

# VALIDITY OF HENRY'S LAW IN DILUTE SOLUTIONS

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According to the generally accepted definition of the ideal solution there are equal interaction forces acting between molecules belonging to the same or different species. (This is equivalent to the statement that the activity of the components equals the concentration.) Strictly speaking this condition is only in exceptional cases fulfilled for mixtures (optical isomers, isotopic mixtures of an element, hydrocarbon mixtures). It is still usual to talk about ideal solutions as limiting cases in reality since very dilute solutions behave ideally with respect to the solvent. This view is further supported by the fact that Raoult's Law empirically found for describing the behaviour of the solvent in dilute solutions can be deduced thermodynamically via the assumption of ideal behaviour of the solvent.

As is commonly known on the basis of the Gibbs—Duhem equation the behaviour of different components of a solution is interdependent.

For example: for a two-component solution the variation of the chemical potential of the components with the composition can be formulated as follows:

$$x_1 \left( \frac{\partial \mu_1}{\partial x_1} \right)_T dx_1 = - x_2 \left( \frac{\partial \mu_2}{\partial x_2} \right)_T dx_2 \quad (1)$$

Since  $\mu = \mu^\circ + RT \ln a$  and  $x_1 + x_2 = 1$  having  $\mu^\circ$  defined independent of pressure expression (1) transforms into (2)

$$\frac{d \ln a_1}{d \ln x_1} = \frac{d \ln a_2}{d \ln x_2} \quad (2)$$

Considering that  $a = \gamma \cdot x$  we arrive at the Duhem—Margules equation:

$$\frac{d \ln \gamma_1}{d \ln x_1} = \frac{d \ln \gamma_2}{d \ln x_2} \quad (3)$$

It follows from the equality of the activity and concentration ( $\gamma = 1$ ) for ideal mixtures that

$$\frac{d \ln \gamma}{d \ln x} = 0 \quad (4)$$

for both components.

On the basis of the Duhem—Margules equation the observation of ideal behaviour of the solvent in dilute, real solutions has resulted in far-reaching inferences regarding the behaviour of the solute known as Henry's Law because

$$\frac{d \ln \gamma_1}{d \ln x_1} = 0 \quad (5)$$

(Subscripts 1 and 2 refer to the solute and solvent, resp.) gives  $\gamma_1 = \text{const.}$  as a result of non-definite integration, i.e. as long as  $a = x$  equality is true for the solvent one gets  $a = \text{const. } x$  as the necessary consequence for the solute. This line of reasoning giving the connection between the characteristics of solute and solvent is frequently found in textbooks on chemistry [1–3]. It should be kept in mind, however, that if two components do not form ideal solutions in any given ratio than even in dilute solutions the forces acting among molecules cannot be described in terms of ideal condition. It is, of course, quite a different matter that in very dilute solutions due to the overwhelming majority of solvent molecules over those of the solute the deviation from ideal behaviour can be such a minute effect that it cannot be detected by measurements.

In the following we shall point out, provided  $\delta$  is the deviation from ideality for the solvent not feasible for observation, but it can still be defined as a finite small quantity, that the same  $\delta$  deviation will manifest itself as a measurable quantity for the solute. Let us write:

$$\frac{d \ln \gamma_1}{d \ln x_1} = \frac{d \ln \gamma_2}{d \ln x_2} = \delta \quad (6)$$

That is  $\frac{d \ln \gamma_2}{dx_2} = \frac{\delta}{x_2}$  for the solvent and  $\frac{d \ln \gamma_1}{dx_1} = \frac{\delta}{x_1}$  for the solute.

Assuming a very dilute solution  $x_2$  is very near to unity but  $x_1$  is almost zero, therefore,  $\delta/x_2 \approx \delta$  for the solvent and so it is negligible, however,  $\delta/x_1$  can easily be quite a great number for the solute.

