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Developed Correlations for Prediction of The Enthalpies of Saturated Vapor – Liquid Coexisting Phases

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Abstract

In this study a new criteria is adopted by the use of Rectilinear Diameter principle to express the saturated vapor and liquid enthalpies at the coexisting phases for pure substances and mixtures, this requires another relation that used to calculate enthalpies of vaporization at the corresponding temperatures.

The relationships between saturated vapor enthalpy, saturated liquid enthalpy and pressure are investigated for many pure substances. These investigations show that the saturated vapor and liquid enthalpies cannot be described by pressure as a simple general relation.

New simple correlations are developed for pure substances and mixtures. These correlations are based on the principle of Rectilinear Diameter depending on the law of corresponding states, where DH is introduced as a dimensionless term including the average reduced saturated enthalpies. The relations developed are:

For Pure Substances $DH = A + B\tau$

For Mixtures $DH_m = A_m + B_m\ \tau$

The constants A and B are correlated by the following relations:

$$A = \left(T_b/T_c\right) - B\left[1 - \left(T_b/T_c\right)\right]$$

$$A = 0.601206 - 0.412371\ B - 0.013378\ B^2$$

The second relation developed by fitting of literature values using Maximum Likelihood Principle for twenty pure substances out of thirty, and then applying them successfully to the remaining components, which indicates the generality of this correlation. These correlations can be applied successfully up to the critical region.

To use this method it requires the values of critical temperature and normal boiling point temperature, and any suitable correlation used to calculate enthalpies of vaporization.

The present new method of calculation of saturated enthalpies compares favorably with any equation of state, for example when using Lee – Kesler equation of state. The comparison shows that the accuracy of the proposed method is better than that of Lee and Kesler at the saturation region. This is in addition to the fact that the present correlations are straight forward, easier, and simpler as compared with that of Lee and Kesler method.

These correlations can be further developed to be used directly for design purpose of distillation operations, and other processes that involves vaporization, condensation phenomena.

Keywords: vapor-Liquid Equilibria, Saturated Enthalpy, Rectilinear Diameter principle

Introduction

Enthalpy is one of the most important thermodynamic properties of fluids, which can be explicitly defined for any system by the mathematical expression;

$$H = U + PV \qquad (1)$$

where U = internal energy, P = absolute pressure, V = volume. The units of all terms of this equation must be the same. Though enthalpy is often applied to a unit mass or to a mole, like volume and internal energy, enthalpy is an extensive property (i.e. depends on the quantity of the material involved); also it is a state function which is independent on the path followed.

Enthalpy is used as a thermodynamic property because the *U* + *PV* group appears frequently, particularly in problems involving a flow processes such as extraction, distillation, humidification, absorption, petroleum refinery processes, refrigeration cycles, power plants.

For pure fluids the equation used to calculate enthalpy is not satisfactory when applied at the saturated region; in addition to the fact that for mixtures, most of the equations used to estimate pure fluid saturated enthalpies can not be applied or if they applied the results is in an enormous deviation from the experimental data. Thus, in order to estimate the saturated vapor and liquid enthalpies for pure components and mixtures, it is essential to introduce a suitable correlations.

It is the aim of this work to develop these correlations for prediction of coexisting saturated vapor and saturated liquid enthalpies for pure components and mixtures. Employing the principle of rectilinear diameter based on the law of corresponding states which greatly facilitate the procedure for correlating the enthalpies of saturated vapor and saturated liquid at the coexisting phases for pure components and mixtures within the temperature, using the reduced parameters (reduced temperature, and reduced saturated enthalpies).

The correlations developed by this method can be used for the prediction of saturated enthalpies at the coexisting vapor and liquid phases for pure components and mixtures, together with any other correlation used for the estimation of the latent heat of vaporization, without direct reference to the nature of the vaporization process, the magnitude and type of the intermolecular forces, and the molecular structure.

It should be pointed out, that serious efforts have been made to get literature data for saturated vapor and saturated liquid enthalpies which are required in developing a generalized correlations for enthalpies of the saturated coexisting phases. Unfortunately, such data are limited in the literature, and are available only for a few components and mixtures.

Theory

Rectilinear Diameter Principle

Many years ago Cailletat and Mathias [1] observed that for pure fluid the arithmetic average of the densities of saturated vapor and saturated liquid is, to a close approximation, a linear function of the temperature; this observation is known as the law (principle) of rectilinear diameter.

Won and Prausnitz [2] reported their observation that an analogous relation appears to exist for some binary mixtures; when the arithmetic average of the molar densities of the saturated liquid and the equilibrium saturated vapor is plotted against pressure at a constant temperature, a nearly straight line is obtained. In a two phase region for a binary mixture the two saturated phases at equilibrium have different compositions, thus at a constant temperature,

$$D_{AV} = \frac{1}{2}\left|D_{sl}(x) + D_{sv}(x)\right| = A + B \cdot P \qquad 2$$

where *P* is the pressure, *A* and *B* are constants, D_{sl} and D_{sv} are the saturated liquid and vapor densities respectively, and *x* is mole fraction in the liquid phase. It follows that:

$$A = D_C - BP_C \qquad 3$$

where subscript *c* refers to the critical state. The accuracy of the critical density determined by means of *Rectilinear Diameter Principle* (*RDP*) has been seriously questioned owing to the relatively poor precision of the measured saturated densities close to the critical state.

