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# Gas Solubilities Near the Solvent Critical Point

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An estimation of gas solubilities in liquids at high temperatures is required for a number of industrial process calculations and geological investigations. Few experimental data, however, are available, and such a lack of information has justified attempts of extrapolations by means of correlations (Hayduck and Laudie, 1973; Cysewski and Prausnitz, 1976; de Ligny et al., 1976). Extrapolations to high temperatures can be subject to large errors, mainly owing to the presence of a minimum in the variation of solubilities with temperature. Here a limiting condition based on thermodynamics is found. All correlations must be consistent with this limit in order to allow reasonable estimations.

Hayduk and Laudie (1973) observed that all gas solubilities in a given solvent have a common value as the solvent critical temperature is approached. Extrapolating bilogarithmic curves of gas solubilities vs. temperature to the solvent critical temperature, they determined reference solubilities in a number of polar and apolar solvents. It is shown here that their observation is true for all gases and solvents, and an exact value of the reference solubility is derived from thermodynamic considerations. It is also shown that enthalpies of solution of all gases are infinite at the solvent critical temperature.

## THERMODYNAMIC FRAMEWORK

Let the solubility of a gas (2) in a solvent (1) at a given temperature $T$ be defined as follows:

$$S_{21} = \lim_{x_2 \to 0} \left( \frac{x_2}{P y_2} \right) \tag{1}$$

The fugacity of the gas in the liquid phase can be written as

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$$f_2^L(T,P,x_2) = H_{21}(T,P_1^S)\,x_2\gamma_2^*\exp\left[\int_{P_1^S}^{P}\frac{\bar{v}_2^\infty}{RT}\,dP\right] \tag{2}$$

where $P_1^S$ is the saturation pressure of the solvent, $\bar{v}_2^\infty$ the partial molal volume of the gas at infinite dilution in the solvent, and $\gamma_2^*$ an activity coefficient normalized by

$$\lim_{x_2\to 0}\gamma_2^* = 1 \tag{3}$$

The vapor-phase fugacity of the gas is given by

$$f_2^G(T,P,y_2) = Py_2\varphi_2(T,P,y_2) \tag{4}$$

The expression of equilibrium

$$f_2^L = f_2^V \tag{5}$$

leads, according to relations (1) to (4), to

$$S_{21} = \frac{\varphi_2^\infty(T,P_1^S)}{H_{21}(T,P_1^S)} \tag{6}$$

where $\varphi_2^\infty$ is the fugacity coefficient of the gas infinitely diluted in the vapor of the solvent. While the quantity $S_{21}$ can be derived directly from measurements of $P$, $y_2$, and $x_2$, the determination of Henry's constant, as shown by the relation above, requires a model of the vapor phase.

## COEXISTENCE EQUATION

Let us consider the coexistence equation derived by Hala et al. (1967) for a two-phase binary system:

$$(x_2-y_2)\left(\frac{\partial^2G^L}{\partial x_2^2}\right)_{T,P}dx_2 + \left[(V^G-V^L)+(x_2-y_2)\left(\frac{\partial V^L}{\partial x_2}\right)_{T,P}\right]dP + \left[(y_2-x_2)\left(\frac{\partial S^L}{\partial x_2}\right)_{T,P} + (S^L-S^G)\right]dT = 0 \tag{7}$$

The molar Gibbs free energy $G^L$ is related to the chemical potentials $\mu_1$, $\mu_2$ of the components

$$G^L = x_1\mu_1 + x_2\mu_2 \tag{8}$$

$$\left(\frac{\partial^2G^L}{\partial x_2^2}\right)_{T,P} = \frac{\partial}{\partial x_2}(\mu_2-\mu_1) \tag{9}$$

with

$$\frac{\partial\mu_1}{\partial x_2} = RT\frac{\partial}{\partial x_2}(\ln\gamma_1x_1) \tag{10}$$

$$\frac{\partial\mu_2}{\partial x_2} = RT\frac{\partial}{\partial x_2}(\ln\gamma_2^*x_2) \tag{11}$$

which gives the following forms to Equation (9):

$$\left(\frac{\partial^2G^L}{\partial x_2^2}\right)_{T,P} = RT\frac{\partial}{\partial x_2}\left(\ln\frac{\gamma_2^*}{\gamma_1} + \ln\frac{x_2}{1-x_2}\right) \tag{12}$$

$$(y_2-x_2)\left(\frac{\partial^2G^L}{\partial x_2^2}\right)_{T,P} = RT\left(\frac{y_2}{x_2}-1\right)\left[1+\frac{x_2}{1-x_2}+x_2\frac{\partial\ln(\gamma_2^*/\gamma_1)}{\partial x_2}\right] \tag{13}$$

