A REACTION MODEL
FOR THE HOT
CARBONATE SWEETENING
PROCESS

By

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NOMENCLATURE

C	solution concentration, equivalent K_2CO_c, wt. fraction.
F	extent of conversion of K_2CO_3, fraction.
F_B	weight fraction bicarbonate, g. per 1 g. solution.
F_C	weight fraction carbonate, g. per 1 g. solution.
F_W	weight fraction water, g. per 1 g. solution
H_{CO_2}	"pseudo-Henry's Law" constant for CO_2, mm H_g/(gmole/lit)
H_{H_2S}	"pseudo-Henry's Law" constant For H_2S, mm Hg/(gmole/lit)
K_i	equilibrium constants in the ionic equations, gmions/lit.
M	solution concentration, gmoles K_2CO_3/lit. soln.
P_{CO_2}	equilibrium partial pressure of Co_2, mm Hg.
P_{H_2S}	equilibrium partial pressure of H_2S, mm Hg.
T	temperature, °R
V_X	volume of solution, lit.
W_B	moles of bicarbonate, gmoles per 1000g. H_2O.
W_C	moles of carbonate, gmoles per 1000 g. H_2O.
W_S	moles of bisulfide, gmoles per 1000 g. H_2O.
$[CO_2]$	free CO_2 concentration in solution, gmoles/lit.
$[CO_3^=]$	carbonate ion concentration, gmoles/lit.
$[HCO_3^-]$	bicarbonate ion concentration, gmoles/lit.
$[HS^-]$	bisulfide ion concentration, gmoles/lit.
$[H_2S]$	free H_2S concentration in solution, gmoles/lit.
MW_i	molecular weight of compound i.
α	equivalent CO_2 loading in solution, gmoles CO_2/gmole K_2CO_3.

β	equivalent H_2S loading in solution, gmoles H_2S/gmole K_2CO_3.
ρ_s	solution density, g/lit.

N.B. subscript 'a' refers to the CO_2/K_2CO_3 system.

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INTRODUCTION

The removal of carbon dioxide from mixtures of gases by liquid absorbents is an important industrial process. Among the many large applications (7, 12) are the following:

i) Sweetening of natural gas (produced form a condensate field or as associated gas from an oil reservoir) which usually contains water vapor and frequently hydrogen sulfide and/or carbon dioxide,
ii) Purification of ammonia synthesis gas,
iii) Upgrading of fuel gases manufactured from gasification of coal or reforming of petroleum fractions.

A few of the other applications include:

i) Manufacture of methanol and synthetic gasolines,
ii) Manufacture of solid carbon dioxide (dry ice),
iii) Manufacture of carbon dioxide for industrial organic chemicals, etc.

The most common means of removal is by absorption into solution with which carbon dioxide reacts, usually aqueous amine or carbonate solutions. Potassium, rather than sodium carbonate is invariably used when aqueous carbonate solutions are used to remove carbon dioxide. This is because of the higher solubility of the potassium carbonate (7). Perhaps the main reasons (2) in favor of the hot potassium carbonate processes are the favorable costs and availability of the absorbents when bulk removal is desired.

In specific applications, hydrogen sulfide is often an impurity which must be removed (such as in gasification of coal to produce synthesis gas). Tests (4) made with feed gases containing hydrogen sulfide and carbon dioxide showed that a high degree of absorption of both gases could be achieved in hot potassium carbonate solutions.

Many experimental determinations have been done on the equilibrium of carbon dioxide, hydrogen sulfide and hydrogen sulfide and carbon dioxide mixtures over potassium carbonate solutions (17, 18).

The purpose of this work is to present an approach for correlating the published data which results in a model that can be used to extrapolate outside the range of existing data with reasonable accuracy.

LITERATURE REVIEW

A literature survey was undertaken for two main reasons:

i) to see if a 'reaction model' approach as that for amines had been undertaken for the potassium carbonate system and,

ii) to check for availability of data for model development.

The review indicated that a lot of work had been done in correlating vapor-liquid equilibria data for absorption of acidic gases in amines.

McNeil and Dankwerts (6) proposed a model in which the vapor pressure of the acid gas species was related to the free acid gas concentration in the liquid phase by a Henry's Law relationship, and the free acid gas concentration was determined by liquid phase ionic equilibria.

Kent and Eisenberg (10) found substantial deviations in predicted equilibrium values and thus modified the McNeil-Dankwerts approach by forcing the amine equilibrium constants to fit published data for the hydrogen-sulfide/amine and carbon-dioxide/amine systems. Thus, they developed a model capable of predicting equilibrium for the hydrogen-sulfide/carbon-dioxide/amine systems.

Vaz, Mains and Maddox (20) improved upon the Kent-Eisenberg approach and developed the Amine Process Model (APM) which not only predicted equilibrium with better accuracy but incorporated other features as well.

Akashah (1) extended the above "reaction model" concept to predict equilibrium for the carbon-dioxide/potassium-carbonate systems for the first time using equilibrium data published by the US Bureau of Mines (17, 18) (Tosh, Field, Benson, and Hayes). However, the predicted equilibrium values were found to deviate from experimental values.

The present work is a modified extension of Akashah's work and it follows the amine-process approach closely. Besides predicting the carbon-dioxide/potassium carbonate system with better accuracy it is extended to predict the carbon-dioxide/hydrogen-sulfide/potassium-carbonate (mixture) system too.

THE REACTION MODEL

CONCEPT

The Bureau of Mines (17, 18) conducted an experimental study of the K_2CO_3-$KHCO_3$ - CO_2 - H_2O and the K_2CO_3 - $KHCO_3$ - KHS-CO_2 - H_2S - H_2O systems with solutions of varying equivalent potassium carbonate concentrations.

Their attempt to correlate the equilibrium data comprised of defining empirical constants, relating the equilibrium concentrations of the carbonate, bicarbonate and bisulfide and the partial pressures of carbon dioxide and hydrogen sulfide.

These so called constants were reported to be functions of temperature and concentration; a conclusion which held good only for low concentrations. The constants seemed to vary with the extent of conversion for higher concentrations of the solution. Besides averaged values of the constants were used for data correlation. All in all, the correlation bordered on pure empiricism.

Since carbonate solutions react chemically with hydrogen sulfide and carbon dioxide, their removing these acid gases from natural gas streams is not simple "absorption in liquid solutions". Equilibrium data indicate that there is an interactive relationship between the quantity of carbonate reacted and the relative amounts of hydrogen sulfide and carbon dioxide present. The concept of the "reaction equilibria model" stems precisely from the above fact.

A set of independent reactions occuring in the liquid phase with the acid gas constituents is postulated and the partial pressure of the acid gas species is related to the free acid gas concentration in the liquid phase by a Henry's Law type relationship. The use of the "actual" Henry's Law constant for the concentrations involved would at best be unconventional; hence the approach is to force "pseudo-Henry's constants" to fit the published vapor pressure data for the two systems. This approach is analogous to forcing the amine equilibrium constants to fit data in the amine-processes.

The two systems are discussed next.

A. The CO_2/K_2CO_3 System

Equations describing the CO_2/K_2CO_3 system are as follows:

$$H_2O + CO_2 \overset{K_1}{\rightleftharpoons} H^+ + HCO_3^-$$

$$H_2O \overset{K_1}{\rightleftharpoons} H^+ + OH^-$$

$$HCO_3^- \overset{K_3}{\rightleftharpoons} H^+ + CO_3^=$$

$$P_{CO_2} = H_{CO_2}\ [CO_2]$$

Equations (1) through (3) represent the ionic dissociation reactions for CO_2 and H_2O. Equation (4) relates the equilibrium partial pressure of CO_2 to the free concentration of CO_2 in solution by the Henry's Law type relationship (using a "psuedo-Henry's Law constant).

