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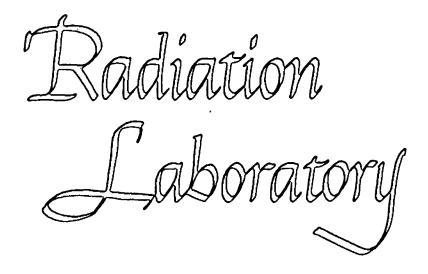https://escholarship.org/uc/item/1jv2c94n

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ABSTRACT

Henry's Law is modified and extended to higher concentrations by considering the solution as a continuum during the addition of the solute component. The expression obtained by this treatment is $P_A = -k' \ln (1 - x_A)$, where A denotes the solute component and k' is the Henry's Law constant at infinite dilution. This relation shows an improvement over Henry's Law in solutions for which the fugacity correction is very small.

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It is properly known that Henry's Law, in general, is valid only for very dilute solutions. The linear relation between the partial pressure of the solute and its mole fraction in the solvent probably begins to break down at the concentration at which any one solute molecule becomes aware of the presence of neighboring solute molecules. For a binary solution in which we denote the solute and solvent species by the letters A and B respectively, Henry's Law becomes

$$P_A = k(x_A). \tag{1}$$

Following Brinkman[1] in his work on the viscosity of suspensions, or Bruggeman[2] in his study of the dielectric constant of mixtures, one can extend Henry's Law to higher concentrations. That is, it is possible to develop an expression analogous to Eq. (1) in which the experimentally determined constant k holds over a wider range of x_A.

To begin with let us propose the following nomenclature:

Let n_0, n_1, n_2, $\cdots$, n_j represent the total number of moles of A and B in the solution after 0, 1, 2, $---$, j moles of A have been added to the solvent. That is, n_0 represents the number of moles of solution before any A has been added (i.e. pure B), and $n_1 = n_0 + 1$; $n_2 = n_1 + 1$; etc. In a similar manner let P_0, P_1, P_2, $\cdots$, P_j be the resulting total pressure of the system after we have respectively added 0, 1, 2, $\cdots$, j moles of A to the system.

Restricting ourselves to binary solutions, where Dalton's Law of additive pressures applies, we may write for the total pressure of the system

$$P = P_A + P_B, \tag{2}$$

where P_A and P_B are the partial pressures of components A and B respectively. If the amount of A in the solution is quite small compared with the amount of

B, then Eq. (1) holds and we may substitute it into Eq. (2) to obtain

$$P = P_B + kx_A. \tag{3}$$

Equation (3) holds for very dilute solutions of A, and therefore it holds for 1 mole of A if we are working with a very large number of moles of B. Thus, using the above nomenclature, we may write

$$P = P_B + k(1)/(n_0 + 1). \tag{4}$$

Since P_B is P_0 and $(n_0 + 1)$ is n_1, by definition, we may write Eq. (4) as

$$P = P_0 + k(1)/n_1. \tag{5}$$

Note, however, that the left-hand side of the above equation is equal to the pressure exerted by the pure solvent plus 1 mole of A and is therefore P_1 by definition. We may write Eq. (5) as

$$P_1 = P_0 + k(1)/n_1. \tag{6}$$

Now, on the addition of the second mole of A, we have a total pressure of P_2, by definition. This pressure may be visualized as being equal to the pressure exerted by the system when 1 mole of A is present plus the increase due to the contribution from the second mole of A. In effect we are treating the solution that results after the addition of the first mole of A as a continuum or a pure solvent with an effective vapor pressure of P_1 so far as the second mole of A is concerned. Therefore we may write

$$P_2 = P_1 + k(1)/(n_1 + 1), \tag{7}$$

or

$$P_2 = P_1 + k(1)/n_2. \tag{7a}$$

This addition procedure may be continued until we have added the jth mole of A and obtain

$$P_j = P_{j-1} + k(1)/n_j. \tag{8}$$

After we added the j-1th mole of A the mole fraction of A in the solution was

$$x_{A_{j-1}} = (j - 1)/n_0 + j - 1), \tag{9}$$

and in a similar manner the mole fraction of A after the $\underline{j}$th mole of A was added is

$$x_{A_j} = (j)/(n_0 + j). \tag{10}$$

The differential changes in the mole fraction of A in going from the $\underline{j-1}$th to the $\underline{j}$th mole of A is then