## APPLICATION TO ISOTHERMAL EQUILIBRIUM AT THE SOLVENT CRITICAL TEMPERATURE

The solvent critical point is reached at the temperature $T_{C_1}$ when $x_2$ goes to zero. It is characterized by the following relations (Rowlinson, 1969):

$$(V^G-V^L)_{C_1} = 0 \tag{14}$$

$$\left(\frac{dP}{dx_2}\right)_{C_1} = 0 \tag{15}$$

The liquid volume can be written as

$$V^L = (1-x_2)\bar{v}_1 + x_2\bar{v}_2 \tag{16}$$

and partial molal volumes $\bar{v}_1$, $\bar{v}_2$ have finite value under nonzero pressure. Hence, the derivative

$$\left(\frac{\partial V^L}{\partial x_2}\right)_{C_1} = \bar{v}_2^\infty(T_{C_1},P_{C_1}) - v_{C_1} \tag{17}$$

has a finite value.

The coexistence Equation (7), when applied to isothermal equilibrium at the temperature $T_{C_1}$, may therefore be written, at the limit $x_2 = 0$

$$\lim_{x_2\to 0}(y_2-x_2)\left(\frac{\partial^2G^L}{\partial x_2^2}\right) = 0 \tag{18}$$

or, according to Equation (13)

$$\lim_{x_2\to 0}\left(\frac{y_2}{x_2}-1\right)\left\{1+x_2\left[\frac{\partial\ln(\gamma_2^*/\gamma_1)}{\partial x_2}\right]_{T_{C_1},P}\right\} = 0 \tag{19}$$

If we assume the continuity of both the function $\ln\gamma_2^*/\gamma_1$ and its partial derivative with respect to $x_2$ [it is equivalent to assume the continuity of the function $(\partial^2G^L/\partial x_2^2)_{T_{C_1},P}$], the product $x_2[\partial\ln(\gamma_2^*/\gamma_1)/\partial x_2]_{T_{C_1},P}$ goes to zero with $x_2$. Therefore

$$\lim_{x_2\to 0}\left(\frac{y_2}{x_2}\right)_{T_{C_1}} = 1 \tag{20}$$

Hala (1975) already used the following equivalent relation for other purposes:

$$\lim_{x_1\to 1}\left(\frac{dy_1}{dx_1}\right)_{T_{C_1}} = 1 \tag{21}$$

An important result concerning gas solubilities is derived from relation (20) according to definition (1)

$$S_{21}(T_{C_1}) = \frac{1}{P_{C_1}} \tag{22}$$

which can also be written as

$$H_{21}(T_{C_1},P_{C_1}) = P_{C_1}\varphi_2^\infty(T_{C_1},P_{C_1}) \tag{23}$$

This equation, derived from thermodynamics only, gives a precise, rigorous content to the concept of reference solubility $S_{21}(T_{C_1})$. It provides also an exact value of $S_{21}$ which differs from the results of evaluations by graphical extrapolations, as shown by Table 1. Actually, it is seen on Figure 1 that experimental data on gas solubilities in water are in better agreement with the limiting value calculated here from thermodynamics. The curves on the figure also suggest a slope of infinite negative value at the limit. It will be shown that thermodynamics also predicts this behavior.

## LIMITING SLOPE AT THE CRITICAL POINT

Let us now consider the binary equilibrium under a total pressure $P_{C_1}$. As $x_2$ approaches zero, equations expressing the equilibrium take the simpler forms