The equilibrium constants were accepted from the literature (values shown in Table 1) and algebraic manipulations (details of which are shown in Appendix A.1) were carried out on the above equations to work out the concentration of free CO_2. The "pseudo-Henry's Law constant" was then determined by forcing a fit with the published data. Complete ionization of the solution was assumed.

The "constant", H_{CO_2}, was found to be a function of temperature and concentration of solution for the CO_2/K_2CO_3 (pure) system.

TABLE 1

Equilibrium constants for the ionic reactions. (References (9) and (10))

$$K_i = \exp [A + B/T + C/T^2 + D/T^3 + E/T^4]$$

with T in °R

Equilibrium constant	Units	A	$BX10^{-4}$	$CX10^{-8}$	$DX10^{-11}$	$EX10^{-13}$
K_1···	gmions/lit.	-241.818	53.6855	-4.8123	1.94	-2.96445
K_2···	$(\text{gmions/lit.})^2$	39.5554	-17.7822	1.843	-0.8541	1.4292
K_3···	gmions/lit.	-294.74	65.5893	-5.9667	2.4249	-3.7192
K_4···	gmions/lit.	-304.689	69.6979	-6.31007	2.5551	-3.91757

The "constant" determined is as follow:

$$H_{CO_2} = exp \{ \frac{1}{C^{0.01}} [X_1 + \frac{X_2}{T} + \frac{X_3}{T^2} + \frac{X_4}{T^3}]\}$$

where $X_1 = 684.69471$

$X_2 = -13.58785 \times 10^5$

$X_3 = 91.72634 \times 10^7$

$X_4 = -20.68227 \times 10^{10}$

C is the concentration of solution, wt. fraction.

T is the temperature, °R.

H_{CO_2} is the "pseudo-Henry's Law constant", mm Hg/(gmoles/lit.soln.)

This result covers a temperature range from 70°C and a solution concentration range from 20% to 40% equivalent K_2CO_3.

Typical fits of the data obtained using this approach for the CO_2/K_2CO_3 system are shown in Figures (1), (2) and (3). Loadings, α, given are for total equivalent CO_2 in solution. Table (2) shows a summary of errors in predicting P_{CO_2} for the CO_2/ K_2CO_3 systems.

The CO_2/K_2CO_3served as a "starter" for the more general $H_2S/CO_2/K_2CO_3$ system.

B. The $H_2S/CO_2/K_2CO$ System

Equations describing the $H_2S/CO_2/K_2CO$ system are as follow:

$$H_2O + CO_2 \xrightleftharpoons{K_1} H^+ + HCO_3^- \qquad (1)$$

$$H_2O \xrightleftharpoons{K_2} H^+ + OH^- \qquad (2)$$

$$HCO_3^- \xrightleftharpoons{K_3} H^+ + CO_3^= \qquad (3)$$

$$H_2S \xrightleftharpoons{K_4} H^+ + HS^- \qquad (4)$$

$$P_{CO_2} = H_{CO_2} [CO_2] \qquad (5)$$

$$P_{H_2S} = H_{H_2S} [H_2S] \qquad (6)$$

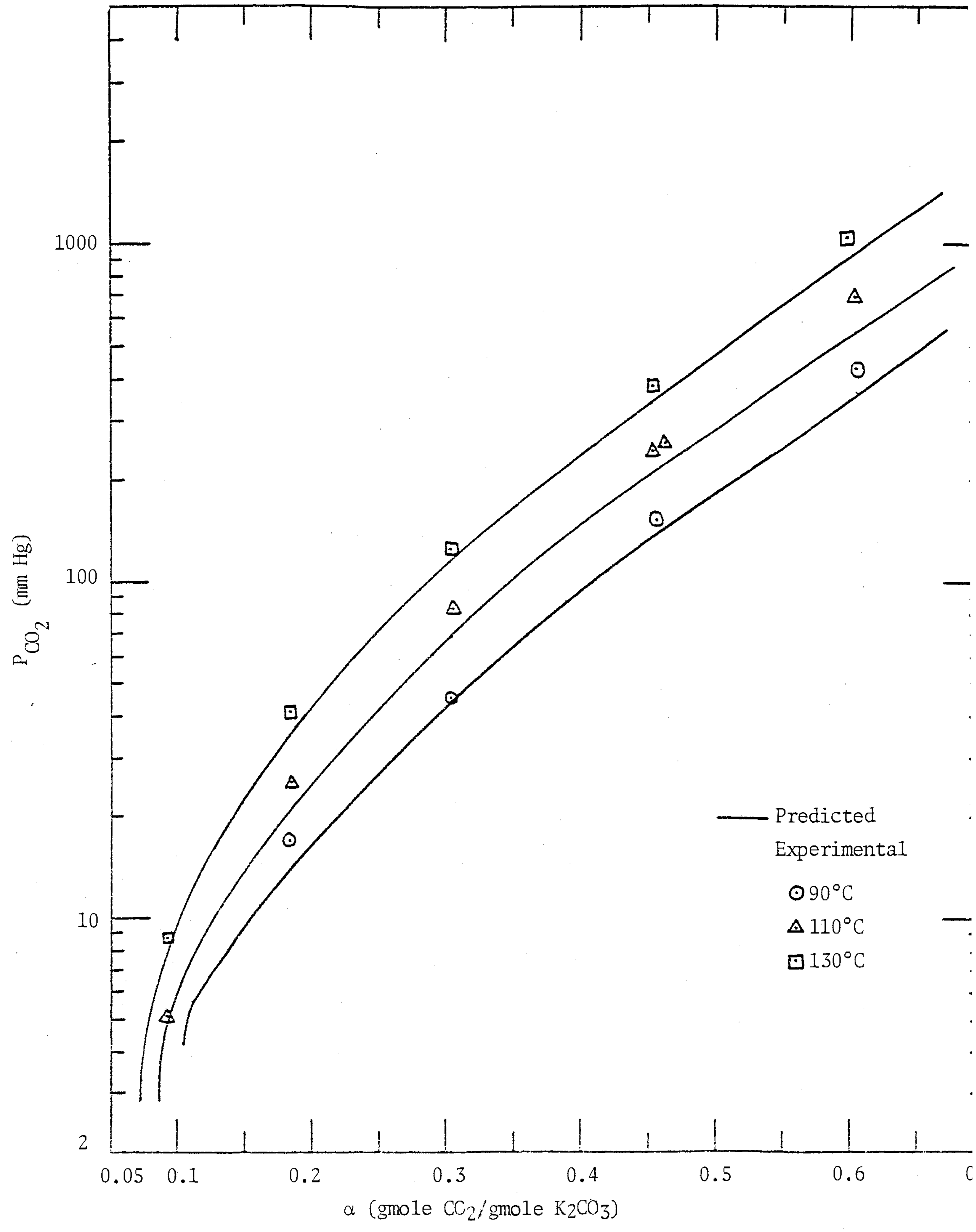

Fig.1: Partial Pressure of CO$_2$ over 20% equiv. K$_2$CO$_3$.