At the same time that we have proven Henry's Law to be invalid even in approximation along with the existence of the approximately valid Raoult's Law we shall try to prove that the distribution ratio for a compound as defined by the concentrations in the two phases can be approximately constant even if the activity coefficients are not constant in the separately considered

phases. In case we succeed in proving the above statement we have already proved that the behaviour of the solute as required by the classical Henry's Law is not a necessary condition for the constancy of  $K_x$ . In other words we give a new interpretation of the Henry domain according to which *it is the constancy of the distribution ratio of the solute as given by the concentration data that characterizes the Henry domain.*

For proof let us examine a system composed of two non-miscible solvents and a solute distributed between them. Considering the thermodynamical condition of an equilibrium it is certain that the ratio of equilibrium activities of the solute in the phases (designated by ' and '') is constant and independent of the concentrations.

$$K_a = \frac{a'}{a''} = \frac{\gamma' x'}{\gamma'' x''} = K_\gamma \cdot K_x = \text{const.} \quad (7)$$

In the following we are going to prove that  $K_\gamma$  is approximately constant and we do not need the assumption that  $\gamma$  is constant. For that purpose we have to know the concentration dependence of the activity coefficients ( $\gamma'$ ,  $\gamma''$ ) for the solute in both phases which is given in a general form by the interpretation of the finite small quantity  $\delta$  defined in (6).

A number of generally valid statements can be made about the finite small  $\delta$ :

1. We have no reason to assume that  $\delta$  is independent of the concentration of the solute ( $x_1$ ).
2. The form of  $\delta(x_1)$  cannot be given exactly but similarly to any function it can be approximated by a series expansion to any degree of accuracy.

Let that series be chosen as  $\delta = A + Bx_1 + Cx_1^2 + \dots +$  where  $A$ ,  $B$  and  $C$  are constants. Using this form the concentration dependence of the activity coefficient of the solute is given by

$$\frac{d \ln \gamma_1}{d \ln x_1} = A + B x_1 + C x_1^2 + \dots \quad (8)$$

Since at  $x_1 = 0$  the ratio:

$$\frac{d \ln \gamma_1}{d \ln x_1} = 0$$

we obtain as the limiting condition:  $A = 0$ .

Taking further into account that for dilute solutions  $x_1$  has very small values, the second and higher order members of the series can be neglected:

$$\frac{d \ln \gamma_1}{d \ln x_1} = B x_1$$

Integrating the above expression over the interval:  $x_1$  and 0 the result is:

$$\ln \frac{\gamma_1}{\gamma_0} = Bx_1 \quad (9)$$

that is  $\gamma_1 = \gamma_0 e^{Bx_1}$  where  $\gamma_0$ , the activity coefficient of the solute at  $x_1 = 0$ , is therefore constant.

About the coefficient  $B$  it can only be stated that it is constant. In some actual problems  $B$  can be correlated with certain physical quantities.

For example in regular mixtures the form of the function whereby the activity coefficient of the solute is related to the mole fraction is known:

$$\gamma_1 = e^{q(1-x_1)^2}$$

or in another form:

$$\ln \gamma_1 = q(1 - x_1)^2$$

Differentiating that expression with respect to  $x_1$ :

$$\frac{d \ln \gamma_1}{d \ln x_1} = 2q(1 - x_1) \cdot x_1 \quad (10)$$

As  $x_1$  is rather small  $1 - x_1$  is approximately a unity so it follows that

$$\frac{d \ln \gamma_1}{d \ln x_1} = -2q x_1$$

On comparing the above formula with (9) it is concluded that  $B = -2q$ ; i.e. for regular solutions the value of  $B$  can be numerically given provided the interaction coefficient is known.

Returning to expression (7)  $K\gamma$  can be formulated as:

$$K = \frac{\gamma'_0 e^{B'x'}}{\gamma''_0 e^{B''x''}} \quad (11)$$

Expanding the exponentials in the numerator and denominator into series and neglecting second and higher order members we get:

$$K = \frac{\gamma'_0}{\gamma''_0} \frac{1 + B' x'}{1 + B'' x''} \quad (12)$$

It has to be emphasized that the problem is that of a very dilute solution. Using data in the denominator of (12) relating to the phase less concentrated

for the solute it is possible to rewrite the expression of  $K\gamma$  using the approximation:

$$\frac{1}{1 + B'' x''} = 1 - B'' x''$$

i.e.

$$K_\gamma = \frac{\gamma'_0}{\gamma''_0} (1 + B' x') (1 - B'' x'') = \frac{\gamma'_0}{\gamma''_0} (1 + B' x' - B'' x'') \quad (13)$$

In deducting (13) the member  $B'' B' x'' x'$  being small in the second order has been omitted.

