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COMMUNICATIONS

Oxygen Solubility in Brines

The solubility of oxygen in water and brines, expressed as the Henry's law constant, is reported for temperatures from 0 to 300 °C. A smoothing and interpolation formula based upon a widely used heat capacity equation fit the solubility data well over this temperature range and may be extrapolated to somewhat higher temperatures. The solubility of oxygen in water and brines exposed to air saturated with water vapor is given for temperatures from 0 °C to the normal boiling point.

As part of Federal Bureau of Mines research on corrosion in geothermal and mineral processing environments, the solubility of oxygen in sodium chloride brines and in mixed-chloride geothermal brines was determined by Cramer (1980) over the temperature range 0 to 300 °C. The smoothing and interpolation formula used to describe the effect of temperature (T) on the Henry's law constant (k) was an empirical five-term power series in reciprocal temperature ($1/T$). While this approach is useful, the smoothing and interpolation formula is more often developed from heat capacity equations of the form

$$\Delta C_p = \Delta\alpha^\circ + 2\Delta\beta^\circ T + 6\Delta\lambda^\circ T^2 \qquad (1)$$

and the application of thermodynamic principles (Gokcen, 1975; Gokcen and Chang, 1975; Hougen et al., 1959; Smith and Van Ness, 1959). This latter approach gives the smoothing and interpolation formula a thermodynamic basis. Thermal effects are more readily evaluated from an equation of this form since heat capacity data for a wide variety of materials have been expressed in this way (Hougen et al., 1959; Smith and Van Ness, 1959). Finally, analytic expressions for the partial molal enthalpy, entropy, and Gibbs energy of solution are readily obtained from eq 1 (Gokcen, 1975; Hougen et al., 1959; Smith and Van Ness, 1959).

The mathematical development of the smoothing and interpolation formula from eq 1 is well established (Gokcen, 1975; Hougen et al., 1959; Smith and Van Ness, 1959), and only the final equation will be given here

$$\ln k^\circ = \frac{(\Delta\alpha^\circ - \Delta S^\circ{}_0)}{R} + \frac{\Delta H^\circ{}_0}{RT} - \frac{\Delta\alpha^\circ \ln T}{R} - \frac{\Delta\beta^\circ T}{R} - \frac{\Delta\lambda^\circ T^2}{R} \qquad (2)$$

where $\Delta S^\circ{}_0$ and $\Delta H^\circ{}_0$ are constants of integration and R is the gas constant, 1.9872 cal/K g-mol. The coefficients $\Delta\alpha^\circ$, $\Delta\beta^\circ$, and $\Delta\lambda^\circ$ are the differences between corresponding terms that describe the state of the gas molecules in the vapor and the solution. ΔC_p represents the difference between the heat capacity of the gas in solution and that in the vapor and can be merged with known thermodynamic functions for the vapor-phase gas behavior to obtain a description of the gas properties in solution.

The Henry's law constant in eq 2 is

$$k^\circ = \phi P/\gamma x \qquad (3)$$

where ϕ is the fugacity coefficient for the gas in the vapor phase evaluated at the temperature and total pressure of the system, P is the partial pressure of the gas in the vapor phase, x is the mole fraction of the gas dissolved in solution, and γ is the activity coefficient for the dissolved gas. Since γ was not known except for the case of pure water where $\gamma \simeq 1$, k° was not measured in the study but rather a "practical" or modified Henry's law constant

$$k = \gamma k^\circ = \phi P/x \qquad (4)$$

which is composed of readily determined quantities. It defines the solubility of gases in nonideal, as well as ideal, solutions (Cramer, 1980). In the limit of dilute solutions, for example, oxygen dissolved in water or in very dilute salt solutions at oxygen partial pressures of 100 atm or less, $\gamma \simeq 1$ and k° and k are equal. However, the salt solutions considered in this study are not dilute. The reference state for the dissolved oxygen is oxygen dissolved in water at infinite dilution. The activity coefficient for the oxygen in the salt solutions is, thus, not unity and k° and k are not equal.