The rectilinear behavior observed for the various saturated properties in the coexistence phases leads one to believe that the rectilinear diameter principle can be applied to other saturated properties (transport and thermodynamic) for pure compounds and mixtures [3].

Development of Correlations

In order to develop a correlation for certain thermodynamic property, one has to determine all the parameters that influence this property and then studies the influence of each of these parameters on the property under consideration, using literature data available for this purpose.

Saturated enthalpies of coexisting vapor and liquid phases are highly influenced by temperature, pressure, and volume. Thus, the first approach is to plot saturated enthalpies of coexisting vapor and liquid phases against saturated pressure and against saturated temperature. These procedures have been made for twenty three pure compounds.

Figure 1 shows a typical of these literature data of saturated enthalpies of coexisting vapor and liquid phases for ethane and propane (as non-polar hydrocarbons), and for freon-12 and ammonia (as polar compounds) against saturated temperature. Figure 2 shows the same property plotted against saturated pressure for the same two groups compounds.

Applying The Rectilinear Diameter Principle

The arithmetic average of saturated vapor and liquid enthalpies are plotted against saturated vapor temperatures and saturated pressures for twenty three pure components. Figures 3 and 4 show typical of these relations, namely ethane and propane (non-polar compounds), and ammonia and refrigerant-12 (polar compounds).

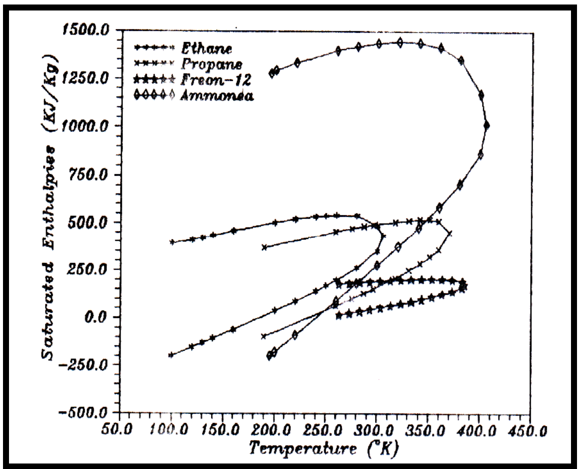

Figure (1) Typical relations between saturated enthalpy and temperature

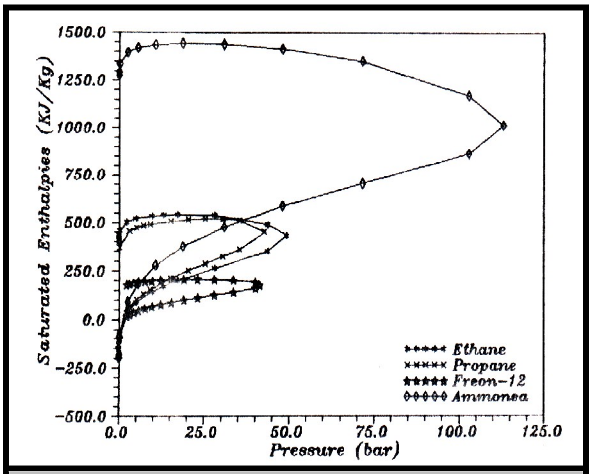

Figure (2) Typical relations between saturated enthalpy and pressure

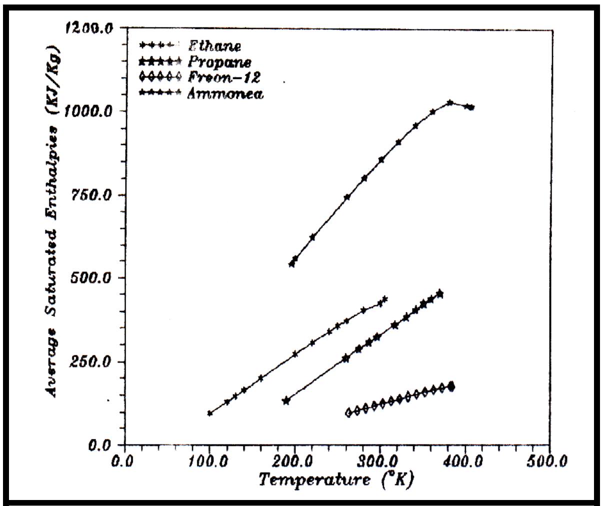

Figure (3) Typical relations between average saturated enthalpies and temperature

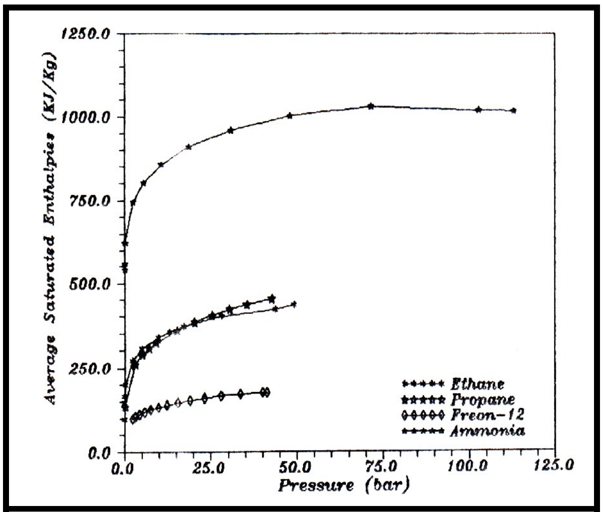

Figure (4) Typical relations between average saturated enthalpies and pressure

As seen from figures 3 and 4 that some of these relations are simple linear relations, this is especially true for enthalpy – temperature relations for many non-polar compounds.

