear from Equation (29) that solubility data will become an increasingly unreliable source of the information desired as y approaches zero. One of the great advantages of the direct chromatographic method is that it gives G^* directly and not as a quotient whose experimental precision vanishes in the very interesting limiting case, $y \rightarrow 0$.

Evaluation of Equilibrium Constants

Initial attempts to fit the experimental results to a specific theoretical model were confused by the anomolous values of G and G^* at $y = 0$. The possibility of weak ionization of the product carbamide allowed rationalization of this point. Ionization is apparently so limited that only the infinite dilution data are affected.

All the data for $y \geqq 0.10$ can be fitted with the two constants α and K_E. The appropriate equations derived from Equations (10), (11), and (25), are

$$G^* = \frac{\alpha + K_E\, x_B{}^2}{1 + y\,[K_E\, x_B{}^2 - \alpha]} \tag{30}$$

and

$$x_B = 1 - x_A - x_C = 1 - y\,[\alpha + K_E\, x_B{}^2] \tag{31}$$

The solid lines in Figure 4 were obtained from Equations (30) and (31) by using the best fit constants shown. Again the agreement seems to be with experimental scatter, confirming the assumption that the solution is reasonably ideal (for $y \geqq 0.10$, at least).

The variation of α with temperature is sufficient only to indicate that the heat of solution of carbon dioxide in DEA reaction mixture is quite small. A plot of log K_E vs. reciprocal absolute temperature is shown in Figure 5. The indicated heat of reaction is 17.5 Kcal./mole carbon dioxide, which includes the heat of solution because of the definition (*11*).

Anomolous Infinite Dilution Data

The intercepts at $y = 0$ of the theoretical curves in Figure 4 are clearly inconsistent with the experimental G^* data, as shown in Table 3. One explanation could be nonideality at low concentration, which cannot be disproved in any case. One activity coefficient would be sufficient to absorb the discrepancies, since G^* was the only independent function measured.

A more interesting possibility is the weak ionization of the carbamide product in solution. This mechanism was included in the general theory by Equations (9) and (12). For sufficiently small values of y, Equations (11) and (12) combined with Equation (25) lead to

$$G^* \cong \alpha + K_E + \sqrt{\frac{K_E\, K_D}{y}}, \quad y \rightarrow 0 \tag{32}$$

The theory thus predicts a singularity in G^* at $y = 0$. It can be shown, in general, that this is characteristic of any stoichiometry which produces more than one net molecular species in solution per gas phase molecule. It is also true for any reasonable stoichiometry that the liquid solubility $S = y\, G^*$ still vanishes at $y = 0$. For this particular case

$$S \sim \sqrt{y} \text{ as } y \rightarrow 0 \tag{33}$$

Since the infinite dilution experiments were run with pure helium as carrier gas, the finite values of G^* obtained would seem to indicate that ionization is not the explanation for the discrepancies in Table 3. If, however, the pure helium contained a finite concentration of carbon dioxide, the ionization hypothesis becomes plausible again. The supplier of the helium indicated a maximum carbon dioxide content of 0.2 p.p.m., although no accurate analysis was available.

TABLE 3. INFINITE DILUTION G^* VALUES

T, °C.	75	85	95	105
$(G^*)_{\text{theo, Equation (30)}}$	1.61	0.83	0.47	0.28
$(G^*, G)_{\text{exp}}$	2.96	1.36	0.67	0.34
$\Delta G^*/\sqrt{K_E}$	1.10	0.61	0.33 ± 0.02	0.14 ± 0.02

The only direct evidence to support the ionization hypothesis was the dependence of K_D on temperature. Near $y = 0$, Equation (32) gives

$$\frac{G^* - (\alpha + K_E)}{\sqrt{K_E}} \cong \sqrt{\frac{K_D}{y}}, \quad y \to 0 \qquad (34)$$

The quantity on the left is given as the last line in Table 3 and is plotted vs. reciprocal absolute temperature in Figure 5. Since the same helium bottle was used for all four infinite dilution runs, y may be taken as constant. The slope of the curve gives an apparent ionization energy of 34 Kcal./mole carbamide.

