Theoretical Interpretation of Gas Oil Selectivity Data on X-Sieve Catalyst

A six-parameter multiresponse model based on the catalyst aging theory of Wojciechowski (1968) is applied to experimental selectivity data in gas oil cracking. Within the range of conditions studied, the model gave an adequate fit to the data. It was found that the selectivity curves at various cat/oil ratios were contained within optimum and minimum performance envelopes but that the relationships between these envelopes and the selectivity curves were not quite as simple as had previously been reported for a theoretical example (Campbell and Wojciechowski, 1969). The optimum time-on-stream for each of the cat/oil ratios was about one minute. Maximum gasoline production was 59 weight % at 81 weight % total cumulative conversion, resulting in a gasoline efficiency of 72.8%.

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SCOPE

Since its introduction in 1968 by Wojciechowski, the time-on-stream theory of catalyst decay has been successfully applied to catalytic cracking of both pure cumene and gas oil in static bed reactors. Previous papers by Wojciechowski and co-workers have dealt with the various aspects of catalytic conversion. This paper is concerned with the selectivity of a cracking catalyst. Although this is the most important aspect of catalyst behavior from the point of view of the petroleum industry, very little work has been published to date concerning selectivity behavior. The major difficulty in the development of suitable kinetics for selectivity has been the lack of adequate mathematical expressions to describe catalyst aging.

In 1961 Froment and Bischoff discussed the effect of various types of catalyst decay on the theoretical selectivity patterns in fixed bed reactors. Their analysis was then successfully applied to a set of data obtained by the same authors (1962). Unfortunately the approach proposed by Froment and Bischoff is experimentally cumbersome and as a result has not been widely used since. Subsequently in 1967, Sagara et al. treated selectivity for both isothermal and nonisothermal reactions in terms of time dependent effectiveness factors. The first attempt at applying a kinetic analysis based on time-on-stream to describe selectivity in gas oil cracking was that of Weekman in 1969 where an exponential decay function was used to account for aging.

Also in 1969, Campbell and Wojciechowski proposed an application of the time-on-stream theory of catalyst decay to describe theoretical patterns of selectivity in gas oil cracking in a fixed bed reactor. Their approach was somewhat simplified in that no volume expansion or refractivity phenomena were included. Some interesting patterns in selectivity were nevertheless observed and generalizations were drawn from the simplified model.

In 1970 Weekman and Nace extended Weekman's fixed bed selectivity model (Weekman, 1969) to account for gas oil cracking selectivity in fluidized and moving bed reactors.

In this paper we correlate experimental data on gas oil selectivity, a portion of which has previously been reported and correlated by Weekman (1969) and Weekman and Nace (1970).

CONCLUSIONS AND SIGNIFICANCE

A general selectivity model which includes terms to account for catalyst aging, volume expansion during reaction, and refractivity of the feed is presented. An *F*-test performed on the gasoline yield model indicates that the experimental data supports the proposed model.

The selectivity curves in gas oil cracking are bounded by optimum and minimum performance envelopes, but the relationship between the minimum envelope and the selectivity curves is not as straightforward as was earlier reported for a simplified model (Campbell-Wojciechowski, 1970).

For the *X*-sieve catalyst used and at the operating temperature of 481°C (900°F) the Ultimate Gasoline Efficiency is 82.9. The maximum gasoline yield of 59% occurs at a total cumulative conversion of 81% and results in a gasoline efficiency of 72.8.

Since the model enables us to obtain the optimum performance envelope for a particular gas oil and catalyst, selectivity can readily be predicted for moving and fluidized bed units. This conclusion is based on the fact that selectivities in moving and fluidized bed reactors are coincident with the static bed optimum performance envelope.

Although the particular gas oil and specific results reported here may be of little interest, they illustrate the fact that the method of approach presented here is useful and can be used as a basis for correlation of gas oil cracking data.

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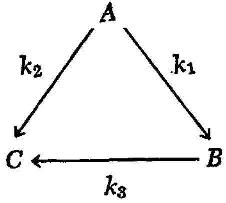
THEORY

In previous publications (Pachovsky, 1971; Best, 1971; Campbell, 1969) it has been proposed that gas oil cracking can be represented by the mechanism



Previously, we have only been concerned with the disappearance of A (gas oil) and thus only the value of the sum of rate constants ($k_{10} + k_{20}$) was obtained from fitting our model to experimental conversion data. Here we concern ourselves with selectivity and will isolate the individual rate constants k_{10}, k_{20}, and k_{30}, where k_{10} is the rate constant for the appearance of B (C_5 + gasoline) and k_{20} and k_{30} are the rate constants for the appearance of C (coke and C_4 − gas), from gas oil and gasoline respectively.