A generalized smoothing and interpolation formula for the modified Henry's law constant, having the same form as eq 2, can be obtained by combining eq 2 and 4

$$\ln k = \frac{(\Delta\alpha - \Delta S_0)}{R} + \frac{\Delta H_0}{R} - \frac{\Delta\alpha \ln T}{R} - \frac{\Delta\beta T}{R} - \frac{\Delta\lambda T^2}{R} \qquad (5)$$

Table I. Brine Characteristics

brine	molality, *m*	molarity, M	ionic strength[a]	constituents
NaCl-1	0.87	0.85	0.87	NaCl
NaCl-2	2.97	2.78	2.97	NaCl
NaCl-3	5.69	5.09	5.69	NaCl
East Mesa geothermal brine (EMGB)	0.57	0.56	0.60	alkali and alkaline-earth metal chlorides[b]
Salton Sea geothermal brine (SSGB)	4.87	4.19	7.34	alkali and alkaline-earth metal chlorides[b]

[a] Based on molal concentrations. [b] Composition given by Cramer (1980).

Table II. Solubility Constants for Oxygen

brine	ΔS_0, cal/K g-mol	ΔH_0, cal/g-mol	$\Delta\alpha$, cal/K g-mol	$\Delta\beta$, cal/K^2 g-mol	$\Delta\lambda$, cal/K^3 g-mol	std error of est, %
water	−21.1537	−7561.7	−10.6578	0.107708	-0.32942×10^{-4}	6.0
NaCl-1	−22.2338	−5918.3	−7.9075	0.081094	-0.22453×10^{-4}	4.7
NaCl-2	−12.6251	−3888.2	−8.1155	0.070532	-0.23145×10^{-4}	5.5
NaCl-3	−8.0613	−5224.7	−13.7075	0.140559	-0.79595×10^{-4}	5.3
EMGB	−11.4186	−9290.6	−18.8512	0.208580	-1.17803×10^{-4}	4.0
SSGB	−32.1306	−5575.1	−25.7905	0.205121	-1.18354×10^{-4}	5.9

It is assumed in doing this that the effect of temperature on the logarithm of the activity coefficient can also be described by an equation similar to eq 2. Mean experimental values of the modified Henry's law constant (in MPa) reported by Cramer (1980) for water and the five brines characterized in Table I and obtained at temperatures ranging from 0 to 310 °C were fit to this smoothing and interpolation formula by the method of least squares. The resulting values for the solubility constants in eq 5—ΔS_0, ΔH_0, $\Delta\alpha$, $\Delta\beta$, and $\Delta\lambda$—are given in Table II. The standard error of the estimate for each set of data, expressed as a percentage of the smoothed Henry's law constant, ranged from 4 to 6%. These values are similar to those computed for the five-term power series and to the relative experimental error for measurements of the Henry's law constant, 5.8% (Cramer, 1980). For the oxygen-water data, an analysis of residuals (Miller and Wichern, 1977) showed that the experimental data were normally distributed about the smoothed values and the residuals were not biased by the magnitude of the smoothed variable (the modified Henry's law constant). Thus, the generalized smoothing and interpolation formula gave a good fit to the experimental data.

Smoothed values of the modified Henry's law constant are given in Table III for water and for the five brines at temperatures from 0 to 300 °C. The smoothed values for water, NaCl-1, NaCl-2, NaCl-3, and EMGB agreed within 2% of the earlier reported values (Cramer, 1980) except at the upper and lower ends of the temperature range, where the differences were about 5%. These differences are not significant. On the other hand, the smoothing and interpolation formula fit the SSGB data at the lower end of the temperature range considerably better than the five-term power series, and the differences between the smoothed values for SSGB reported here and the earlier values (Cramer, 1980) were significant. Moderate extrapolation of the curves for the Henry's law constant using eq 5 to temperatures above 300 °C is reasonable since the slope of the ln k–T curves is only slowly changing in the temperature range 200 to 300 °C.