Thus it seems more convenient to develop a simple generalized relations based on enthalpy – temperature relations rather than enthalpy – pressure relations.

Development of The Generalized Correlations of Rectilinear Diameter Principle

In order to develop generalized correlations of Rectilinear Diameter Principle based on the law of corresponding state conditions, the average saturated enthalpies will be replaced by reduced average saturated enthalpies and the temperature will be replaced by reduced temperatures.

Figure 5 represents the relations between average reduced saturated enthalpies and reduced temperatures for the four components (ethane, propane, ammonia and freon-12).

It is more convenient to plot reduced average saturated enthalpies against (1-T_r) rather than against T_r. This is because the reduced average saturated enthalpies at critical point can be obtained from the intercept point only.

Figure 6 represent the relations between average reduced saturated enthalpies and 1-T_r (which can be indicated as τ), for these four components (ethane, propane, ammonia and freon-12).

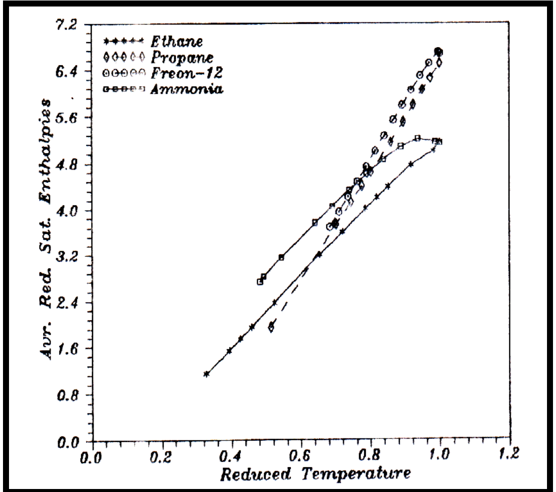

Figure (5) Typical relations between average reduced saturated enthalpies and reduced temperature

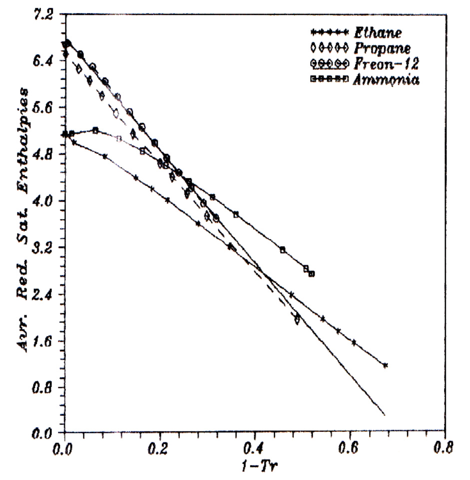

Figure (6) Typical relations between average reduced saturated enthalpies and 1-T_r

The fruitful result achieved, based on reduced rectilinear diameter principle, is the relation obtained between DH and τ. This relation is almost a linear relation for twenty three pure components, and can be represented by the following equations:

$$DH = A + B\tau \qquad (4)$$

$$DH = \frac{(H_{sv}+H_{sl})_T / 2RT_C}{(H_{sv}+H_{sl})_b / 2RT_b} = \frac{(H_{sv}+H_{sl})_T}{(H_{sv}+H_{sl})_b} T_{rb} \qquad (5)$$

$$\tau = 1 - \frac{T}{T_C} \qquad (6)$$

H_{sv}, H_{sl} = saturated vapor and liquid enthalpies respectively
R = gas constant.
T_c = critical temperature.
T_b = normal boiling point temperature.
T_{rb} = reduced temperature at the normal boiling point.
A and B are constants.

Figures 7 through 11 show the relation between DH and τ for twenty three pure components classified to the following groups of substances, as shown in table 1.

The reason for dividing the average reduced saturated enthalpies of coexisting vapor and liquid at any temperature by the same values at the normal boiling point temperature is to obtain a mathematical relation between constant A and constant B of eq.(4). When eq.(4) is applied at the normal boiling point temperature the following equations will result:

$$DH = \frac{(H_{sv}+H_{sl})_b}{(H_{sv}+H_{sl})_b} T_{rb} = A + B\tau \qquad (7)$$

$$T_{rb} = A + B(1 - T_{rb}) \qquad (8)$$

thus the following simple relation is obtained:

$$A = T_{rb} - B(1 - T_{rb}) \qquad (9)$$

Attempts have been made to relate the constant A and B of eq.(4) with the other parameter characteristics of pure components such as acentric factor ω, Z_c, P_c, T_c and V_c. No simple workable relation could be obtained.