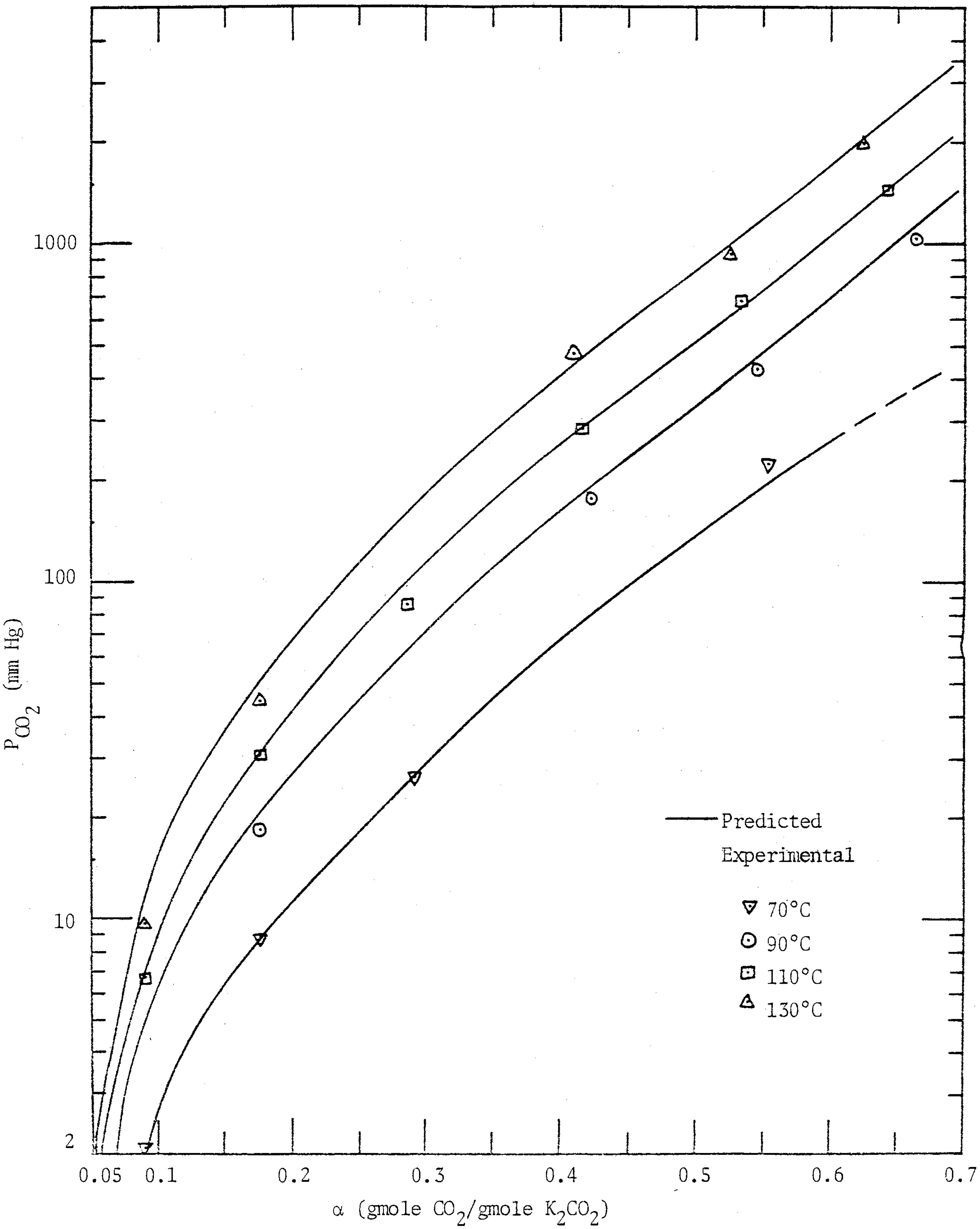

Fig.2: Partial Pressures of CO_2 over 30% equiv. K_2CO_3

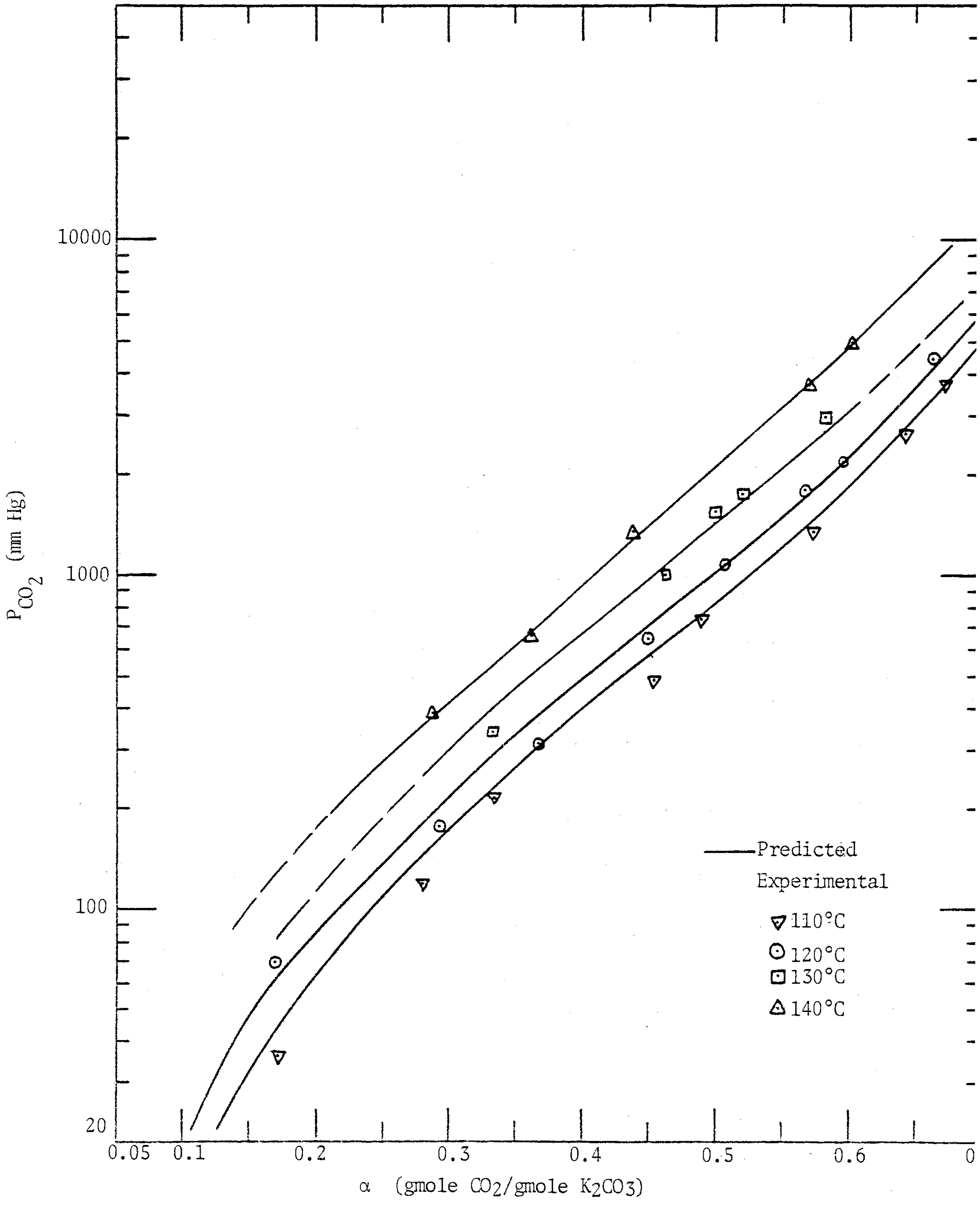

Fig.3: Partial Pressures of CO_2 over 40% equiv. K_2CO_3.

