

# APPLICATION OF THE 'QUASI-CRYSTALLINE' MODEL FOR PREDICTING THE VAPOUR-LIQUID EQUILIBRIUM OF SOME BINARY MIXTURES BY USING THEIR BOILING POINTS

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## ABSTRACT

It is shown that the boiling points of the systems (1) Carbon tetrachloride/Toluene, (2) Carbon tetrachloride/Carbon disulphide, (3) Benzene/Ethylene dichloride, (4) Benzene/Carbon disulphide, (5) Benzene/Chloroform, (6) Chloroform/Carbon tetrachloride, and (7) Cyclohexane/Carbon tetrachloride are in very good agreement with the quasi-crystalline model proposed by Guggenheim (1952).

The possibility of using this model for the prediction of the vapour-liquid equilibrium data for the above systems has been discussed.

## INTRODUCTION

It is well known that the vapour-liquid equilibrium data can be evaluated from a knowledge of the activity coefficients. Guggenheim (1952) has shown that the activity coefficients of regular binary mixtures can be evaluated from the Quasi-Crystalline model. According to this model the partial vapour pressures  $p_A$  and  $p_B$  of a regular binary mixture of two components  $A$  and  $B$  respectively are given by

$$\left. \begin{aligned} p_A &= p_A^\circ x e^{\frac{w}{RT} (1-x)^2} ; p_B = p_B^\circ (1-x) e^{\frac{w}{RT} x^2} \\ \gamma_A &= e^{\frac{w}{RT} (1-x)^2} ; \gamma_B = e^{\frac{w}{RT} x^2} \end{aligned} \right\} \dots \dots (1)$$

where  $\gamma_A$  and  $\gamma_B$  are the activity coefficients of components  $A$  and  $B$ ,  $x$  is the mole fraction of the component  $A$  in the mixture, and  $w$  is the measure of interaction energy of the unlike molecules. It is obvious from the above relation (1) that for ideal solution where there is no interaction, partial pressures are linear functions of  $x$ . As a very good example of an ideal system one can cite the case of Benzene/Toluene for which the partial pressures are directly proportional to their concentration at all temperatures. For other pairs of molecules however, the partial pressures deviate from linearity. The magnitude of the deviations are given by the multiplying factor  $e^{\frac{w}{RT} (1-x)^2}$  and  $e^{\frac{w}{RT} x^2}$  (i.e. the activity coefficients). For any pair of molecules the activity coefficient decreases rapidly with increase in temperature and hence at higher temperatures, the deviation decreases rapidly and the partial vapour pressures then approach those of ideal solutions. The sign and magnitude of the deviations at any temperature, however, depend upon the magnitude and the sign of the interaction constant  $w$ . For  $w$  positive the deviations are positive and the observed partial pressures are larger than the corresponding linear values (i.e. ideal partial pressures). Examples of this type are Cyclohexane/

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Carbon tetrachloride, Carbon tetrachloride/Carbon disulphide, Ethylene dichloride/Benzene, Benzene/Carbon disulphide and Carbon tetrachloride/Chloroform. On the other hand if  $w$  is negative the observed vapour pressures are smaller than the ideal values. Examples of this type are binary mixtures of Chloroform/Acetone (Guggenheim), Carbon tetrachloride/Toluene, and Benzene/Chloroform. Heats of mixing are positive with the former and negative in the latter case.