The solubility of oxygen (expressed in ppm by weight) in water and in the five brines exposed to air saturated with water vapor at a total pressure of 760 mmHg was computed from values of the modified Henry's law constant generated by the smoothing and interpolation formula. These values are computed for temperatures ranging from 0 °C to the normal boiling point of the brine and are given in Table IV. The values for water at 0 to

Table III. Smoothed Values of the Modified Henry's Law Constant, MPa

temp, °C	water	NaCl-1	NaCl-2	NaCl-3	EMGB	SSGB
0	2620	4130	9810	19900	3340	15360
20	4040	5780	11970	23900	5040	19360
40	5450	7300	13600	26390	6560	21870
60	6600	8450	14560	27310	7630	22920
80	7320	9130	14870	26880	8120	22610
100	7540	9310	14590	25470	8070	21330
120	7310	9040	13860	23460	7620	19460
140	6730	8430	12810	21170	6910	17350
160	5940	7600	11580	18840	6100	15250
180	5060	6650	10270	16620	5280	13290
200	4190	5680	8970	14600	4520	11570
220	3370	4760	7740	12830	3860	10110
240	2660	3910	6610	11300	3280	8890
260	2070	3170	5590	10020	2820	7910
280	1580	2540	4700	8960	2440	7140
300	1190	2010	3930	8090	2140	6560

Table IV. Oxygen Solubility (ppm) in Brines Exposed to Air Saturated with Water Vapor at a Total Pressure of 760 mmHg (Basis: 20.93 vol % Oxygen in Dry Air)

temp, °C	water	NaCl-1	NaCl-2	NaCl-3	EMGB	SSGB
0	14.29	8.89	3.60	1.70	11.05	2.23
5	12.61	8.07	3.39	1.61	9.79	2.08
10	11.23	7.37	3.21	1.53	8.77	1.95
15	10.08	6.77	3.05	1.46	7.92	1.84
20	9.11	6.25	2.91	1.40	7.21	1.75
25	8.29	5.79	2.78	1.35	6.61	1.67
30	7.58	5.40	2.66	1.30	6.10	1.60
35	6.96	5.04	2.55	1.26	5.66	1.54
40	6.41	4.71	2.44	1.22	5.26	1.48
45	5.91	4.40	2.34	1.18	4.90	1.43
50	5.45	4.11	2.24	1.14	4.57	1.37
55	5.01	3.83	2.13	1.10	4.25	1.32
60	4.58	3.54	2.01	1.06	3.93	1.26
65	4.15	3.24	1.88	1.01	3.61	1.20
70	3.71	2.93	1.74	0.95	3.27	1.12
75	3.24	2.59	1.58	0.88	2.89	1.04
80	2.73	2.21	1.39	0.80	2.48	0.94
85	2.17	1.79	1.17	0.71	2.00	0.82
90	1.54	1.30	0.91	0.59	1.46	0.67
95	0.82	0.75	0.61	0.45	0.83	0.50
100	0	0.11	0.25	0.28	0.08	0.29
101	*a*	*a*	0.17	0.25	*a*	0.24
102	*a*	*a*	0.09	0.21	*a*	0.19
103	*a*	*a*	0.01	0.17	*a*	0.14
104	*a*	*a*	*a*	0.13	*a*	0.08
105	*a*	*a*	*a*	0.08	*a*	0.03

[a] Temperature exceeds the normal boiling point.

40 °C are in better agreement with the published data than those computed from the five-term power series (Cramer, 1980). The most extreme example of this improvement is the result for water at 0 °C where the oxygen solubility measured by Truesdale et al. (1955) was 14.16 ppm, that determined from the generalized smoothing and interpolation formula (eq 5) was 14.29 ppm, and that from the five-term power series was 15.36 ppm. Except for SSGB, there was less than a 5% difference between the atmospheric pressure solubility values given by the two equations at temperatures above 40 °C.