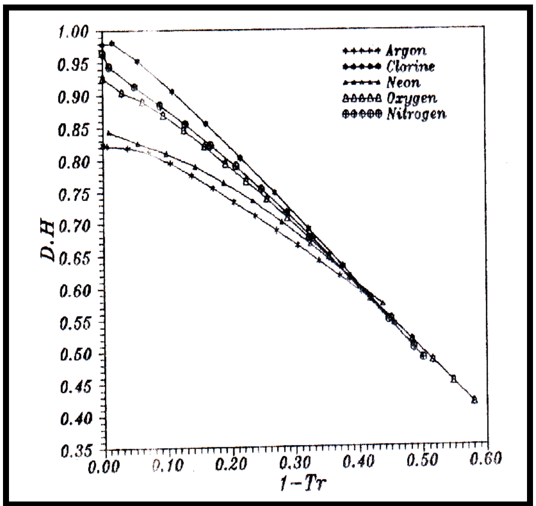

Figure (7) Relation between *D.H* and 1-T_r of group *A*

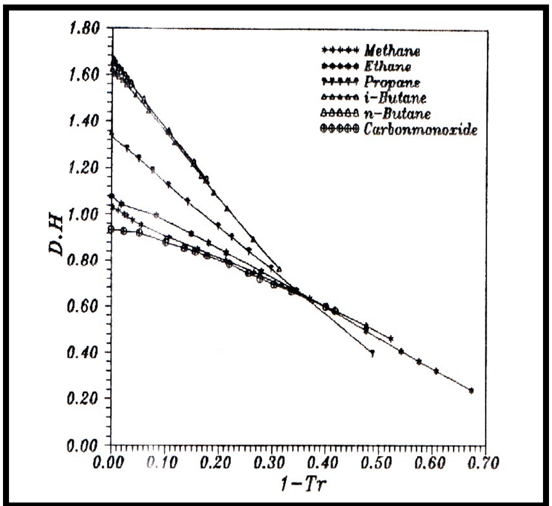

Figure (8) Relation between *D.H* and 1-T_r of group *B*

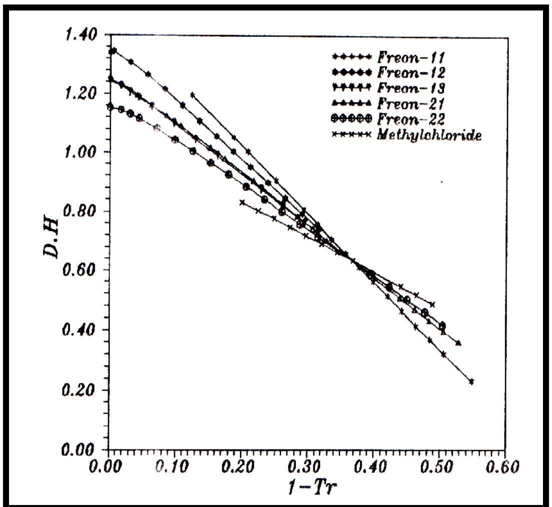

Figure (9) relation between *D.H* and 1-T_r of group *C*

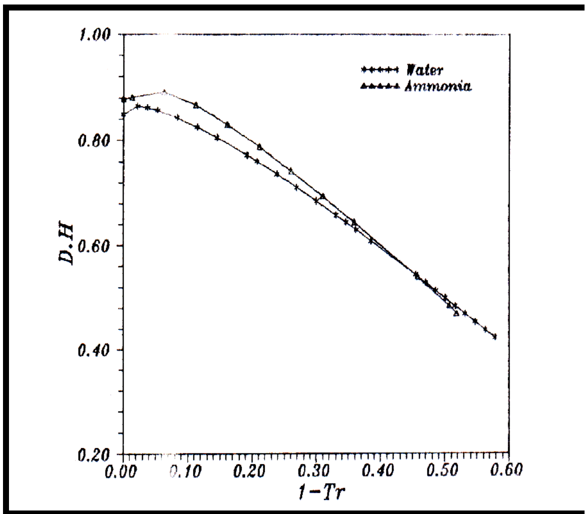

Figure (10) relation between *D.H* and 1-T_r of group *D*

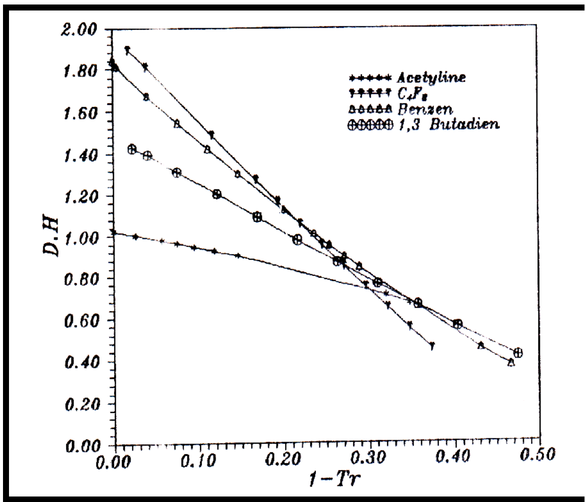

Figure (11) Relation between *D.H* and 1-T_r of group *E*

Values of the constant *A* are plotted against the values of constant *B* for the twenty components used in this investigation including (methane, ethane, propane, n-butane, i-butane, nitrogen, oxygen, argon, chlorine, freon-11, freon-12, freon-13, freon-21, freon-22, methyl chloride, benzene, octaflouro cyclobutane, 1,3-butadiene, water and ammonia) [1-2, 4-6] as shown in figure 12