The activity coefficients can be determined from the corresponding vapour pressure data. Guggenheim (1952) has analysed the partial vapour pressure data of Scatchard *et al.* (1939, 1940) for two systems, viz. Benzene/Carbon tetrachloride and Cyclohexane/Carbon tetrachloride, at different temperatures and has shown that the partial vapour pressures over the whole range of concentration and temperature are very well represented by (with an accuracy of one in 5,000) a temperature dependent  $w$ ,

$$w = 71.8 \text{ cal. mole}^{-1} \text{ (at } 70^\circ\text{C.)}; \quad dw/dt = -0.15 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

for the first and

$$w = 56.3 \text{ cal. mole}^{-1} \text{ (at } 70^\circ\text{C.)}; \quad dw/dt = -0.23 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

for the second system. Thus for predicting the  $V-L$  equilibrium of binary mixtures which can be treated from the Quasi-Crystalline model, an accurate value of  $w$  and its temperature variation  $dw/dt$  is necessary. This can normally be obtained if the variations of the partial pressures with concentration are determined at various temperatures. Due to the elaborate experimental technique necessary for obtaining vapour pressure data suitable for comparison with this model and the determination of  $w$  and  $dw/dt$ , this data is available up to this time only for the above two systems.

Recently measurements on the variation of heats of mixing of the above systems with concentration have been made at different temperatures by Adcock and McGlashan (1954), Cheesman and Whitaker (1952) and others. Their results have been in very good agreement with the Quasi-Crystalline model relation, viz.

$$\left. \begin{aligned} \Delta_m H &= x(1-x)NU \\ U &= w - T \frac{dw}{dt} \end{aligned} \right\} \dots \dots \dots (2)$$

where

We have been exploring the possibility of using the boiling points of binary mixtures for comparison with the theory and hence for the prediction of the  $V-L$  equilibrium data for such mixtures. In an earlier paper (Katti, 1955) we have shown that the observed boiling points\* for Benzene/Carbon tetrachloride systems are in excellent agreement with the relation

$$760 = p_A^\circ x e^{\frac{w}{RT} (1-x)^2} + p_B^\circ (1-x) e^{\frac{w}{RT} x^2} \dots \dots \dots (3)$$

where  $p_A^\circ$  and  $p_B^\circ$  are given by the relation

$$\log_{10} p = -\frac{0.05223}{T} \alpha + \beta \dagger \dots \dots \dots (3a)$$

\* Observed Boiling Points quoted in this paper have been taken from Ju Chin Chu (1950) and Vapour pressure data from International Critical Tables (1938).

† This formula has been used for all liquids except for Carbon disulphide for which the pressures (in atmospheres) are given by the relation

$$\log_{10} p = (A + 2B + 3C) - \frac{T}{T_B} (A + B + C) - \frac{T_B}{T} (B + 3C) - C \left( \frac{T_B}{T} \right)^2$$

where  $T_B$  is the boiling point in  $^\circ\text{K}$  and  $A, B, C$  are constants.

and  $T$  is the boiling point of the mixture. Young's (1938) values of  $\alpha$  and  $\beta$ , and Scatchard's values of  $w$  and  $\frac{dw}{dt}$  had been used.

*Determination of  $T$  ideal and  $T$  calculated from relation (3):*

As  $T$  in relation (3) occurs both in the vapour pressures of the pure components  $p_A^\circ$  and  $p_B^\circ$  as well as in the activity coefficients  $e^{\frac{w}{RT}(1-x)^2}$  and  $e^{\frac{w}{RT}x^2}$ , it is not possible to express  $T$  as a simple function of the parameters  $x$  and  $w$ . Therefore the following steps were adopted to evaluate the value of  $T$  that satisfies relation (3) for a given value of  $x$ . The partial pressures

$$p_A = p_A^\circ x e^{\frac{w}{RT}(1-x)^2}; \quad p_B = p_B^\circ (1-x) e^{\frac{w}{RT}x^2}$$

were calculated for a given value of  $x$  (between  $x = 0$  and  $x = 1$ ) at various temperatures lying between the boiling points of the two pure components by using relation (3a), and known values of  $w$  at those temperatures. The total pressures ( $p_t = p_A + p_B$ ) were then plotted against the corresponding temperatures and from the graph the boiling points for the concentration (i.e. the temperature corresponding to  $p_t = 760^{\text{mm}}$ ) were read off. This procedure was adopted for values of  $x$  from zero to one at small intervals of 0.1.