In summary, the generalized smoothing and interpolation formula (eq 5) fit the experimental oxygen solubility data well. It is based upon a widely used heat capacity equation and the application of thermodynamic principles, which facilitates further interpretation of the results. The solubility of oxygen in water, in three sodium chloride brines, and in two geothermal brines, expressed in terms of the Henry's law constant, is reported for temperatures from 0 to 300 °C. The solubility of oxygen in these brines at atmospheric pressure is reported for temperatures from 0 °C to their normal boiling point.

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Optimal Policy for a Consecutive Reaction in a CSTR with Concentration-Dependent Catalyst Deactivation

An optimal time-temperature policy to maximize the cumulative yield of the desired product has been developed for a first-order consecutive reaction, subject to concentration-dependent catalyst deactivation conducted in a continuous stirred tank reactor. A graphical methodology utilizing Pontryagin's Minimum Principle has been used. In general, the optimal policy is a nonconstant conversion policy. This technique can be extended to include various deactivation mechanisms.

Introduction

In commercial catalytic reactors undergoing slow catalyst deactivation, it is the usual practice to gradually increase the reactor temperature to maintain a constant conversion at the outlet. This constant conversion policy constitutes a rigorous optimal policy only for the simple reaction A → B.

Commercial reactions are generally more complex and selectivity considerations are usually more important. The optimal temperature policy for complex reactions has been investigated by several authors (Dalcorso and Bankoff, 1972; Ogunye and Ray, 1971; Reiff and Kittrell, 1981). In general, numerical solutions are necessary. Recently, Reiff (1981) presented a graphical methodology for obtaining the optimal temperature policy for a series reaction undergoing concentration-independent deactivation in a CSTR.

Except for a few cases, concentration-independent deactivation is not applicable and usually the deactivation is concentration dependent. This note extends his analysis to the case of concentration-dependent deactivation for the first-order series reaction A → B → C conducted in a CSTR.

Problem Formulation and Solution

The objective is to maximize the yield of B for the first-order series reaction A → B → C undergoing catalyst deactivation in an isothermal, continuous stirred tank reactor. For convenience, the nomenclature of Reiff (1981) will be retained. For no products present in the feed and assuming that the pseudo-steady-state approximation is valid, we have

$$\frac{C_A}{C_{A_0}} = \frac{1}{1 + k_1 a \tau} \tag{1}$$

$$\frac{C_B}{C_{A_0}} = \frac{k_1 a \tau}{(1 + k_1 a \tau)(1 + k_2 a \tau)} \equiv -F \tag{2}$$

where, in general

$$-\frac{da}{dt} = k_D C_A{}^n C_B{}^m a \equiv f; \quad a(0) = 1 \tag{3}$$

The aim is to find an optimal temperature policy such that the total yield of B over the catalyst life is maximized subject to the constraints on the reaction temperature. In order to find the optimal temperature policy for this problem, the run length, θ, has to be specified (Reiff, 1981). Thus, the objective is to minimize $\int_0^\theta F\,dt$ subject to $k_{D*} \le k_D(t) \le k_D{}^*$ where k_D rather than T is taken as the control variable because of mathematical convenience in calculating the partial derivative of the Hamiltonian with respect to the independent variable.

The graphical solution has been discussed in detail by Reiff (1981). Briefly, the Hamiltonian, H, is defined as

$$H = F + \lambda f \tag{4}$$

The first necessary condition for optimally can be obtained from Pontryagin's Minimum Principle as

$$\frac{\partial H}{\partial k_D} = 0 = \frac{\partial F}{\partial k_D} + \lambda \frac{\partial f}{\partial k_D} \tag{5a}$$

or

$$\lambda = -\frac{\partial F/\partial k_D}{\partial f/\partial k_D} \tag{5b}$$

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