TABLE 2

Summary of Errors in predicting P_{CO_2} for the CO_2/K_2CO_3 system.

1.	Total number of observations	65
2.	Temperature range	70°C to 140°C
3.	Concentration range	20 to 40% eq. K_2CO_3
4.	Conversion range	10 to 70%
5.	Maximum -ve error	23.3%
6.	Maximum +ve error	29.2%
7.	Average absolute error	10.2%

Note: a) Percent error = $\frac{\text{(Predicted value - Expt. value)}}{\text{Expt. value}}$ 100

b) P_{CO_2} predicted in mm Hg.

Once again equations (1) through (4) represent the ionic dissociation reactions for CO_2, H_2O and H_2S and equations (5) and (6) relate the equilibrium partial pressures of $CO_2$and H_2S to the free concentrations of the two special in solution, by the Henry's Law type relationship (again, using a "pseudo - Henry's Law constant" for each)

As before, the equilibrium constants were accepted from literature (shown in Table 1) and algebraic manipulations (details of which are relegated to Appendix A.2) were carried out on the above equations to work out the free acid species concentrations. "Pseudo - Henry's Law constants" were then determined for each species by forcing a fit with the published data-

C ionization was assumed here, also.

For this "mixture" system, H_{CO_2}, was found to be a function of temperature and concentration.

A fit for H_{CO_2} using the $H_2S/CO_2/K_2CO_3$ system vapor pressure data yielded the following equation:

$$H_{CO_2} = exp \{ \frac{1}{C^{0.01}} [X_1 + \frac{X_2}{T} + \frac{X_3}{T^2} + \frac{X_4}{T^3}] \} \qquad (I)$$

where: $X_1 = 207.08040$

$X_2 = -37.35059 \times 10^4$

$X_3 = 24.21064 \times 10^7$

$X_4 = -53.0998 \times 10^9$

C is the concentration of solution, wt. fraction

T is the temperature, °R

H_{CO_2} is the "pseudo constant", mm Hg /(gmoles/lit.soln.)

A fit for H_{H_2S} had to be carried out next. Analysis of the data indiccated that H_{H_2S} had to be, logically, a function of temperature and solution concentration.

A fit using the $H_2S/CO_2/K_2CO_3$ system vapor pressure data resulted in the following equation:

$$H_{H_2S} = exp \left\{ X_1 + \frac{X_2}{C^{0.2}T} + \frac{X_3}{C^{0.2}T^2} \right\} \tag{II}$$

where $X_1 = 14.07121$

$X_2 = 939.10254$

$X_3 = -12.53656 \times 10^5$

C is the concentration of solution, wt. fraction

T is the temperature, °R

H_{H_2S} is the "pseudo constant," mm Hg/(gmole/lit.soln.)

The above results cover a temperature range from 70°C to 130°C, a solution concentration range from 30% to 40% equivalent K_2CO_3 and total H_2S loadings greater than about 250-300 grains H_2S per gallon of solution.

Typical fits of the data are shown in Figures (4) through (7). Table (3) shows a summary of errors in predicting P_{CO_2} and P_{H_2S} for the $H_2S/CO_2/K_2CO_3$ system.

The two "constants," H_{CO_2} and H_{H_2S}, as determined above apply to the $H_2S/CO_2/K_2CO_3$ system only.

The particular type of dependence of the "pseudo - constants" on temperature and solution concentration can be explained with the help of thermodynamic derivations.

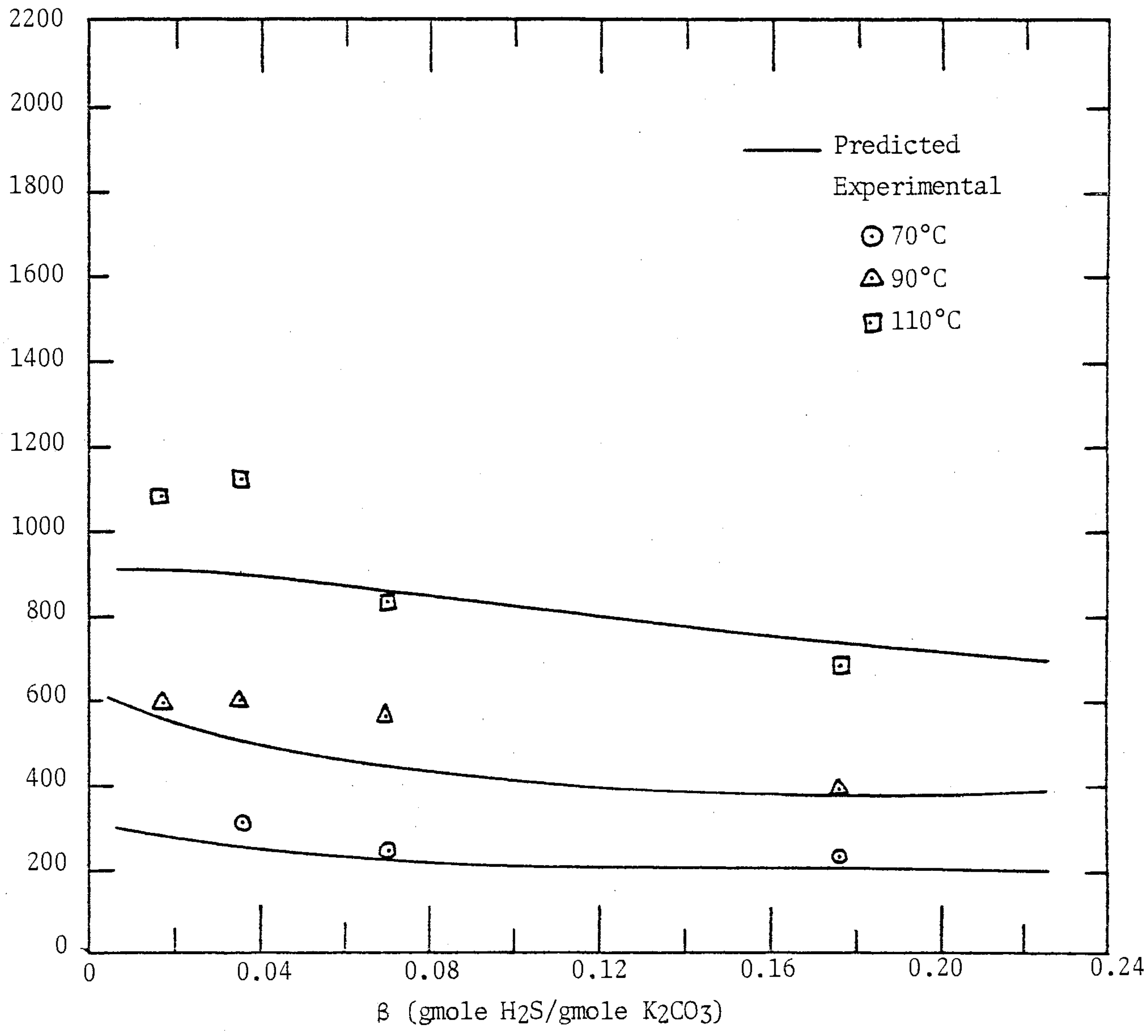

Fig.4: Partial Pressures of CO_2 over 30% equiv. K_2CO_3. with total loading, (α + β), ≃ 0.56 gmole/gmole K_2CO_3.