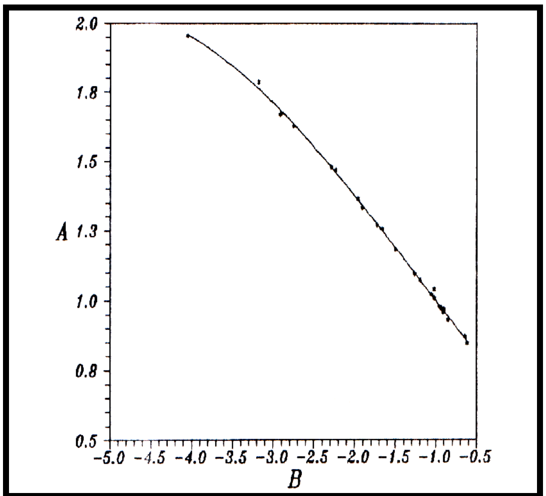

Figure (12) relation between the constants *A* and *B* which appears at eq.(4) for the pure compounds

The generalized mathematical relation between constant *A* and constant *B* can be represented by the following equation:

$$A = 0.601206 - 0.412371B - 0.0133827B^2 \qquad (10)$$

Each of the eq.(9) and eq.(10) represents the relation between the constant *A* and constant *B*, from the two equations, it can be recognized that *A* and *B* constants are independent of temperature. Solving these two equations simultaneously for twenty three pure components to obtain the values of *A* and *B* for each component.

Table (1) Groups of substances

Group A	Group B	Group C	Group D	Group E
Nitrogen	Methane	Freon-11	Water	Acetylene
Oxygen	Ethane	Freon-12	Ammonia	Benzene
Neon	Propane	Freon-13		1,3-Butadiene
Argon	i-Butane	Freon-21		Octaflouro Cyclobutane
Chlorine	n- Butane	Freon-22		
	Carbon Monoxide	Methyl Chlorine		

Extension of The Correlations to The Mixtures

The generalized correlations for pure compounds can be extended to involve also mixtures. Saturated enthalpies data are rarely available in the literature especially for the saturated coexisting vapor and liquid phases for mixtures. Experimental data for saturated coexisting enthalpies of mixtures have been taken from literature and sometimes it was necessary to interpolate or extrapolate mathematically those data.

The same procedure that is used for pure compounds has been also used for mixtures with the exception of using mixing rules to calculate thermodynamic properties of mixtures from the thermodynamic properties of pure components. Thus, the procedure is as follows:

$$DH_m = A_m + B_m \tau_m \qquad (11)$$

where

$$A_m = \sum_i Z_i A_i \qquad (12)$$

$$B_m = \sum_i Z_i B_i \qquad (13)$$

Z_i = mole percent of component *i* in the feed.

$$DH_m = \frac{(H_{svm}+H_{slm})_T}{(H_{svm}+H_{slm})_b} T_{rbm} \tag{14}$$

$$T_{rbm} = \frac{T_{cm}}{T_{bm}} \tag{15}$$

where

$(H_{svm}+H_{slm})_T$ = Addition of saturated vapor and liquid enthalpies at any temperature T of the mixture.

$(H_{svm}+H_{slm})_b$ = Addition of saturated vapor and liquid enthalpies at the normal boiling point temperature of the mixture.

$$T_{cm} = \sum_i \sum_j Z_i Z_j T_{cij} \tag{16}$$

$$T_{cij} = (T_{ci} T_{cj})^{0.5} \tag{17}$$

$$\omega_m = \sum_i \sum_j Z_i Z_j \omega_{ij} \tag{18}$$

$$\omega_{ij} = \sum_k Z_k \omega_k \tag{19}$$

$$\mathrm{Mt}_m = \sum_i \sum_j Z_i Z_j \mathrm{Mt}_{ij} \tag{20}$$

$$\mathrm{Mt}_{ij} = \sum_k Z_k \mathrm{Mt}_k \tag{21}$$

$$T_{bm} = \sum_i \sum_j Z_i Z_j T_{bij} \tag{22}$$

$$T_{bij} = (T_{bi} T_{bj})^{0.5} \tag{23}$$

$$\Delta H_{vbm} = \sum_i Z_i \Delta H_{vbi} \tag{24}$$

A and *B* constants are not functions of temperature as indicated before, so, they can be used at any temperature desired to calculate saturated coexisting vapor and liquid enthalpies. Thus, using the same procedure of calculations (*To use this method it requires the values of critical temperature and normal boiling point temperature, and any suitable correlation used to calculate enthalpies of vaporization*); figures 13 through 22 are prepared to show the relation between the enthalpies of saturated vapor and saturated liquid with temperatures for a typical pure components using the data from literatures and the developed method.