$$\Delta x_A = (n_0)/(n_0 + j)(n_0 + j - 1). \tag{11}$$

Since j is assumed to be a large number in comparison with 1, we may set j approximately equal to $j-1$ in the above expression. This is equivalent to neglecting lower-order terms in the denominator of Eq. (11). We thus obtain for Δx_A

$$\Delta x_A = (n_0)/(n_0 + j)^2. \tag{12}$$

Noting $x_B = (1 - x_A) = (n_0)/(n_0 + j)$, we see that Eq. (12) may be written as

$$\Delta x_A = (1 - x_A)/(n_0 + j), \tag{13}$$

or

$$\Delta x_A = (1 - x_A)/n_j \tag{13a}$$

The corresponding change in pressure in passing from the $\underline{j-1}$th to the $\underline{j}$th mole of A is

$$\Delta P = P_j - P_{j-1}. \tag{14}$$

Upon substituting Eq. (13a) and (14) into Eq. (8) we obtain

$$\Delta P = k(\Delta x_A)/(1 - x_A). \tag{15}$$

Passing to the limit and integrating x_A from 0 to x_A while P goes from P_0 to P, we obtain

$$\int_{P_0}^{P} dP = k \int_{0}^{x_A} dx_A/(1 - x_A), \tag{16}$$

which yields

$$P = P_0 - k \ln(1 - x_A).$$ (17)

We note that P_0 is identical to the vapor pressure of pure B, and by use of Eq. (2) we may simplify (17) to

$$P_A = -k \ln(1 - x_A).$$ (18)

The value of K in the above equation will in general agree with the value in Eq. (1) only at infinite dilution, therefore the above expression is better written as

$$P_A = -k' \ln(1 - x_A).$$ (19)

Equation (19) is the desired extension of Henry's Law. Since our model has neglected fugacity corrections, the results are best tested on systems in which this correction is known to be small or negligible. Table I shows a comparison of the k's in Eqs. (1) and (19) for three systems in which the fugacity correction is very small.[3] Columns 3 and 4 of the table show the Henry's Law constant required by Eq. (1) and the corresponding variation in its value based on the lowest value given. Columns 5 and 6 show the constant required by Eq. (19) and its resulting variation. It can be seen that the constant in the "Henry's Law Extension" undergoes much less variation in the data given than does the constant in Henry's Law.

Table I

Comparison of Henry's Constant and Modified Henry's Constant

1	2	3	4	5	6
P_A mm Hg	x_A	k $x\ 10^{-4}$ mm Hg	% var. in k	k' $x\ 10^{-4}$ mm Hg	% var. in k'
		H_2 in H_2O at 19.4°C			
900	0.0101	8.24	0.00	8.21	0.00
2000	0.0240	8.32	0.97	8.28	0.85
3000	0.0356	8.41	2.06	8.28	0.85
4000	0.0472	8.49	3.04	8.30	1.09
5000	0.0582	8.59	4.25	8.34	1.58
6000	0.0689	8.74	6.07	8.45	2.92
7000	0.0790	8.86	7.52	8.52	3.78
		O_2 in H_2O at 23°C			
900	0.0196	4.58	0.00	4.55	0.00
2000	0.0436	4.59	0.22	4.51	0.88
3000	0.0652	4.60	0.44	4.47	1.76
4000	0.0855	4.68	2.20	4.50	1.10
5000	0.1060	4.73	3.26	4.47	1.76
6000	0.1250	4.80	4.80	4.47	1.76
7000	0.1440	4.88	6.40	4.47	1.76
		H_2 in H_2O at 23°C			
2000	0.0259	7.76	0.00	7.65	0.00
3000	0.0386	7.77	0.13	7.65	0.00
4000	0.0511	7.81	0.65	7.65	0.00
5000	0.0634	7.89	1.68	7.65	0.00
6000	0.0750	8.00	3.10	7.70	0.65
7000	0.0860	8.16	5.15	7.80	1.96

Nomenclature

A   A symbol used to denote the solute.

B   A symbol used to denote the solvent.

k   Henry's Law constant.

k'   A constant defined by Eq. (19).

n   Number of moles of solution.

P   Pressure symbol.

References

1. H. D. Brinkman, J. Chem. Phys. 20, No. 4, 571 (1952).

2. D. A. G. Bruggeman, Ann. Physik 24, 636 (1935).

3. W. J. Moore, Physical Chemistry, 2nd Ed. (Prentice-Hall, New York, 1955).