We assume that the cracking reaction is taking place in an ideal fixed bed reactor where the catalyst is static and the reactant passes through in plug flow. If we say that the time taken for a differential segment of reactant to pass through the reactor is τ, then it has been shown (Pachovsky, 1971) that we can write the differential equation describing the instantaneous disappearance of gas oil as

$$-r_A = (k_1 + k_2)\, C_A \tag{1}$$

Similar equations can be written describing the instantaneous formation of gasoline and coke plus dry gas. In particular these are

$$r_B = k_1 C_A - k_3 C_B \tag{2}$$

$$r_c = k_2 C_A + k_3 C_B \tag{3}$$

Pachovsky and Wojciechowski (1971) have shown that each rate constant in the above equations is modified by taking into account catalyst aging. Furthermore, in the case of gas oil, the rate constant is modified by a refractivity term (Blanding, 1953). Incorporating these features in Equations (1), (2), and (3), allowing for volume expansion, and rewriting Equation (1) in terms of fraction of feed converted, we write

$$\frac{dX_A}{d\tau} = (k_{10} + k_{20}) \left(\frac{1}{1 + Gt}\right)^N \left(\frac{1 - X_A}{1 + \epsilon_A X_A}\right)^{1+W} \tag{4}$$

It should be noted that in gas oil cracking volume expansion may not vary linearly with conversion as has been assumed in Equation (4). However, over a wide range of conversions the linear expansion assumption appears to be adequate. The decay function has been previously derived (Wojciechowski, 1968) and is based on the premise that the rate of loss of active sites on surface of a catalyst can be described as following an mth order decay. This suggestion was first reported by Schlaffer et al. in 1957 and more recently by Szepe and Levenspiel (1968).

For the recracking of gasoline we do not include a term for refractivity since the gasoline fraction is a more homogeneous cut. For this reaction the rate constant is modified only by the inclusion of the catalyst aging and expansion terms. We can now rewrite Equation (2) in terms of fraction of gasoline produced,

$$\frac{dX_B}{d\tau} = \left(\frac{1}{1 + Gt}\right)^N \left\{ k_{10}\left(\frac{1 - X_A}{1 + \epsilon_A X_A}\right)^{1+W} - k_{30}\left(\frac{1 + \epsilon_A}{1 + \epsilon_A X_A}\right) X_B \right\} \tag{5}$$

And for the undesirable products, we can rewrite Equation (3) as

$$\frac{dX_c}{d\tau} = \left(\frac{1}{1 + Gt}\right)^N \left\{ k_{20}\left(\frac{1 - X_A}{1 + \epsilon_A X_A}\right)^{1+W} + k_{30}\left(\frac{1 + \epsilon_A}{1 + \epsilon_A X_A}\right) X_B \right\} \tag{6}$$

Equations (4) to (6) then are the coupled differential equations which must be solved to compare theory to experimental results. Each of these equations is true only for a particular catalyst age t and hence the values of X_A, X_B, and X_c are instantaneous values. In a static bed reactor, however, all measured values of yields are time averaged over the duration of the experimental run to give $\overline{X}_A$, $\overline{X}_B$, and $\overline{X}_c$. In order to compare the experimental values with those predicted by the model, all the calculated instantaneous values X at the various catalyst ages t must be time averaged from $t = 0$ to $t = t_f$ to yield average $\overline{X}$ values.

It should be noted that in a fixed bed reactor

$$\tau = bPt_f$$

where P is the cat/oil ratio. The above system of equations can then be solved for a variety of cat/oil ratios.