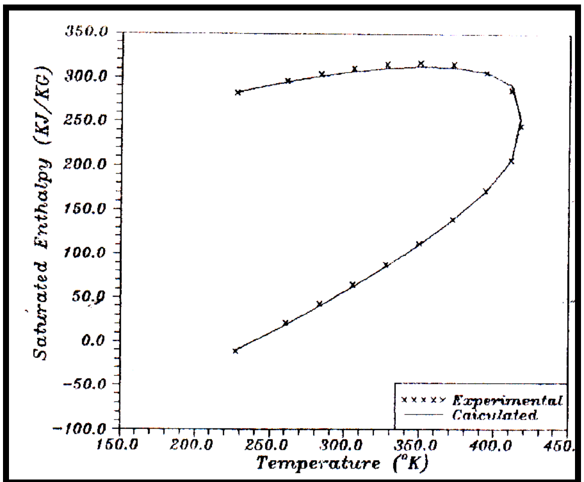

Figure (13) Enthalpy temperature diagram for chlorine

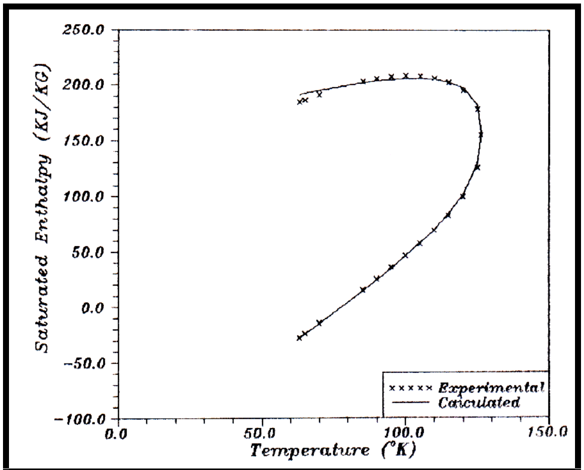

Figure (14) Enthalpy temperature diagram for nitrogen

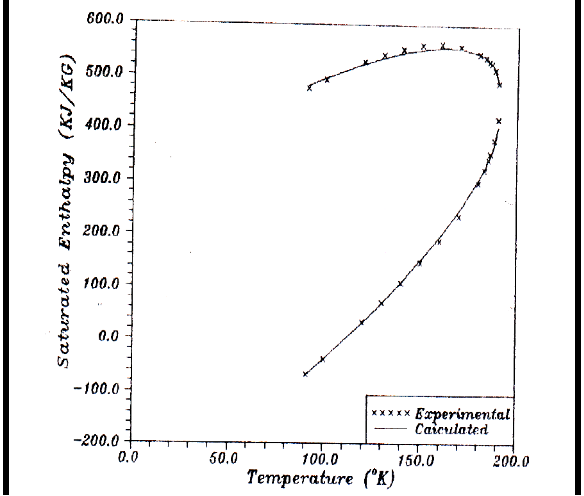

Figure (15) Enthalpy temperature diagram for methane

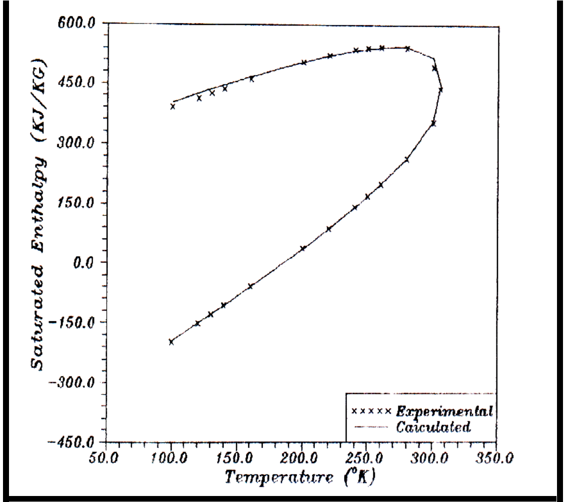

Figure (16) Enthalpy temperature diagram for ethane

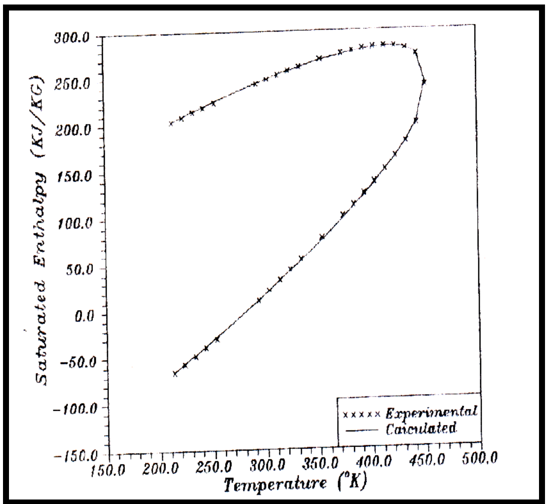

Figure (17) Enthalpy temperature diagram for Freon-21 ($CHFCl_2$)

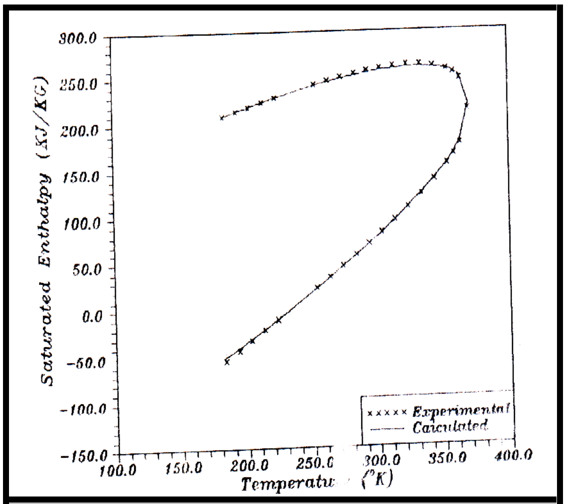

Figure (18) Enthalpy temperature diagram for Freon-22 (CHF_2Cl)