For calculating  $T$  ideal values,  $w$  was put equal to zero in the above relations for partial pressures  $p_A$  and  $p_B$ .

The correctness of the boiling points thus obtained was checked by calculating the pressure  $p_t$  from the relation (3) using the value of  $T$  in  $p_A^\circ$ ,  $p_B^\circ$  and the activity coefficient to verify that

$$p_t = 760^{\text{mm}}.$$

Relation (3) could not be verified for the other system (Carbon tetrachloride/Cyclohexane) although  $w$  and  $dw/dt$  are available, as the experimental boiling points for this system are not readily available. This made it necessary to determine the boiling points in the laboratory.

#### *Experimental Determination of the boiling points of Carbon tetrachloride and Cyclohexane mixtures:*

The apparatus (Fig. 1) is in principle similar to that recommended for measuring the elevation of boiling points of solutions by using a Beckman Thermometer. The three-necked container  $D$  has a capacity of about 50 c.c. A thermometer reading up to 0.1°C. is introduced just above the liquid surface through the neck  $A$ . At  $B$  there is a ground joint to fit the spiral condenser for the vapours to condense and fall back into the liquid again. Through  $C$  a syringe is introduced into the liquid. The vessel containing the liquid is held in a glycerine bath, the temperature of which was adjusted to be just above the boiling point of the solution by controlling the current in the electric heater. The boiling points which can be determined to an accuracy of 0.1°C. were noted after the steady state persisted for an hour. The exact composition of the liquid mixture was then determined by drawing a few c.c. of the liquid in the steady state through the syringe and measuring its refractive index on an Abbey Refractometer. The apparatus was first tested for the boiling points of mixture of Benzene/Toluene and Carbon tetrachloride/Chloroform.

Merck's analar Cyclohexane and Carbon tetrachloride from freshly opened bottles were dried for a day over Calcium Chloride and used for the boiling points

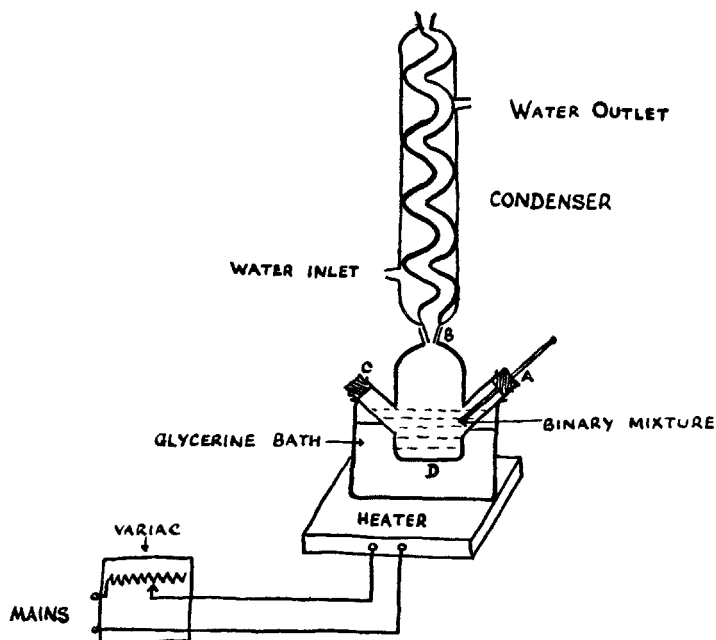


Fig. 1. Experimental Arrangement for the Determination of the Boiling Points

measurement without further purification as the refractive indices and the boiling points of the pure liquids agreed closely with the standard values.

It can be noticed from Table 1 that the observed boiling points are in good agreement with those calculated from the Quasi-Crystalline model.

