A Restriction Implicit in the Theory of Conformal Solutions

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Özet: «Conformal» çözeltiler teorisine göre, polar olmayan ve molekül-leri küresel simetriyi haiz bulunan saf sıvıların aynı temperatür ve basınçta-ki birim hacım başına buharlaşma enerjilerinin genleşme katsayılarına oranla-rının aynı değerde olması gerekmektedir· Hakikatte ise, bunun nadiren ger-çekleştiği müşahede edildiğinden bu teorinin reel çözeltilere tatbik kabiliye-tinin pek mahdut olacağı anlaşılmaktadır.

Extending the assumptions on interaction potential energies of molecules, introduced by Pitzer[1] to account for the law of corresponding states in pure fluids, to the interactions between unlike molecules, Longuet-Higgins[2] has correlated the excess free energies of mixing of liquid and gaseous multicomponent mixtures of spherically symmetrical non-polar molecules to the molar fractions, configurational energy of one of the pure components and one adjustable parameter for each pair of species. This theory which is called the theory of "conformal solutions", has been verified by experimental results fairly well in some cases[2], [3], [4].

The non-ideal Gibbs free energy ΔG, non-ideal entropy ΔS, heat ΔH and volume change ΔV of mixing per mole of a liquid conformal mixture at constant temperature T and pressure P are related by the equations

$$\frac{\Delta G}{Q_0 - RT} = \frac{\Delta S}{R - \dfrac{dQ_0}{dT}} = \frac{\Delta H}{Q_0 - T\dfrac{dQ_0}{dT}} = \frac{\Delta V}{V_0(T\alpha_0 - P\beta_0)}$$

$$= -\sum_{r<s}\sum x_r x_s d_{rs} \qquad (1),$$

where Q_0, V_0, α_0 and β_0 are the molar latent heat of vaporiza-tion, molar volume, coefficient of thermal expansion and iso-

thermal compressibility of the reference liquid at T, P, which
can be taken as any one of the pure components. x_r and x_s are
the molar fractions of components r and s in the mixture. d_{rs}
is the interaction parameter which depends only on the chemi-
cal nature of species r and s and the reference species.

Taking first a component r then a component s as the refe-
rence component, from eqns. (1) we obtain following three
equations.

$$\frac{Q_r - RT}{Q_s - RT} = \frac{R - \dfrac{dQ_r}{dT}}{R - \dfrac{dQ_s}{dT}} = \frac{Q_r - T\dfrac{dQ_r}{dT}}{Q_s - T\dfrac{dQ_s}{dT}} = \frac{V_r(T\alpha_r - P\beta_r)}{V_s(T\alpha_s - P\beta_s)} \cdots (2)$$

However, the first two equations in (2) are not independent of
each other. Omitting, for instance, the second equation, we have

$$\frac{Q_r - RT}{Q_s - RT} = \frac{R - \dfrac{dQ_r}{dQ}}{R - \dfrac{dQ_s}{dT}} = \frac{V_r(T\alpha_r - P\beta_r)}{V_s(T\alpha_s - P\beta_s)} \quad \cdots \cdots (3).$$

If pure liquids 1, 2,$\cdots$, etc. are to form a conformal solution,
then all the pairs of liquids r, s must   satisfy the eqns. (3) at
any temperature and pressure. The success of the theory should
depend primarily on these restrictive conditions. Therefore, it is
interesting to see how far these conditions are satisfied by non-
polar liquids.

One of these conditions, i. e.

$$\frac{Q_r - RT}{Q_s - RT} = \frac{V_r(T\alpha_r - P\beta_r)}{V_s(T\alpha_s - P\beta_s)} \quad \cdots \cdots \cdots (4),$$

lends itself to direct testing. At moderate pressures and not
too low temperatures, $P\beta$ terms are quite negligible   compared
to $T\alpha$ terms. Hence, eqn. (4) can be put into the following form,

$$\frac{Q_r - RT}{V_r \alpha_r} = \frac{Q_s - RT}{V_s \alpha_s} \quad \cdots \cdots \cdots \cdots (5),$$

which means that all the pure components of a liquid confor-
mal solution should have identical $(Q - RT)/V\alpha = K$ values.

In Table 1 we tabulate the values of this ratio at 25°C and
1 at., for certain non-polar liquids calculated from the data given
in the literature[5], [6], [7]. It will be seen that the ratio K varies

Table 1

Substance	K, at 25°C, 1 at. KCal. deg. cc.$^{-1}$	Substance	K, at 25°C, 1 at KCal. deg. cc.$^{-1}$
Tetrachloro ethylene	93	Carbon tetrachloride	61
Carbon disulphide	84	Cyclohexane	56
m-Xylene	75	n-Octane	48
Toluene	74	n-Heptane	44
Ethyl benzene	74	Silicon tetrachloride	40
Cumene	73	n-Hexane	39
Benzene	69	n-Pentane	30
Stannic chloride	64	iso-Pentane	28

greatly. Only very similar compounds, such as substituted benzenes and stannic and carbon tetrachlorides, form groups of almost identical K values. Although Table 1 contains some liquids of non-spherical molecules, such as normal paraffin hydrocarbons, it is not possible to attribute the large differences observed in this table to the absence of spherical symmetry in the molecules concerned, since, as it will be seen, the smaller the chain length of these hydrocarbons the more is the deviation from perfectly spherical molecules such as stannic and carbon tetrachlorides, and silicon tetrachloride differs significantly from the latter compounds. Unexpectedly, silicon tetrachloride and n-hexane have almost identical K values.

The condition that the K values of pure liquids should be the same for their mixtures to be conformal is also shown in Table 2.

Table 2

Component 1 (ref. species)	Component 2	$-d_{12}(\Delta V)$	$-d_{12}(\Delta H)$	$|d_{12}(\Delta V)-d_{12}(\Delta H)|$	$|K_2-K_1|$
CCl$_4$	Cyclohexane	0.009	0.013	0.004	5
Benzene	CCl$_4$	0.002	0.010	0.008	8
Benzene	Cyclohexane	0.077	0.066	0.011	13
Benzene	Toluene	0.020	0.007	0.013	5
CS$_2$	CCl$_4$	0.058	0.034	0.024	23
CS$_2$	Toluene	0.071	0.042	0.029	10
Benzene	CS$_2$	0.080	0.048	0.032	15

The third and fourth columns of this table contain the interaction constants of certain non-polar binary mixtures calculated

by Longuet-Higgins[2] by eqns. (1) from experimental ΔV and ΔH data, respectively. The differences between these two inte-raction constants, which characterize the deviations of the mix-tures concerned from the theory, are tabulated in the fifth co-lumn. In the sixth column we tabulated the difference between the K values of pure components taken from Table 1 for each system. It will be observed that (i) where the agreement bet-ween the theory and experiment appears to be good, as in the case of CCl_4 - cyclohexane, the difference $| K_2 - K_1 |$ is small, (ii) where the difference $| K_2 - K_1 |$ is large, the deviation from the theory is also large as in the case of $CS_2 - CCl_4$ and benzene - CS_2, and that (iii) there are cases where this devia-tion is appreciable in spite of a small $| K_2 - K_1 |$ such as in benzene - toluene. It follows, therefore, that the condition re-presented by eqn. (5) is a necessary but not a sufficient condi-tion for "conformality". This is expected since eqn. (5) is a relationship between the properties of pure components. It con-tains only the assumptions concerning the interactions between the molecules of the same species.

It appears, therefore, that even the requirements for inter-actions between similar molecules inherent in the theory of con-formal solutions limit the applicability of the theory to actual systems seriously.

Bibliography

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