Experiments were undertaken recently to investigate ionization in the DEA-carbamide solution in order to confirm the foregoing analysis. At 85°C., the electrical conductance of DEA was found to increase by a factor on the order of 50 as the carbon dioxide pressure over the solution was increased from 0 to 0.01 atm. An additional five-fold increase in conductivity followed as the carbon dioxide pressure was raised to 1 atm. More precise experiments are in progress.

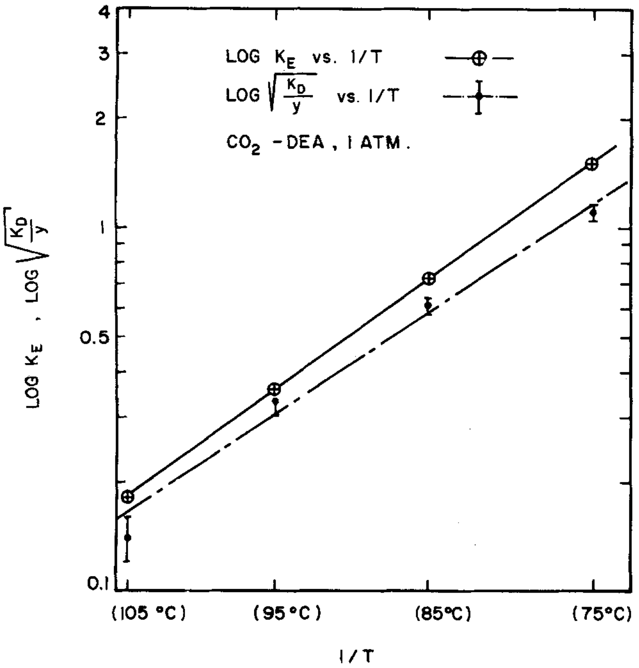

Fig. 5. Temperature dependence of derived equilibrium constants.

SUMMARY

The direct perturbation method of employing chromatographic effects is clearly well suited to the system studied here. Data at low carbon dioxide partial pressure is difficult to obtain accurately by static methods and is of course not available at the very low concentrations where this system shows anomalous behavior. The dynamic method was qualitatively as well as quantitatively useful here, as it should be in many systems where certain mechanisms are only important at low concentrations.

Although not indicated here, the theory is applicable to systems in which both gas and liquid phases are in motion. Provided suitable contacting devices can be found, this variation of the technique will allow the method to be used in systems where all components are volatile.

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NOTATION

F = local reaction rate, moles carbon dioxide removed per mole gas phase-time
G = relative excess residence time, concentration peak
G^* = relative excess residence time, radioactive peak
K_D = dissociation constant for carbamide, Equation (12)
K_E = equilibrium constant for DEA formation, Equation (11)
R_{CO_2} = local source of carbon dioxide in the flowing phase, moles/mole gas phase-time
S = equilibrium solubility, total moles carbon dioxide per mole original DEA
t = (real) time, retention time if subscripted
t_G = bulk gas retention time, column length divided by $\overline{V_z}$
V_c = characteristic velocity
$\overline{V_z}$ = bulk (flowing) gas phase velocity
w_i = fixed phase concentration of component i, moles/mole gas phase
$w_B{}^o$ = initial DEA concentration, moles DEA originally per mole gas phase
x_i = mole fraction of component i in the fixed phase
y = mole fraction of carbon dioxide in the gas phase
y^* = mole fraction of $C^{14}O_2$ in the gas phase
z = distance in the flow direction
α = physical solubility constant for carbon dioxide, Equation (10)

Subscripts

A = carbon dioxide
B = diethanolamine
C = carbamide product of reaction between A and B
D^+, E^- = products of carbamide ionization
DEA = diethanolamine
RA = radioactive counter detection
TC = thermal conductivity cell detection

LITERATURE CITED

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