TABLE 1

Cyclohexane (1) and Carbon tetrachloride (2)

$\alpha_1 = 30175$ ;  $\alpha_2 = 32229$ ;  $w = 58.6 \text{ cal. mole}^{-1} (70^\circ\text{C.})$   
 $\beta_1 = 7.3279$ ;  $\beta_2 = 7.6944$ ;  $dw/dt = -0.23 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$   
 Pressure = 749.50 mm.

$X_1$ (mole fraction of component 1)	$T$ ideal	$T$ calculated	$T$ observed
0.00	76.70	76.70	76.70
0.20	77.08	76.71	76.70
0.30	77.51	76.90	77.00
0.40	77.95	77.35	77.35
0.50	78.41	77.75	77.75
0.60	78.86	78.25	78.25
0.70	79.35	78.75	78.80
0.80	79.84	79.34	79.40
1.00	80.90	80.90	80.90

This showed that it is worth while extending these investigations to the determination of  $w$  and  $\frac{dw}{dt}$  for different pairs of molecules which will be useful for predicting the  $V$ - $L$  equilibria of these systems.

*Computation of Boiling Points from the Quasi-Crystalline Model:*

For this purpose we have adopted the following procedure: From equation (2) and (3) it can be easily shown that

$$(w_b)_{x=0.5} = 4RT_b \log_e \frac{1520}{(p_A^\circ + p_B^\circ)} \quad \dots \quad (4)$$

$$(\Delta_m H)_T^{x=0.5} = 0.25 \left( w_T - T \frac{dw}{dt} \right) \quad \dots \quad (5)$$

and

$$w_T = w_b + (T - T_b) \frac{dw}{dt} \quad \dots \quad (6)$$

where  $w_b$  is the value of  $w$  at  $T_b$ , the boiling point of an equimolecular mixture and  $(\Delta_m H)_T^{x=0.5}$  is the heat of mixing of an equimolecular mixture at temperature  $T$ .

For the given system  $w_b$  was determined from the relation (4) from observed values of  $T_b$  and the corresponding values of  $p_A^\circ$  and  $p_B^\circ$ , obtained from Young's data.  $w$  and  $\frac{dw}{dt}$  were then obtained by using (5) and (6) from the experimentally observed value of  $(\Delta_m H)_T^{x=0.5}$ . The variations of boiling points with concentration are then calculated with the observed changes in the boiling point over the whole range of concentration.

*Discussion of the Results:*

The following tables (2), (3), (4), (5), (6) and (7) show the results for the systems given below:

- (a) Carbon tetrachloride/Toluene.
- (b) Carbon tetrachloride/Carbon disulphide.
- (c) Benzene/Ethylene dichloride.
- (d) Benzene/Carbon disulphide.
- (e) Benzene/Chloroform.
- (f) Chloroform/Carbon tetrachloride.

The first column shows the mole concentration of one of the components, the second and third columns give the corresponding boiling points of the solution as given by the ideal solution theory and the Quasi-Crystalline model respectively.

The last column shows the observed boiling points. The values of  $w$  and  $\frac{dw}{dt}$  and the corresponding constants which are used for the computations of the boiling points in columns 2 and 3, are also shown in each table.

Comparison of the corresponding boiling points in columns 2, 3 and 4 in each table shows that there is a very close agreement between the observed boiling points and those calculated from the Quasi-Crystalline model over the whole range of investigations. It may be noted that the systems Cyclohexane/Carbon tetrachloride,

TABLE 2

Carbon tetrachloride (1) and Toluene (2)

$$\alpha_1 = 32229; \quad \alpha_2 = 35271; \quad w = -54.62 \text{ cal. mole}^{-1} (70^\circ\text{C.})$$

$$\beta_1 = 7.6944; \quad \beta_2 = 7.6807; \quad dw/dt = 0.565 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$X_1$ (mole fraction of component 1)	$T$ ideal in $^\circ\text{C.}$	$T$ calculated in $^\circ\text{C.}$	$T$ observed in $^\circ\text{C.}$
0.00	110.20	110.20	110.20
0.10	104.70	105.30	106.00
0.20	100.40	101.20	101.40
0.30	96.30	97.20	97.30
0.40	92.10	93.30	93.50
0.50	89.35	90.10	90.10
0.60	86.30	87.00	86.90
0.70	83.50	84.20	83.80
0.85	79.90	80.30	80.40
1.00	76.70	76.70	76.70