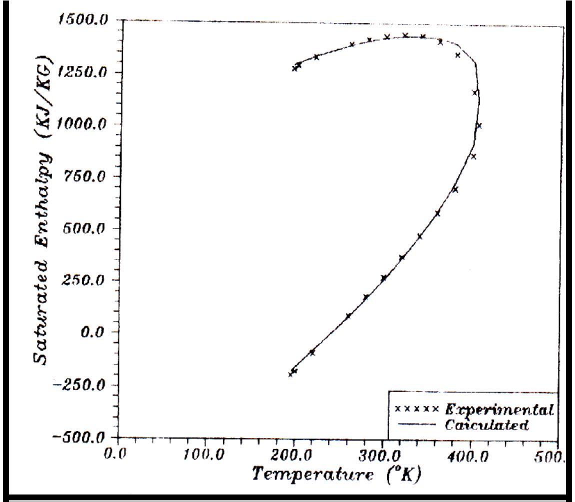

Figure (19) Enthalpy temperature diagram for ammonia

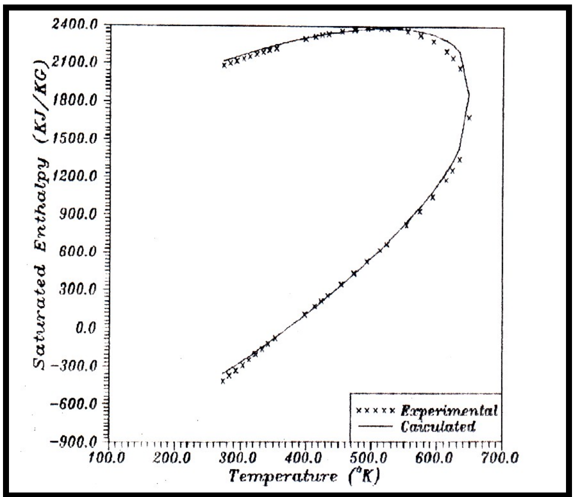

Figure (20) Enthalpy temperature diagram for water

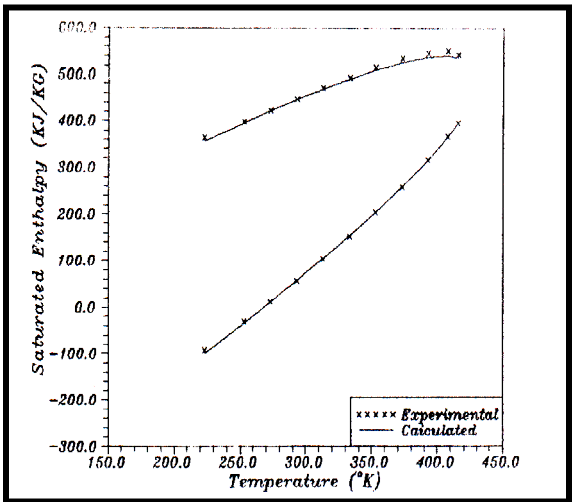

Figure (21) Enthalpy temperature diagram for 1,3-butadine

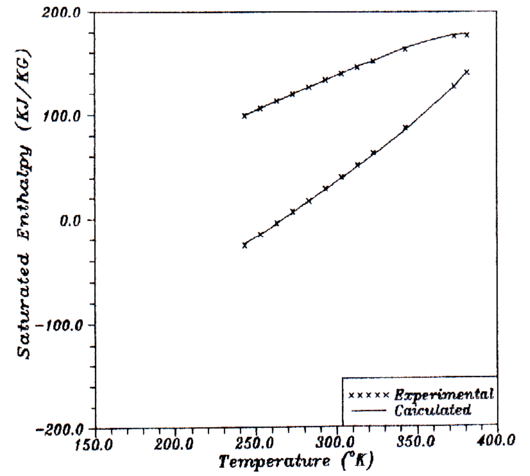

Figure (22) Enthalpy temperature diagram for Octafluoro Cyclobutane

Figures 23 through 26 have been prepared to show the relation between the enthalpies of saturated vapor and saturated liquid with temperatures for typical system mixtures using the data from literatures and the developed method.

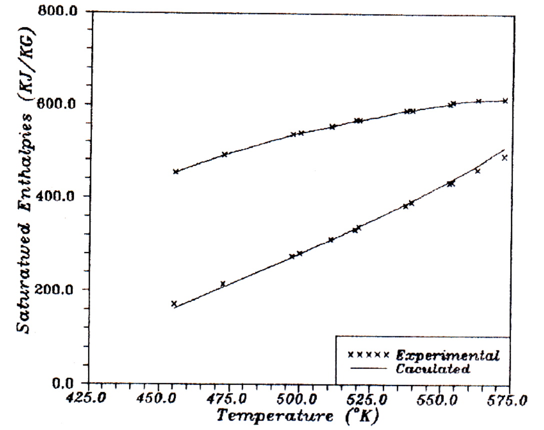

Figure (23) Enthalpy temperature diagram for (90 percent) benzene – hexadecane system