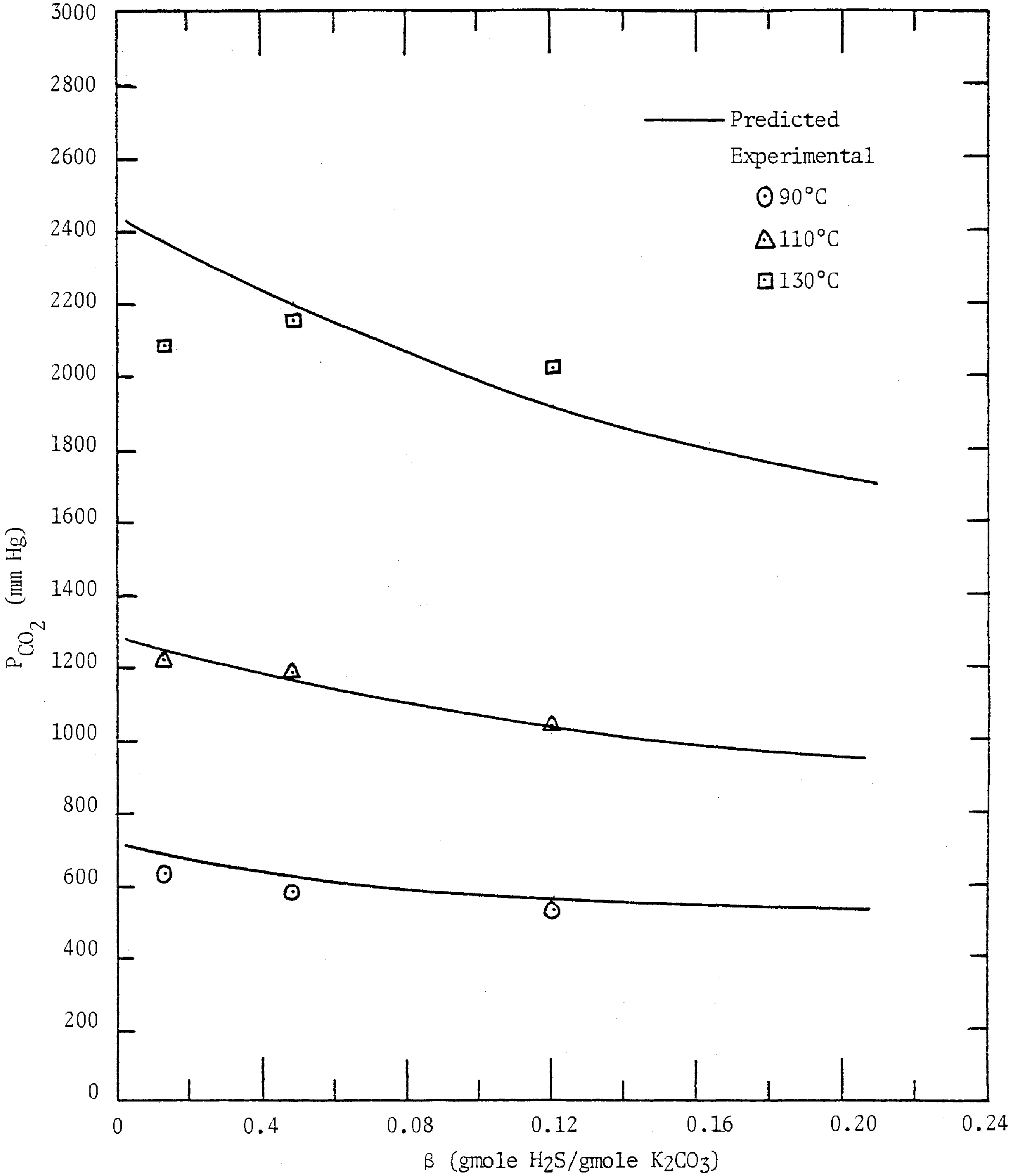

Fig.5: Partial pressures of CO_2 over 40% equiv. K_2CO_3. with total loading, (α + β), ≃ 0.56 gmole/gmole K_2CO_3

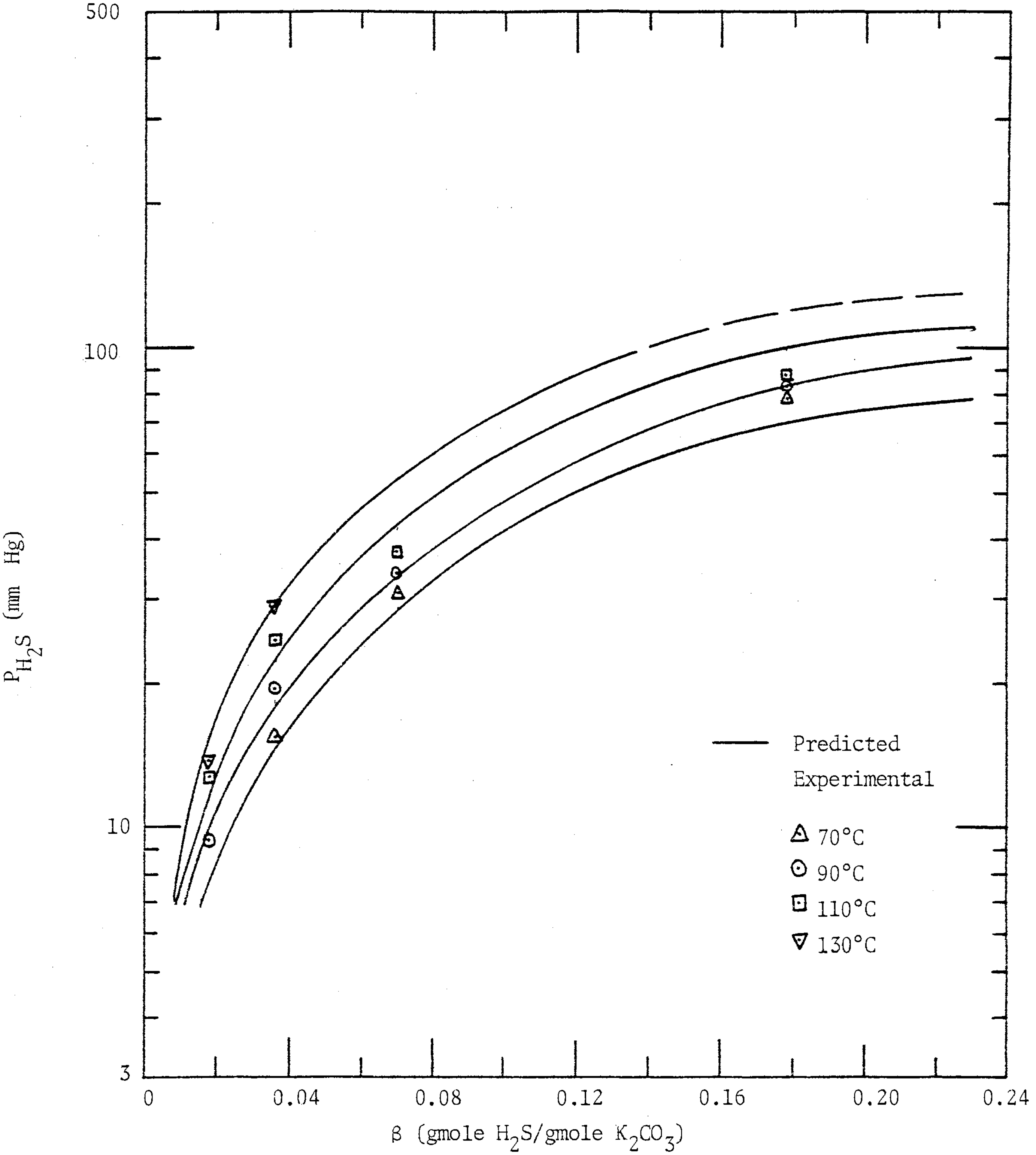

Fig. 6: Partial pressures of H_2S over 30% equiv. K_2CO_3 with total loading, $(\alpha + \beta)$, $\simeq$ 0.56 gmole/gmole K_2CO_3.