PROCEDURE

Although there are several methods for solving systems of first-order ordinary differential equations, we chose to use the Hamming predictor-corrector method since it appears to be best suited to our needs. Two different procedures were used in the determination of the parameters. The first procedure involved taking the previously known values of N, G, $k_{10} + k_{20}$, and W (Pachovsky, 1971) and determining the values of the individual rate constants k_{10}, k_{20}, and k_{30}. The G's and N's were taken to be the same in all the branches of the catalytic cracking mechanism. For each set of three data points (that is, $\overline{X}_A$, $\overline{X}_B$, and $\overline{X}_c$) determined from a single experimental run, catalyst times-on-stream ranging from $t = 0$ to $t = t_f$ (final time-on-stream for that run) were chosen and at each of these times the system of Equations (4), (5) and (6) was solved to give instantaneous values of X_A, X_B, and X_c. These were then time averaged over the interval $0 - t_f$ and the resulting time averaged values compared with the corresponding experimental ones. The above procedure was repeated for new values of k_{10}, k_{20}, and k_{30} until optimum values for these parameters were obtained. The second procedure was tried on only one set of data and was performed in a similar manner to that of the first except that all parameters (that is, including N, G, and W) were left to be optimized. In both cases similar final values of the parameters resulted. However, the second procedure was considerably more expensive in computer time. All computations were performed on on IBM 360 model 50 computer. The criterion for fit in this case consisted of minimizing the determinant of the covariance matrix between calculated and experimental results (Box-Draper, 1965).

Table 1. Comparison of Model Fittings
Stock: Mid Continent Gas Oil
Catalyst: 30/60 Mesh REHX
Temperature: 481°C (900°F)

	Fit of Weekman-Nace model (1970) (16 data pts. 2 response treatment)	Fit of Weekman-Nace model (this work) (41 data pts. 3 response treatment)	This model (41 data pts. 3 response treatment)
k_0 $(= k_{10} + k_{20})$	210.8 hr^{-1}	292.9 hr^{-1}	1443.8 hr^{-1}
k_{10}	164.8 hr^{-1}	231.6 hr^{-1}	1180.1 hr^{-1}
k_{20}	46.0 hr^{-1}	61.2 hr^{-1}	234.7 hr^{-1}
k_{30}	8.96 hr^{-1}	11.2 hr^{-1}	19.8 hr^{-1}
α	18.2 hr^{-1}	26.6 hr^{-1}	$G =$ 18.2 hr^{-1}
			$N =$ 3.6 hr^{-1}
			$W =$ 0.72 hr^{-1}

		Conversion response	Gasoline response	Conversion response	Gasoline response
F—test @ 95% confidence level	F—Tabulated	2.15	2.28	2.27	2.36
	F—Calculated	9.29	10.61	1.92	1.69

DISCUSSION

Figure 1 shows the predicted conversion for various cat/oil ratios and the experimental conversion data. It was shown by Pachovsky-Wojciechowski (1971) that an F-test performed on the model proved that the model adequately described the conversion data at the 95% confidence level. Figure 2 shows the model gasoline yield for various cat/oil ratios along with experimental gasoline yield data. Table 1 shows that an F-test performed on the gasoline yield model indicates that the model adequately describes the gasoline data at the 95% confidence level.

The procedure for model fitting reported here is correct, although some confusion might result from the fact that previously (Pachovsky, 1971) we used a minimum sum of squares of residuals as the criterion of fit whereas here we are minimizing a covariance matrix determinant. A residual is defined in both cases as the difference between a value predicted by the model and the corresponding experimental value. In the present case, the value of the minimum sum of squares of residuals is not the correct criterion of fit due to potential interactions between $\overline{X}_A$, $\overline{X}_B$, and $\overline{X}_c$. The correct optimum fit in such a case is obtained by using the criterion suggested by Box and Draper (1965) for determining parameters from multiresponse data. When using this criterion, not the sum of squares of residuals for the individual responses but the determinant of the covariance matrix must be minimized.

From Figure 2 we see that the inclusion of volume expansion and stock refractivity produces theoretical gasoline yield curves which show almost identical shapes to those reported for a simplified theoretical case by Campbell and Wojciechowski (1969).

Figure 3, however, has a feature which is different from that reported by Campbell and Wojciechowski (1969). We noted that the general shape of the curves matches those for class III catalysts in the work of Campbell and Wojciechowski (1969) but that the minimum performance envelope in the present case is defined by long on stream times at a high cat/oil ratio rather than by a coincident envelope which includes all cat/oil ratios at high on stream times.