TABLE 3

Carbon tetrachloride (1) and Carbon disulphide (2)

$$\alpha_1 = 31477; \quad A = 4.525; \quad w = 174.353 \text{ cal. mole}^{-1} (70^\circ\text{C.})$$

$$\beta_1 = 7.5814; \quad B = 0.350; \quad dw/dt = -0.366 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$C = 0.480$$

$X_1$	$T$ ideal	$T$ calculated	$T$ observed
0.00	46.40	46.40	46.40
0.15	49.50	48.70	48.60
0.30	53.00	51.50	51.50
0.50	59.20	56.10	55.90
0.65	62.90	60.50	60.40
0.75	66.50	64.00	64.20
0.85	70.30	68.30	68.50
0.90	72.20	70.90	70.60
1.00	76.70	76.70	76.70

Carbon tetrachloride/Carbon disulphide, Ethylene dichloride/Benzene, Benzene/Carbon disulphide and Carbon tetrachloride/Chloroform show positive deviations in vapour pressures and negative deviations in boiling points give positive value of  $w$ , while Carbon tetrachloride/Toluene and Benzene/Chloroform show the opposite behaviour gives a negative value of  $w$ , the interaction constant.

The large deviations in the observed boiling points of Benzene/Chloroform and Benzene/Carbon disulphide systems, from those calculated from the theory, give large values for the interaction constant  $w$ . It may be noted that the corresponding heats of mixing for these systems is also very large. Even in these two systems the agreement with the Quasi-Crystalline model over the whole range is very close.

TABLE 4

Ethylene dichloride (1) and Benzene (2)

$$\alpha_1 = 32996; \quad \alpha_2 = 32295; \quad w = 20.484 \text{ cal. mole}^{-1} (70^\circ\text{C.})$$

$$\beta_1 = 7.7050; \quad \beta_2 = 7.6546; \quad dw/dt = -0.115 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$X_1$	$T$ ideal	$T$ calculated	$T$ observed
0.00	80.10	80.10	80.10
0.10	80.53	80.43	80.42
0.20	80.90	80.75	80.75
0.30	81.27	81.09	81.09
0.40	81.63	81.43	81.43
0.50	81.95	81.77	81.77
0.60	82.30	82.42	82.40
0.70	82.61	82.45	82.45
0.80	82.91	82.79	82.80
0.90	83.23	83.12	83.15
1.00	83.48	83.48	83.48

TABLE 5

Benzene (1) and Carbon disulphide (2)

$$\alpha_1 = 32295; \quad A = 4.525 \quad w = 627.679 \text{ cal. mole}^{-1} (70^\circ\text{C.})$$

$$\beta_1 = 7.6546; \quad B = 0.350 \quad dw/dt = 0.1856 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$C = 0.480$$

$X_1$	$T$ ideal	$T$ calculated	$T$ observed
0.00	45.75	45.75	45.75
0.20	50.80	47.90	47.60
0.30	53.50	49.00	48.70
0.50	59.30	51.70	51.30
0.60	62.70	53.40	52.90
0.70	66.20	56.00	55.30
0.80	70.50	60.00	59.50
0.90	75.00	66.90	65.70
1.00	79.55	79.55	79.55

It may also be noted that none of the systems rigorously satisfy Guggenheim's condition for strictly regular solution, viz.

(i) That both components should be non-polar and the molecules of the two components should be sufficiently alike.

(ii) That the interactions between the unlike molecules and hence the deviation from ideality must be very small.