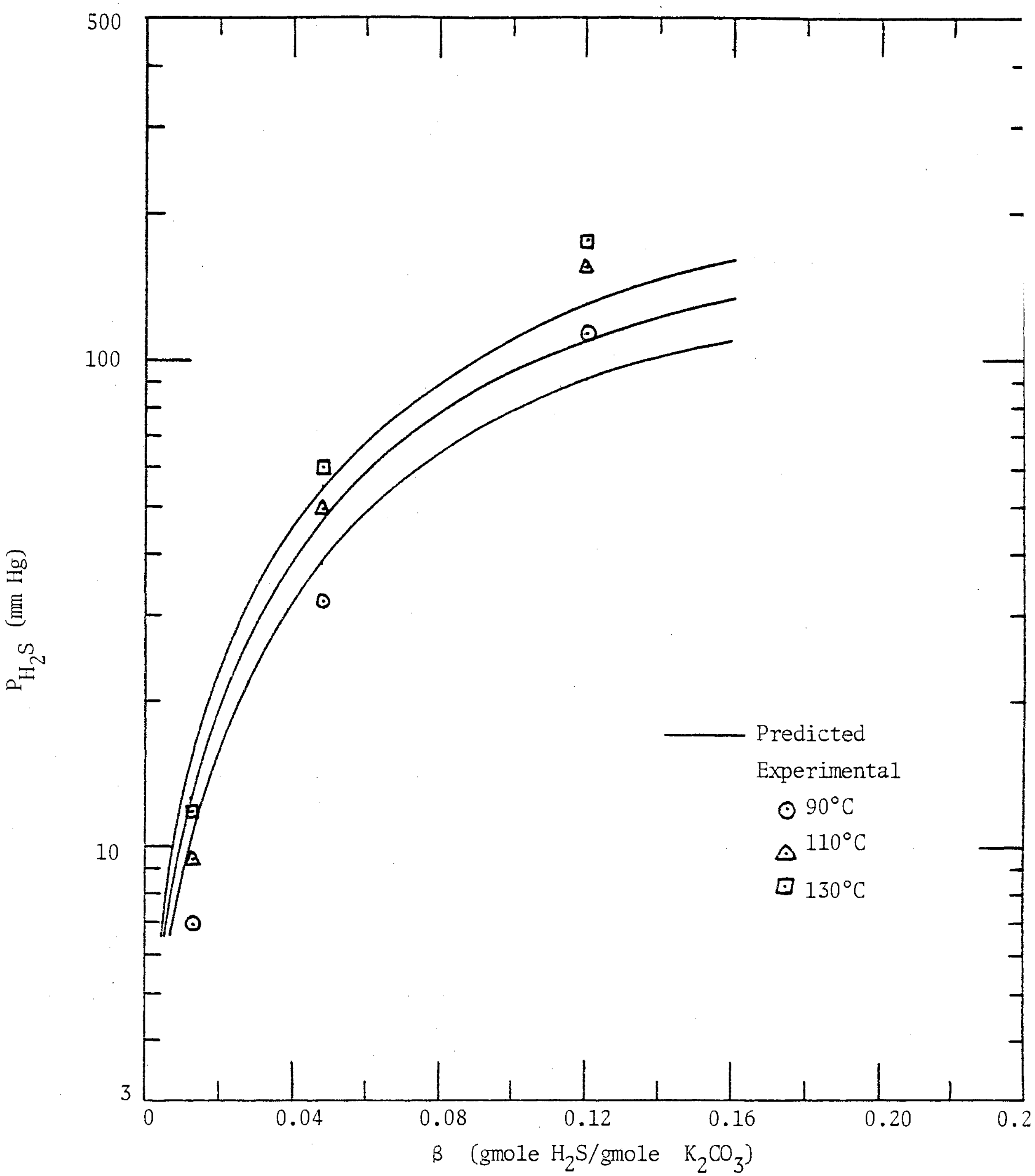

Fig. 7: Partial pressures of H_2S over 40% equiv. K_2CO_3 with total loading, $(\alpha + \beta)$, $\simeq$ 0.56 gmole/gmole K_2CO_3

TABLE 3

Summary of Errors in predicting

P_{CO_2} and P_{H_2S} for the $H_2S/CO_2/K_2CO_3$ system.

1.	Total number of observations	30
2.	Temperature range	70°C to 130°C
3.	Concentration range	30% to 40% eq. K_2CO_3
4.	For P_{CO_2}:	
	a) Maximum -ve error	21.4%
	b) Maximum +ve error	2.98%
	c) Average absolute error	12.8%
5.	For P_{H_2S}	
	a) Maximum -ve error	30.2%
	b) Maximum +ve error	50.4%
	c) Average absolute error	12.4%

Note: a) percent error = $\frac{\text{(Predicted value - Expt. value) 100}}{\text{Expt. Value}}$

b) P_{CO_2} and P_{H_2S} predicted in mm Hg.

Take the CO_2/K_2CO_3 system. H_{CO_2} was computed from (App.A.2)

$$H_{CO_2} = \frac{K_1}{K_3} \frac{[CO_3^{=}]}{[HCO_3^-]^2} P_{CO_2} \tag{1}$$

The temperature dependence of H_{CO_2} would then be due to the temperature dependence of the terms on the right-hand side of the equation. Equation (1) can be rewritten as

$$\ln H_{CO_2} = \ln K_1 - \ln K_3 + \ln P_{CO_2} + \ln C_1 \tag{2}$$

where C_1 incorporates the $[CO_3^{=}]$ and $[H_{CO_3}^{-}]$ values. For a qualitative understanding, assume C_1 to be independent of temperature (which amounts to neglecting the temperature dependence of the activity coefficients of $CO_3^{=}$ and $H_{CO_3}^{-}$, a simplifying assumption) and say P_{CO_2} can be approximated by a Antoine type equation of the type

$$P_{CO_2} = \frac{C_2}{T} \tag{3}$$

then differentiation of equation (2) w.r.t. T gives

$$\frac{d}{dt} \ln H_{CO_2} = \frac{d}{dt} \ln K_1 - \frac{d}{dt} \ln K_3 - \frac{C_2}{T^2} \tag{4}$$