The optimum performance envelope is such an important feature of the selectivity plot that it deserves special

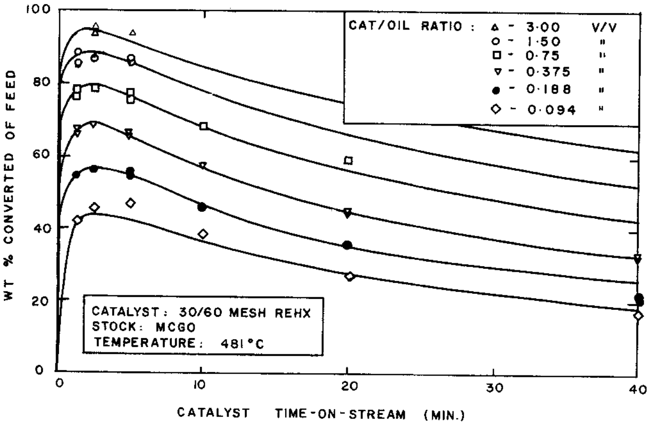


Fig. 1. Comparison of conversion model and experimental data for constant catalyst to oil ratio. Catalyst: 30/60 mesh REHX; Stock: Mid-Continent gas oil; Temperature: 481°C (900°F).

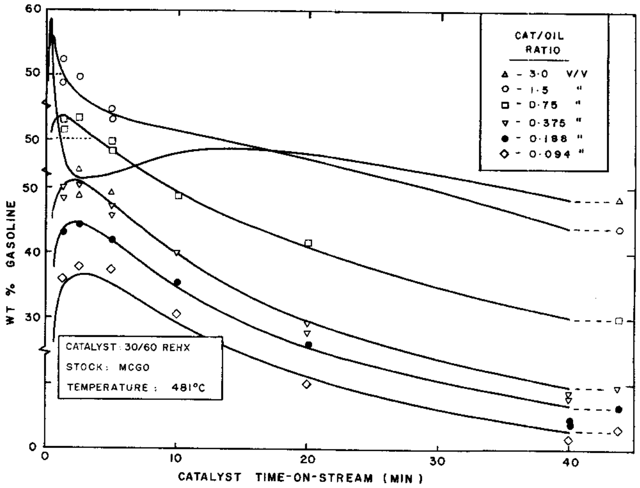


Fig. 2. Comparison of selectivity model and experimental data for constant catalyst to oil ratio. Catalyst: 30/60 mesh REHX; Stock: Mid-Continent gas oil; Temperature: 481°C (900°F).

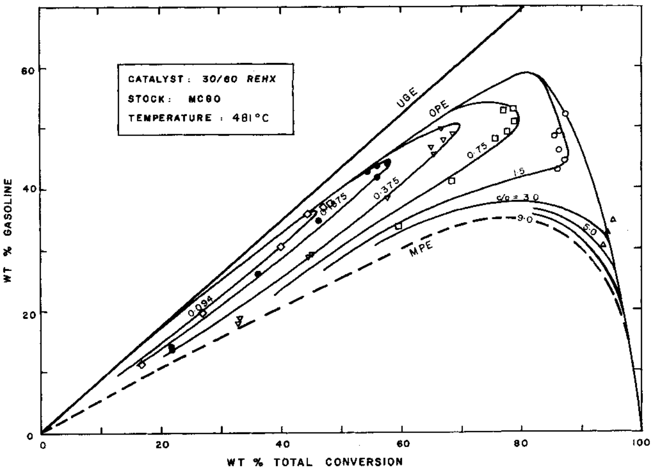


Fig. 3. Comparison of model and experimental data for constant catalyst to oil ratio.

attention. It represents the maximum possible yield of gasoline that can be obtained from a feed stock at a specified conversion. Since the optimum performance envelope was shown by Campbell and Wojciechowski (1969) to be identical to the instantaneous selectivity curve, it is a simple matter to solve equations (4) to (6) to obtain instantaneous yields of X_A, X_B, and X_c at different times-on-stream and hence the instantaneous selectivity. This optimum performance envelope shows that in a fixed bed reactor using REHX catalyst, operating at 481°C (900°F), and cracking mid-continent gas oil, the maximum gasoline yield of 59% occurs at a conversion of about 81% in weight %. From the previous works of Campbell-Wojciechowski (1969) and of Weekman (1969), it would appear that for this catalyst and temperature any cat/oil ratio greater than unity can give this maximum gasoline yield.