Considering the form of (13) it is evident that only if  $B' x' - B'' x''$  is negligibly smaller than unity can  $K\gamma$  be a constant.

Let us examine whether there are such cases. Assuming a solute that forms solutions in both solvents with positive deviations with respect to the ideal case it follows that:

$$\frac{d \ln \gamma'}{d \ln x'} = B' x' < 0 \quad \frac{d \ln \gamma''}{d \ln x''} = B'' x'' < 0$$

as for  $x_1 = 0$  the value of  $\gamma$  is always greater than unity and decreases with increasing  $x_1$ .

This situation can only be achieved if both  $B'$  and  $B''$  are negative quantities from which it follows that in case of positive deviation for both solvents  $B' x'$  and  $B'' x''$  have indeed to be subtracted from each other. If the mole fraction increases in both phases both  $Bx$  type quantities increase simultaneously, however, if  $B'/B''$  is approximately equal to  $x''/x'$  the difference  $B' x' - B'' x''$  can be neglected when compared to unity in the whole interval of the dilute solution. The consequence is that for equilibria between two solutions of a solute behaving as mixtures of positive deviation both  $K\gamma$  and  $Kx$  can be constants even for  $\gamma \neq \text{const}$ . The parallel case for two solutions of negative deviation cannot be assumed since negative deviation results from mixing compounds of similar character and this condition would require great similarity between the two solvents. In such cases, however, there would be a mixing between the two phases which is no longer the case for distribution equilibria.

Let us analyze the correlation between the dependence of the distribution ratio and activity coefficient in a definite example on the concentration. (A distribution equilibrium will be examined between two solutions in which the mole fraction of the solute is 0.01 and 0.001 resp.) These concentration data correspond to molarity 0.5 and 0.05 for aqueous solutions provided the more concentrated or less concentrated solution, resp. is the aqueous one.

(Using cyclohexane as solvent the corresponding molarity figures are: 0.1 and 0.01, resp.) Take  $B$  for the more concentrated solution as  $-1$ . (More precisely let us choose the molar ratio for the more concentrated solution in such a way that for  $K_x = 10$ ,  $Bx'' = -0.01$ .) As the next step calculate the percentage variation of the distribution ratio;  $K_x$  with respect to the infinitely dilute solution for the case when the concentration in the more concentrated solution will increase tenfold. Using the data of the present example this means that according to equ. (12) for infinitely dilute solutions the activity coefficient of the solution denoted by  $\gamma''$  decreases from  $\gamma''_0$  to  $0.9\gamma''_0$  i.e. it changes by 10%. The results of this calculation are tabulated in Table I.

Table I

$B'/B''$	$K_x(B''x'' = 0)$	$K_x(B''x'' = -0.1)$	$100 \frac{\Delta K_x}{K_{x^0}}$
20	10.10	8.88	12.1
15	10.05	9.38	6.7
11	10.01	9.88	1.3
10	10.00	10.00	0.0
9	9.99	10.11	1.2
6	9.96	10.43	4.7
3	9.93	10.72	8.0
1	9.91	10.91	10.1

Let us now choose a more concentrated solution that deviates negatively from the ideal case. For the value previously used  $K_x = 10$  let  $B''x'' = 0.01$ . Results of this calculation are summarized in Table II.

Table II

$B'/B''$	$K_{x^0}$	$K_x(B''x'' = 0.1)$	$100 \frac{\Delta K_x}{K_{x^0}}$
1	10.09	9.27	8.1
0.5	10.095	9.22	8.7
-1	10.11	9.09	10.1
-5	10.15	8.70	14.3
-10	10.20	8.14	20.2

The data tabulated show that for double positive deviation the approximate equality  $B'/B'' \approx K_x$  results in a negligible change in  $K_x$  with changing  $\gamma''$  in the dilute solution concentration range. This means that the validity of

Henry's Law can be extended over and above the range characterized by a constant activity coefficient.