$$P_{C_1}y_1 = P_1^S(T)x_1 \tag{24}$$

$$P_{C_1}y_2\varphi_2^\infty = H_{21}(T,P_1^S)x_2 \tag{25}$$

Differentiating both equations along the isobaric equilibrium curve, we get

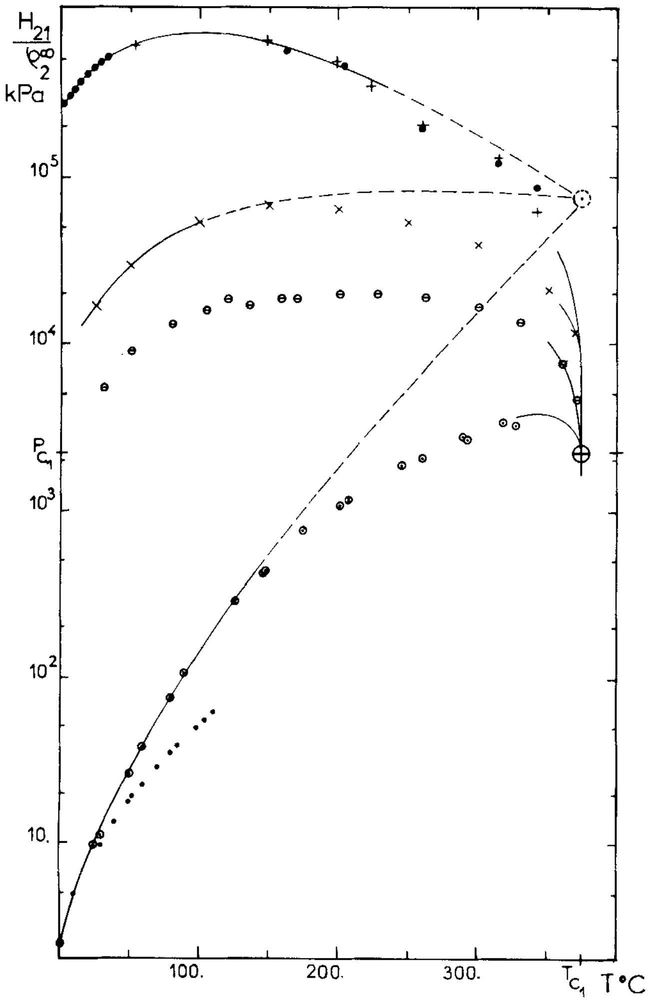

**Fig. 1. Gas solubilities in water:experimental points and extrapolations to the solvent critical temperature.**

+ **hydrogen (Pray et al., 1952).**
● **oxygen (Pray et al., 1952; Benson and Krause, 1976).**
× **carbon dioxide (Houghton et al., 1957; Ellis and Golding, 1963).**
⊖ **hydrogen sulfide (Clarke and Glew, 1971; Selleck et al., 1952; Kozintseva, 1964).**
⊙ **ammonia (Jones, 1963).**
• **sulfur dioxide (Beuschlein and Simenson, 1940).**
⊕ **reference solubility from this work.**
- - - **Hayduk's graphical extrapolations.**
— **real behavior suggested by experimental points and this work.**

$$P_{C_1}\left[\frac{\partial(y_1/x_1)}{\partial x_2}\right]_{P_{C_1}}\left(\frac{\partial x_2}{\partial T}\right)_{P_{C_1}}=\frac{dP_1{}^S}{dT} \qquad (26)$$

$$P_{C_1}\left[\frac{\partial(y_2/x_2)}{\partial x_2}\right]_{P_{C_1}}\left(\frac{\partial x_2}{\partial T}\right)_{P_{C_1}}=\frac{d}{dt}\left(\frac{H_{21}}{\varphi_2{}^\infty}\right) \qquad (27)$$

Taking the ratios of corresponding terms, we get

$$\frac{d}{dT}\left(\frac{H_{21}}{\varphi_2{}^\infty}\right)=\frac{dP_1{}^S}{dT}\left[\frac{\partial(y_2/x_2)}{\partial x_2}\right]_{P_{C_1}}\left[\frac{\partial(y_1/x_1)}{\partial x_2}\right]_{P_{C_1}}^{-1} \qquad (28)$$

Now, the following relations are easily derived from relation (20) and definitions of mole fractions:

$$\lim_{x_2\to 0}\left[\frac{\partial(y_2/x_2)}{\partial x_2}\right]_{P_{C_1}}=\lim_{x_2\to 0}\left[\frac{(y_2/x_2)-1}{x_2}\right] \qquad (29)$$

Table 1. Reference Solubilities in Three Solvents (in kPa$^{-1}$)

| Solvent | $S_{21}(T_C)$ extrapol.* | $S_{21}(T_{C_1}) = 1/P_{C_1}$ |
|---|---|---|
| Water | 1.3 $10^{-5}$ | 4.43 $10^{-4}$ |
| Methanol | 4.8 $10^{-5}$ | 1.23 $10^{-3}$ |
| Chlorobenzene | 1 $10^{-4}$ | 2.17 $10^{-3}$ |

* Hayduk and Laudie (1973).

$$\lim_{x_2\to 0}\left[\frac{\partial(y_1/x_1)}{\partial x_2}\right]_{P_{C_1}}=\lim_{x_2\to 0}\left[\frac{(y_1/x_1)-1}{x_2}\right]=\lim_{x_2\to 0}\left[\frac{1-(y_2/x_2)}{x_1}\right] \qquad (30)$$