In the tables the first four systems contain both non-polar molecules whereas the last two contain one polar and one non-polar molecule. In the recent investigations of the variation of heats of mixing with temperature in case of Carbon tetrachloride/Chloroform, McGlashan and others (1954) have shown that in spite of

TABLE 6

Benzene (1) and Chloroform (2)

$$\alpha_1 = 32295; \quad \alpha_2 = 32996; \quad w = -493.080 \text{ cal. mole}^{-1} (70^\circ\text{C.})$$

$$\beta_1 = 7.6546; \quad \beta_2 = 7.7050; \quad dw/dt = -0.276 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$X_1$	$T$ ideal	$T$ calculated	$T$ observed
0.00	61.40	61.40	61.40
0.20	64.10	68.90	68.90
0.34	66.35	71.90	71.90
0.46	68.40	74.00	74.00
0.56	70.30	75.30	75.30
0.64	71.85	76.40	76.40
0.71	73.25	77.30	77.40
0.74	74.80	78.20	78.20
0.78	76.50	79.00	79.00
0.85	78.20	79.80	79.80
1.00	78.20	78.20	78.20

TABLE 7

Carbon tetrachloride (1) and Chloroform (2)

$$\alpha_1 = 30193; \quad \alpha_2 = 31748; \quad w = 117.477 \text{ cal. mole}^{-1} (70^\circ\text{C.})$$

$$\beta_1 = 7.3896; \quad \beta_2 = 7.8425; \quad dw/dt = -0.298 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$X_1$	$T$ ideal	$T$ calculated	$T$ observed
0.00	61.20	61.20	61.20
0.20	63.55	63.10	63.00
0.40	66.25	65.00	65.00
0.50	67.65	66.60	66.30
0.60	69.15	68.00	67.70
0.70	70.90	69.50	69.30
0.80	72.75	71.50	71.30
0.90	74.65	73.50	73.80
1.00	76.80	76.80	76.80

the fact that Chloroform is a polar molecule, the mixture behaves as a regular solution. Moreover it is seen that Benzene interacts strongly with Chloroform and Carbon disulphide, the interactions being in the opposite direction. The present model is however inadequate to explain this peculiar behaviour of the Benzene molecule.

The usefulness of the above relation in readily computing the  $V-L$  equilibrium data from the above systems at various temperatures and concentration is obvious.

In Table 8 the binary systems for which the  $V-L$  equilibrium data can be evaluated from this model are shown. The second column gives the ready relation for calculating the activity coefficients of the different components obtained from the present investigation.  $T$  in the above relation is the absolute temperature and



$x$  is the mole fraction of the components for which  $\gamma$  the activity coefficient is required.

TABLE 8

Name of the system	$\log \gamma = (1-x)^2 \frac{w_T}{RT} = \frac{(1-x)^2}{T} \left\{ \frac{T}{R} \frac{dw}{dt} + \text{const.} \right\}$
Carbon tetrachloride/Toluene	$\frac{(1-x)^2}{T} \{-125.051 + 0.284T\}$
Carbon tetrachloride/Carbon disulphide	$\frac{(1-x)^2}{T} \{150.964 - 0.184T\}$
Benzene/Ethylene dichloride	$\frac{(1-x)^2}{T} \{30.168 - 0.058T\}$
Benzene/Carbon disulphide	$\frac{(1-x)^2}{T} \{283.926 + 0.093T\}$
Benzene/Chloroform	$\frac{(1-x)^2}{T} \{-200.559 - 0.139T\}$
Chloroform/Carbon tetrachloride	$\frac{(1-x)^2}{T} \{110.592 - 0.150T\}$
Cyclohexane/Carbon tetrachloride	$\frac{(1-x)^2}{T} \{69.212 - 0.116T\}$
Benzene/Carbon tetrachloride	$\frac{(1-x)^2}{T} \{62.044 - 0.076T\}$

Similar work on binary systems of a number of Hydrocarbons is in progress.

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