The van't Hoff equation relates the equilibrium constant to the heat of reaction at constant pressure by

$$\frac{d}{dt} \ln Ki = \frac{\Delta H_i^\circ}{RT^2} \tag{5}$$

Hence equation (4) can be written as

$$\frac{d}{dt} \ln H_{CO_2} = (\Delta H_1^\circ - \Delta H_2^\circ) \frac{1}{RT^2} - \frac{C_2}{T^2} \tag{6}$$

or

$$\frac{d}{dt} \ln H_{CO_2} = \frac{\Delta H_t^\circ}{RT^2} - \frac{C_2}{T^2}$$

$$\text{where } \Delta H_t^\circ = \Delta H_1^\circ - \Delta H_2^\circ$$

ΔH°_t in turn is related to the specific heat at constant pressure as

$$\Delta H^\circ_t = \Delta H^\circ_{o,t} + \int \Delta C_{p_t} dT \qquad (8)$$

and ΔC_{p_t} then (for inorganic salts) is of the type

$$\Delta C_{p_t} = \Delta a + \frac{\Delta b}{T} + \frac{\Delta C}{T^2} \text{ etc} \qquad (9)$$

Hence equations (7) through (9) give

$$\frac{d}{dt} \ln H_{CO_2} = \frac{\Delta H^\circ_{o,t}}{RT^2} + \left(\Delta a + \frac{\Delta b}{T} + \frac{\Delta C}{T^2} \right) \frac{1}{RT^2} dt - \frac{C}{T^2} \qquad (10)$$

integration of which can be approximated as

$$\ln H_{CO_2} = \frac{-\Delta H^\circ_{o,t}}{R} - \frac{\Delta a^1}{RT} - \frac{\Delta b^1}{RT^2} - \frac{\Delta c^1}{RT^3} + \frac{C_2}{T} \qquad (11)$$

or

$$\ln H_{CO_2} = a^1 + \frac{b^1}{T} + \frac{c^1}{T^2} + \frac{d^1}{T^3} \qquad (12)$$

which is the type of temperature dependence depicted by the fitted expression for $\ln H_{CO_2}$.

The dependence of H_{CO_2} on the solution concentration can be explained in terms of the Debye - Hückel theory. A qualitative explanation using the simplified Debye - Hückel equation will be given.

The concentration dependence of H_{CO_2} comes purely from the concentration dependence of the activity coefficients of the $CO_3^=$ and $H_{CO_3}^-$ ions.

The Debye - Huckel equation for single ions gives

$$\ln \gamma_i = A Z^2 \sqrt{I} \qquad (13)$$

where A = constant

Z = charge on ion

I = total ionic strength of solution

Equation (13) written for each of the $CO_3^=$ and $H_{CO_3}^-$ ions gives

$$\ln \gamma CO_3^= = 4 A \sqrt{I} \qquad (]4)$$

and

$$\ln \gamma HCO_3^- = A \sqrt{I} \qquad (15)$$

Equations (14) and (15) can be combined to give

$$\frac{\gamma CO_3^=}{\gamma H^2_{CO_3^-}} = e^{-2 \sqrt{I}} \qquad (16)$$

The ionic strength of solution, I, is a function of the solution concentration, C, in the first place, hence equation (16) can be written as

$$\frac{\gamma CO_3^=}{\gamma H^2_{CO_3^-}} = C_3 e^{-2 \sqrt{C}} \qquad (17)$$

where C_3 = a constant

and H_{CO_2} is proportional to the activity coefficients of the two ions as

$$H_{CO_2} \propto \frac{\gamma CO_3^=}{\gamma H^2_{CO_3^-}} \qquad (18)$$

hence from equations (17) and (18) it can be shown that

$$\ln H_{CO_2} \propto \sqrt{C} \qquad (19)$$

The above conclusion was reached using simplest form of the Debye-Hückel equations. A more general conclusion for the concentration levels being concentration levels being considered would necessitate using the more complex, extended Debye - Hückel equations. The derivations would then need quantities like the salting-out parameters, specific ion constants etc··· which are not readily available for the present system. Hence even though the particular type of solution concentration dependence is obtained through regression of the experimental data, it is evident that it does indeed have a theoritical foundation.

All fits were made using the General Linear Models Procedure (PROC GLM) of the Statistical Analysis System (SAS) package. The goodness-of-fit was checked against the required criteria for PROC GLM and was found to be excellent in each case.

A sample listing of the computer program for the CO_2/K_2CO_3 system is included in Appendix A.3.

CONCLUSIONS AND RECOMMENDATIONS

The reaction model incorporating the fitted "constants", H_{CO_2} and H_{H_2S}, thus enable prediction of equilibrium partial pressure of CO_2 and CO_2 and H_2S for the CO_2/K_2CO_3 and $H_2S/CO_2/K_2CO_3$ systems, respectively. This model development overcomes one of the drawbacks of non-availability of experimental data in a given temperature, concentration or loading range. Besides, it presents a tool that can initiate the development of a package for a detailed simulation/design of an absorption-desportion unit for the hot carbonate process (vis-a-vis, the APM).

A few points must be mentioned in regard to the preceeding work and besides:

In the case of the amine model, two distinct groups of equations enabled the evaluation of amine equilibrium constants for two "pure" systems. These two were then combined to predict the general "mixture" system. The same approach was not possible for the carbonate model. This was because of the fact that no two distinct groups of equations existed for the process. The set of equations for an "only H_2S" system were exactly the same as those for a "mixture" system. Hence constants had to be fitted for the CO_2/K_2CO_3 system and the "mixture" $H_2S/CO_2/K_2CO_3$ system separately.

The other point to be mentioned is in connection with the available data for the "mixture" system. Only three levels of conversion and concentration have been covered and there too the data tends to be erratic and suspect for the lower concentrations and loadings of H_2S Substantial deviations from a possible trend is not explained. More "accurate" data would certainly be a big help in proper data correlation and model development.

Finally, suggestions (14) have been made for equilibrium studies for the H_2S / CO_2 / K_2CO_3 system wherein the K_2CO_3 solution contains small amounts of chemical additives (like amine borates, etc...). These are essentially "catalysed" processes and all that would change would be the rates of the various reactions. Nevertheless, the above approach would most certainly predict equilibria for those systems, provided, of course, substantial vapor pressure data are available or are generated experimentally for such processes.

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APPENDIX A.1

Equations for the CO_2/K_2CO_3 system.

(nomenclature employed is as shown earlier)

Ionic - equilibria equations:

$$H_2O + CO_2 \xrightleftharpoons{K_1} H^+ + HCO_3^- \qquad (1)$$

$$H_2O \xrightleftharpoons{K_2} H^+ + OH^- \qquad (2)$$

$$HCO_3^- \xrightleftharpoons{K_3} H^+ + CO_3^= \qquad (3)$$

"Pseudo-Henry's Law" relation:

$$P_{CO_2} = H_{CO_2}\,[CO_2] \qquad (4)$$

For 1 g. solution given F and C

$$F_{c,a} = (1-F)\,C \qquad (5)$$

$$F_{B,a} = 2\,F\,C\,\frac{MW_{HCO_3}}{MW_{K_2CO_3}} \qquad (6)$$

$$F_{w,a} = \left[\frac{(1-C)}{MW_{H_2O}} - \frac{FC}{MW_{K_2CO_3}}\right] MW_{H_2O} \qquad (7)$$

$$V_{s,a} = \frac{1}{\rho_s}\,(F_{c,a} + F_{B,a} + F_{w,a}) \qquad (8)$$

Hence,

$$[CO_3^=]_{,a} = \frac{F_{c,a}}{MW_{K_2CO_3}}\,\frac{1}{V_{s,a}} \qquad (9)$$

$$[HCO_3^-]_{,a} = \frac{F_{B,a}}{MW_{KHCO_3}}\,\frac{1}{V_{s,a}} \qquad (10)$$

Also, from equations (1), (3) and (4)

$$H_{CO_2,a} = \frac{K_1}{K_3}\,\frac{[CO_3^=]_a}{[HCO_3^-]^2_{,a}}\,PCO_{2,a} \qquad (11)$$