A knowledge of the initial slope of the selectivity curve yields the Ultimate Gasoline Efficiency (U. G. E.) of the catalyst at the operating temperature of 900°F. Campbell and Wojciechowski (1970) have previously shown that the ultimate product efficiency is given by $k_{10}/(k_{10} + k_{20})$ and is equivalent to the ratio of feed converted to desirable product to the total feed converted under initial conditions. In this present case the U.G.E. is found to be 82.9%. This represents the very best selectivity which can be expected in this system. Since this selectivity only occurs at very low conversions it is of little practical importance. The more important value is that representing maximum gasoline production which is shown here to be 59 wt % at an efficiency of 72.8%.

The model of Weekman and Nace (1970) in differential form, in particular their equations 8a and 8b, was also fitted to this data by our method in order to provide a means by which the two models could be compared. Before this could be done, however, a third equation had to be added since in the multiresponse situation which exists in gas oil cracking the correct computational procedure requires the use of all available responses in the estimation of the parameters. The added equation

$$\frac{dy_3}{dx} = \frac{K_3}{s}\phi_3 y_1^2 + \frac{K_2}{s}\phi_2 y_2 \qquad (7)$$

was intended to fit the coke plus gas responses. In this case the exponential decay function proposed by Weekman is used. The only difference between our approach and the one originally used by Weekman and Nace was that we chose not to normalize any of our values (such as time-on-stream, and contact time) but instead retained the absolute values. This difference in procedure, however, should have no effect on the resultant parameter values. Table 1 shows a comparison of the value for the model parameters as obtained by Weekman-Nace (1970) and those obtained by us. It is readily apparent that including the coke and C_4 + dry gas response changes the parameter values to a significant degree.

One further point that needs comment is the fact that from the data reported in Figure 3 in the Weekman-Nace paper (1970) it is readily apparent that a hyperbolic type of decay is more appropriate in this case than is the exponential decay function the authors prefer to use.

In our work an adequate fit of data is obtained using a six-parameter model. We believe this to be the minimum number of parameters required to describe the complex phenomenon of gas oil cracking over a rapidly aging catalyst. This stems from the fact that two parameters are needed to describe the catalyst decay—one for the order of deactivation and one for the deactivation rate constant. Assuming that the gas oil cracking reactions can be described by first-order kinetics eliminates the need for three orders of reaction however it still leaves three conversion rate constants to be determined. Furthermore, this is true only if the simple three reaction gas oil cracking mechanism is used. At least one parameter is also needed to account for feed stock refractivity. This results in the total of six parameters. If volume expansion due to reaction is not assumed to be linear and the value of the expansion coefficient ϵ_A is not known, then at least one additional parameter is required. We feel that the six parameters that have been included in our model are not only sufficient to guarantee adequacy of fit but are also essential.

NOTATION

A = gas oil in cracking mechanism

B = C_5 + gasoline in cracking mechanism

C = coke + C_4 − dry gas in cracking mechanism

C_A = concentration of gas oil feed, atm

C_B = concentration of gasoline, atm

C_c = concentration of coke and dry gas, atm

G = rate constant parameter of the aging function, hr^{-1}

N = exponent of aging function

P = cat/oil ratio (vol. cat/vol. feed)

W = composition parameter for the rate constant function

X_A = instantaneous fraction of deed converted

X_B = instantaneous fraction of gasoline produced

X_c = instantaneous fraction of coke and dry gas produced

$\overline{X}_A$ = time averaged fraction of feed converted

$\overline{X}_B$ = time averaged fraction of gasoline produced

$\overline{X}_c$ = time averaged fraction of coke and dry gas produced

b = proportionality constant (taken equal to unity)

k_{01} = initial rate constant for conversion of gas oil to gasoline, hr^{-1}

k_{02} = initial rate constant for conversion of gas oil to coke and dry gas, hr^{-1}

k_{03} = initial rate constant for conversion of gasoline to coke and dry gas, hr^{-1}

t_f = catalyst time-on-stream, hr

t = any intermediate time-on-stream during an experimental run, hr

ϵ_A = volume expansion correction term

τ = gas oil contact time measured at initial conditions of flow, hr

LITERATURE CITED

Best, D. A., et al., "Diffusion Effects in Catalytic Gas Oil Cracking," *Can. J. Chem. Eng.*, **49**, 365 (1971).

Blanding, F. H., "Reaction Rates in Catalytic Cracking of Petroleum," *Ind. Eng. Chem.*, **45**, 1186 (1953).

Box, G. E. P., and N. R. Draper, "The Bayerian Estimation of Common Parameters from Several Responses," *Biometrika*, **52**, 355 (1965).