Consequently, as $x_2$ goes to zero, Equation (28) gives

$$\left[\frac{d}{dT}\left(\frac{H_{21}}{\varphi_2{}^\infty}\right)\right]_{T_{C_1}}=-\infty \qquad (31)$$

since

$$\left(\frac{dP_1{}^S}{dt}\right)_{T_{C_1}}>0 \qquad (32)$$

The pair of Equations (23) and (31) may be called a limiting law for gas solubilities in liquids. The only mathematical assumption involved in their derivation regards the continuous behavior of all functions of the mole fraction $x_2$ appearing in the coexistence Equation (7) near the solvent critical point ($x_2 = 0$).

## CONCLUSION

As evidenced by Figure 1, estimation of high temperature Henry's constants from data at low temperature is impossible without some other source of information. The limiting law derived here justifies Hayduk's idea of a reference solubility, and any theory or correlation on gas solubilities in liquids should restitute the limiting behavior. For example, scaled particle theory, applied by Pierotti (1963) to gas solubilities, does predict an enthalpy of solution that is positive, infinite at the point $CP_1$, in agreement with Equation (30). It does not verify Equation (23), and such a disagreement should be analyzed in order to develop a better theory.

## NOTATION

$f_i$ = fugacity of component $i$
$G$ = molar Gibbs free energy
$H_{21}$ = Henry's constant of gas 2 in solvent 1
$P$ = pressure
$R$ = gas constant
$S$ = molar entropy
$S_{21}$ = solubility of gas 2 in solvent 1
$T$ = temperature
$V$ = molar volume
$\bar{v}_i$ = partial molal volume of component $i$
$x_i$ = mole fraction of component $i$ in the liquid
$y_i$ = mole fraction of component $i$ in the vapor
$\gamma_1,\gamma_2{}^*$ = activity coefficients
$\mu_i$ = chemical potential of component $i$
$\varphi_i$ = fugacity coefficient of component $i$

### Subscripts

$C_1$ = taken at the critical point of solvent 1

### Superscripts

$G$ = gas-phase quantities
$L$ = liquid-phase quantities
$S$ = quantities evaluated along the saturation curve
$\infty$ = infinite dilution properties

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# Effects of Convection and Brownian Motion on Particle Growth Rate in Colloidal Dispersions

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The particle growth rate due to the monomer diffusion in colloidal dispersions is known to be given by

$$\dot{r} = \frac{DV_m(C - C_r')}{r} \tag{1}$$

This equation has been used as the fundamental equation of particle growth or dissolution in the theories of Ostwald ripening (Wagner, 1961; Mullin, 1972; Sugimoto, 1971, 1978).

The effect of convection is not considered in Equation (1). It is, however, of practical importance to consider the effect of convection, since natural convection and/or forced convection (agitation) are almost always applied in real systems in order to accelerate the mass transfer.

Kahlweit (1975) has proposed use of the following Nernst's equation instead of Equation (1) for diffusion controlled Ostwald ripening under the influence of convection:

$$\dot{r} = \frac{DV_m(C - C_r')}{\delta} \tag{2}$$

where $\delta$ is assumed independent of $r$ and implies the presence of convection. Although this equation is known to be valid for relatively large particles ($> 10^2\ \mu m$), it seems unlikely that it is similarly applicable to the kinetics of Ostwald ripening which ordinarily involves small particles under a few microns in size. In such a small size range, the convection seems to become ineffective, and the Brownian motion of the particles is expected to become the determinant factor. Thus, the object of this work is to propose kinetic equations of $\dot{r}$ due to monomer diffusion when the effects of convection and Brownian motion may both be present.

### EFFECTS OF CONVECTION AND BROWNIAN MOTION

The quantity of monomers diffusing per unit time through the spherical surface at $x$ from the center of a particle ($x \geqq r$) is given by the Fick's law as

$$\dot{n} = 4\pi x^2 D \frac{\partial c(x, t)}{\partial x} \tag{3}$$

If the monomer stream is in the steady state, $\dot{n}$ is independent of $x$. Thus, it follows that

$$\dot{n} = 4\pi r^2\, \dot{r}/V_m \tag{4}$$

and integration of Equation (3) over $x$ gives

$$4\pi D\,[c(x, t) - c(r, t)] = -\dot{n}\left(\frac{1}{x} - \frac{1}{r}\right) \tag{5}$$

Since $c(x, t)$ at $x \geqq r + \delta$ is virtually equal to $C$ from the

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