Further:

$$M = \frac{\rho_s C}{MW_{K_2CO_3}} \tag{12}$$

So,

$$\alpha, a = \frac{1}{M}\{[CO_3^{=}] + [HCO_3^{-}] + [CO_2] - M\} \tag{13}$$

APPENDIX A.2

Equations for the $H_2S/CO_2/K_2CO_3$ system:

(nomenclature employed is as shown earlier)

Ionic equilibria equations:

$$H_2O + CO_2 \underset{}{\overset{K_1}{\rightleftharpoons}} H^+ + HCO_3^- \tag{1}$$

$$H_2O \overset{K_2}{\rightleftharpoons} H^+ + OH^- \tag{2}$$

$$HCO_3^- \overset{K_3}{\rightleftharpoons} H^+ + CO_3^= \tag{3}$$

$$H_2S \overset{K_4}{\rightleftharpoons} H^+ + HS^- \tag{4}$$

"Pseudo-Henry's Law" relations:

$$P_{CO_2} = H_{CO_2} [CO_2] \tag{5}$$

$$P_{H_2S} = H_{H_2S} [H_2S] \tag{6}$$

For 1000g H_2O, given W_B, W_C and W_s

$$V_s = \frac{1}{\rho_s} [W_B \, NW_{KHCO_3} + W_C \, MW_{D_2CO_3} + W_s \, MW_{KHS} + 1000] \tag{7}$$

Hence,

$$[CO_3^=] = \frac{W_c}{V_s} \tag{8}$$

$$[HCO_3^-] = \frac{W_B}{V_S} \tag{9}$$

$$[HS^-] = \frac{W_S}{V_S} \tag{10}$$

Also from equations (1), (3) and (5)

$$H_{CO_2} = \frac{K_1}{K_3} \frac{[CO_3^=]}{[HCO_3^-]^2} P_{CO_2} \tag{11}$$

and from equations (3), (4) and (6)

$$H_{H_2S} = \frac{K_4}{K_3} \frac{[CO_3^{=}]}{[HS^-][HCO_3^-]} P_{H_2S} \tag{12}$$

Further,

$$M = \frac{\rho_s C}{MW_{K_2CO_3}} \tag{13}$$

So,

$$\alpha = \frac{1}{M} \{[CO_3^{=}] + [HCO_3^-] + [CO_2] - M\} \tag{14}$$

$$\beta = \frac{1}{M} \{[HS^-] + [H_2S]\} \tag{15}$$

APPENDIX A.3

```
**************************************************************
*                                                            *
*  S A S PROGRAM TO DEVELOP A CORRELATION FOR HCO2, THE      *
*  'PSEUDO-HENRY'S LAW CONSTANT' FOR THE CO2/K2CO3 SYSTEM.   *
*                                                            *
**************************************************************
*
*
*  READ IN THE SOLUTION CONCENTRATIONS,(WT.FRACTION),
*  TEMPERATURE,(DEG C), CONVERSION,(WT.FRACTION) AND
*  THE PARTIAL PRESSURE OF CO2,(PSIA) AND STORE THESE
*  OBSERVATIONS IN A DATASET LABELED 'DATA PURECO2'.
*
*;
DATA PURECO2;
INPUT C 1-10 T 11-20 F 21-30 CO2PSI 31-40;
PCO2=CO2PSI/14.696*760.0;
TR=(T+273.16)*1.8;
*
*
*  COMPUTE THE DENSITY OF THE SOLUTION FOR DIFFERENT
*  CONCENTRATIONS AND TEMPERATURES.
*
*;
RHOS=1000.0*(1.03346+100.0*0.01096*C-0.000858*((TR/1.8)
-273.16));
*
*
*  COMPUTE THE VALUES OF THE IONIC-EQUILIBRIA CONSTANTS
*  FOR DIFFERENT TEMPERATURES. THESE CONSTANTS ARE TAKEN
*  FROM THE LITERATURE.
*
*;
K1=EXP((-241.818)+(53.6855E+04/TR)-(4.8123E+08/TR**2)+(1.94E
+11/TR**3)-(2.96445E+13/TR**4));
K3=EXP((-294.74)+(65.5893E+04/TR)-(5.9667E+08/TR**2)+(2.4249E
+11/TR**3)-(3.7192E+13/TR**4));
*
*
*  COMPUTE THE CONCENTRATIONS OF THE VARIOUS IONS.
*
*;
M=C*RHOS/138.20535;
CRB=(1.0-F)*C;
BICAR=F*C*2.0*100.11525/138.20535;
H2O=((1.0-C)/18.0152-(F*C/138.20535))*18.0152;
TOTG=CRB+BICAR+H2O;
VOL=TOTG/RHOS;
CCO3=CRB/138.20535/VOL;
CHCO3=BICAR/100.11525/VOL;
*
*
*  COMPUTE THE CONCENTRATION OF FREE CO2 IN SOLUTION
*  AND THUS COMPUTE THE 'PSEUDO-HENRY'S LAW CONSTANT'.
*
*;
```

```
FRCO2=K3*CHCO3*CHCO3/(K1*CCO3);
HCO2=PCO2/FRCO2;
*
*
*  COMPUTE THE EQUIVALENT LOADING OF CO2 IN SOLUTION.
*
*;
ALFA=(CCO3+CHCO3+FRCO2-M)/M;
*;
KEEP C TR PCO2 FRCO2 HCO2 ALFA F T;
*
*
*  THE DATA DECK FOLLOWS AFTER 'CARDS'.
*
*;
CARDS;
DATA TOTAL;
*
*
*  SET THE EQUATIONS FOR THE CORRELATION USING THE ABOVE
*  DATA AND CALL 'PROC G L M' TO DETERMINE THE COEFFICIENTS
*  IN THE EQUATION FOR HCO2
*
*;
SET PURECO2;
Y1=LOG(HCO2);
X1=1/C**0.01;
X2=1/C**0.01/TR;
X3=1/C**0.01/TR**2;
X4=1/C**0.01/TR**3;
PROC GLM DATA=TOTAL;
MODEL Y1=X1 X2 X3 X4/NOINT;
*
*
*  USING THE ABOVE DETERMINED EQUATION FOR HCO2,PREDICT
*  THE PARTIAL PRESSURES OF CO2.  ALSO COMPUTE THE PERCENT
*  ERROR BETWEEN PREDICTED AND EXPERIMENTAL VALUES OF THE
*  CO2 PARTIAL PRESSURES FOR EACH OBSERVATION AND THE
*  CUMULATIVE AVERAGE ABSOLUTE ERROR FOR THE PREDICTIONS.
*
*;
OUTPUT OUT=NEW PREDICTED=PY1;
DATA PRED;
SET NEW;
PHCO2=EXP(PY1);
PPCO2=PHCO2*FRCO2;
PCTERR=ABS((PPCO2-PCO2)*100.0/PCO2);
SUMER+PCTERR;
N+1;
AVERR=SUMER/N;
*
*
*  PRINT OUT THE RESULTS FOR EACH OBSERVATION BY
*  CALLING 'PROC PRINT'.
*
*;
PROC PRINT DATA=PRED;
VAR C T ALFA PCO2 PPCO2 PCTERR AVERR;
*
*
*  END OF PROGRAM
*;
```