Campbell, D. R., and B. W. Wojciechowski, "Theoretical Patterns of Selectivity in Aging Catalysts with Special Reference to the Catalytic Cracking of Petroleum," *Can. J. Chem. Eng.*, 47, 413 (1969).

———., "Selectivity of Aging Catalyst in Static, Moving, and Fluidized Bed Reactors," *ibid.*, **48**, 224 (1971a).

———., "The Catalytic Cracking of Cumene on Aging Catalysts, I. The Mechanism of the Reaction," *J. Cat.*, **20**, 217 (1971a).

———., "The Catalytic Cracking of Cumene on Aging Catalysts, II. An Experimental Study," *ibid.*, **23**, 307 (1971b).

Froment, G. F., and K. B. Bischoff, "Non-Steady State Behaviour of Fixed Bed Catalytic Reactors Due to Catalyst Fouling," *Chem. Eng. Sci.*, **16**, 189 (1961).

———., "Kinetic Data and Product Distribution from Fixed Bed Catalytic Reactors Subject to Catalyst Fouling," *ibid.*, **17**, 105 (1962).

Pachovsky, R. A., and B. W. Wojciechowski, "Theoretical Interpretation of Gas Oil Conversion Data on an X-Sieve Catalyst," *Can. J. Chem. Eng.*, **49**, 365 (1971).

Sagara, S., et al., "Effect of Nonisothermal Operation on Catalyst Fouling," *AIChE J.*, **13**, 1226 (1967).

Schlaffer, W. G., et al., "Aging of Silica-Alumina Cracking Catalysts, I. Kinetics of Structural Changes by Heat and Steam," *J. Phys. Chem.*, **61**, 714 (1957).

Szepe, S., and O. Levenspiel, "Catalyst Deactivation," in Proc. 4th *Eur. Symp. on Chem. Reac. Eng.*, Brussels (1968).

Weekman, V. W., "A Model for Catalytic Cracking Conversion in Fixed, Moving, and Fluid-Bed Reactors," *Ind. Eng. Chem. Process Design Develop.*, **7**, 90 (1968).

———., "Kinetics and Dynamics of Catalytic Cracking Selectivity in Fixed Bed Reactors," *ibid.*, **8**, 385 (1969).

———., Nace, D. M., "Kinetics of Catalytic Cracking Selectivity in Fixed, Moving, and Fluid Bed Reactors," *AIChE J.*, **16**, 397 (1970).

Wojciechowski, B. W., "A Theoretical Treatment of Catalyst Decay," *Can. J. Chem. Eng.*, **46**, 48 (1968).

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Activity Coefficients—Aqueous Solutions of Polybasic Acids and Their Salts

A method of predicting activity coefficients of polybasic acids and their salts in strong aqueous solutions is presented. Application of the calculation of decomposition pressures of SO_2 over sodium sulfite-bisulfite systems and of CO_2 over carbonate-bicarbonate systems is illustrated.

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SCOPE

Correlations have recently been presented (Meissner and Tester, 1972; Meissner et al., 1972; Meissner and Kusik, 1972) whereby the mean ionic activity coefficients of many types of electrolytes, notably neutral salts such as NaCl, $AlCl_3$, etc., can be estimated in both pure and mixed aqueous solutions at temperatures of from 0 to 150°C, and at concentrations up to saturation. It is desirable to extend these simple correlations to more complex ionic soluions.

CONCLUSIONS AND SIGNIFICANCE

It is demonstrated that one may predict the activity coefficients of (1) the strong polybasic acids, namely H_2SO_4, H_3AsO_4, and H_3PO_4, (2) the acid salts of these strong polybasic acids such as $NaHSO_4$, K_2HPO_4, etc., and (3) the acid salts of the weak polybasic acids such as $NaHCO_3$, $KHSO_3$, sodium hydrogen malonate, potassium hydrogen succinate, etc. Such activity coefficients can be employed in the calculation of chemical equilibria, as when the dissociation pressures of CO_2 over aqueous carbonate-bicarbonate solutions and of SO_2 over sulfite-bisulfite solutions are approximated.

STRONG ACIDS

For strong electrolytes, isotherms of log Γ° versus concentration expressed in ionic strength units fall into the curve family of Figure 1 at all temperatures from the freezing point to about 150°C (Meissner et al., 1972). Since there is little curve cross-over, location of one point