This assumption is not a special one but is very plausible. The greater the deviation from ideality the bigger negative value  $B$  interaction coefficient will have. A decrease in solubility will, however, accompany such conditions. Therefore it can be expected that in cases when the solute is less soluble in one of the solvents then the constant  $B$  will have greater absolute value in the latter. Doubly positive  $B$  can occur in physically realizable circumstances for gas absorption phenomena when the gas forms negatively deviating mixtures with the solvent and the temperature is above the Boyle point for the gas in question. For gas absorption the distribution ratio is usually expressed as a function of molarity and the Henry—Dalton Law itself is formulated for such an absorption coefficient. Expressing  $B$  as a function of  $c$  it has the following typical values at the boiling point of normal liquids:  $B \approx -1.2$ , at critical gas temperatures:  $B \approx -0.25$  (at room temperature), at reduced temperature  $\vartheta \approx 2.5$ ,  $B \approx 0$  and it has positive values at higher temperatures. If, therefore, below the Boyle point temperatures  $B(c)l \approx LB(c)_g$  (where  $l$  refers to the solvent and  $L$  is the Henry—Dalton absorption coefficient) the absorption coefficient can be approximately constant even in such concentration intervals where the activity coefficient of the gas dissolved is not constant. This is equivalent to the original interpretation of Henry's Law.

For mixtures of negative deviation there is no physical sense in putting  $B'/B'' > 1$ . It is only for gas absorption that the distribution equilibrium can be interpreted. The  $B(c)$  constant of the gas is positive only above the Boyle point and its maximal value for  $P_k \approx 50$  atm ( $\vartheta = 5$ ) is 0.25. When, therefore, the gas is in the "more dilute" phase  $B(c)$  cannot be greater than 0.25.

When the "more concentrated" phase is the gas the numerator of  $K\gamma$  will be given by the activity coefficient of the solute. In case of negative deviation  $B'/B''$  can, in principle, be any great number ( $B'$  now refers to the solute and  $B''$  to the gas). If the molecular weight of the solvent is about 80 and its density is about 0.8 (e.g. hexane)  $c \approx 10x$  in dilute solution.

For ideal solubility  $x = 1/p^0$  so  $c \approx 10/p^0$ . For room temperature and pressure of 1 atm,  $c_g \approx 1/25$ . Using these data  $K_c \approx p^0/250$ . In the case of  $\vartheta = 5$  the order of magnitude of  $p$  is 1000 atm (this is an extrapolated value) so the value of  $K_c$  is only about 4. For mixtures of negative deviation  $K_c$  can only be smaller, so  $K_c$  the reciprocal of the absorption coefficient can never reach 10.

When  $\mu_0$  is defined as independent of pressure — as remarked in the introduction — the activity coefficient of the pure solvent is not unity but:

$$\exp \left[ \frac{V_2^0}{RT} (p_2^0 - 1) \right],$$

so it can only be unity at the normal boiling point of the solvent. Since this is a constant temperature we need not alter our lines of reasoning. Attention should be paid to the fact, however, that the activity coefficient is a function of not only the composition but of the pressure as well. (Its variation is parallel to that of the pressure.) The effect due to the variations of pressure can, however, be neglected in comparison to the effect of composition because the factor  $V/RT$  is small and the form of the function is exponential.

### Summary

It has been pointed out on the basis of the Duhem—Margules equation that for cases where Raoult's Law is only approximately valid for the solvent the activity coefficient of the solute cannot be regarded as constant even in approximation.

When, however, for mixtures of positive deviation from the ideal behaviour the constants  $B$  characterizing the deviation are in such a ratio, that is, approximately equal to the reciprocal of the distribution ratio for the two mixtures in equilibrium then the validity of Henry's Law can be extended. On the ground of the nearly constant nature of the distribution ratio this extension can be effected over a broader concentration range than that of the constant activity coefficient. Henry's Law can be similarly interpreted in some cases for gas absorptions leading to positively deviating solutions.

### References

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