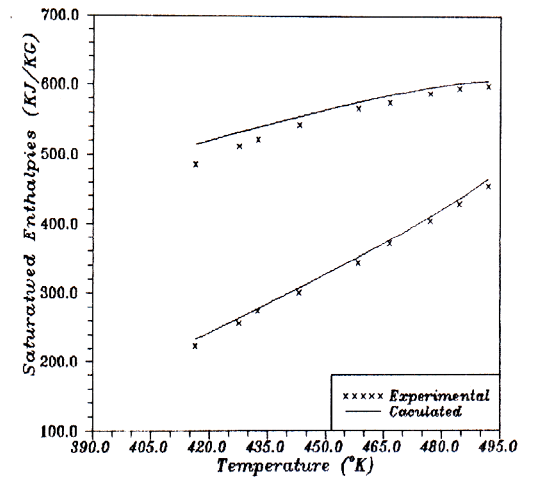

Figure (24) Enthalpy temperature diagram for (61.2 percent) pentane – cyclohexane system

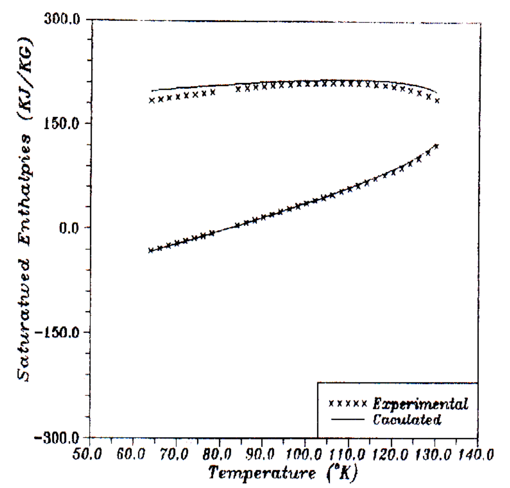

Figure (25) Enthalpy temperature diagram for (79.1 percent) nitrogen – oxygen system

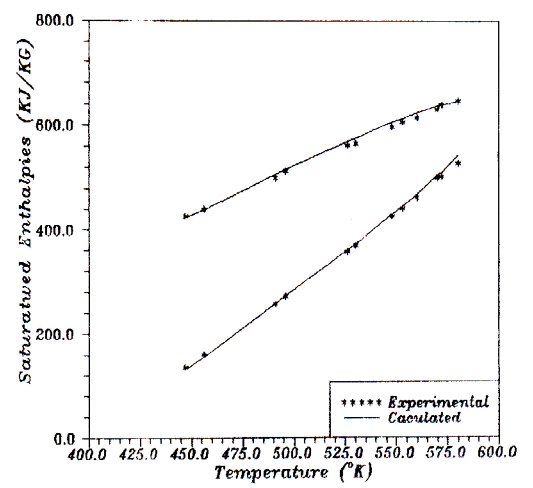

Figure (26) Enthalpy temperature diagram for (35.2 percent) benzene – (51.5 percent) octanecane - tetraline system

Discussion

The correlations of the coexisting saturated vapor and liquid enthalpies that developed in the proposed work are generally on the same line adopted in the literature [4,5] which have reported the correlations of densities of saturated vapor and saturated liquid using the rectilinear diameter principle and the law of corresponding states. The resulted correlation for pure substances in this study is:

$$DH = A + B\tau \qquad 4$$

It should be mentioned that, this relation has been extended to involve mixtures also, by means of using suitable mixing rules. The resulted correlation for mixtures is:

$$DH_m = A_m + B_m \tau_m \tag{11}$$

However, the use of reduced rectilinear diameter principle to determine the saturated vapor, and saturated liquid enthalpies is a new approach which has not been used previously in the literature.

Usually, the method adopted in literature to calculate saturated vapor and liquid enthalpies depended on direct use of the equations of state, most of these equations of state are empirical equations, very complicated, in addition to the fact that these equations of state are not suited to the saturated region which resulted in a large errors when applied to calculate enthalpies at this saturated region if they compares with experimental data.

When using the available correlations in the literature to calculate the saturated enthalpies at coexisting vapor and liquid phases for pure substances and mixtures, the calculation methods using either hand calculator or computer programs are always associated with difficulties compares with the method developed in this study.

Edmister and Lee [6], used Redlich-Kwong equation of state to predict enthalpy using equation:

$$\frac{H-H^*}{RT_C} = Z - 1 - \frac{1.5\,a}{bRT}\left(1+\frac{a}{V}\right) \tag{25}$$

where *a* and *b* are constants. The method requires to obtain six values of constants in order to get the enthalpy, that makes it not simple method as that in the present work, they presented their results as graphs from which reasonable accurate data can not be obtained.

The correlations of this study are based on analyzing the relation between the saturated vapor, saturated liquid enthalpies and temperature, where the values of DH and the values of τ are used as the basic generalized functions. The resulted models of correlations are very simple and can be applied easily to hand calculator or using a computer program.

These correlations can be applied successfully up to the critical region and for some of the examined substances and mixtures (especially the polar substances) the deviation of the experimental data increases with linear relation of eq.(4) and eq.(11).

For pure substances, the AAD of saturated vapor enthalpy fall in range of 0.3292 % to 3.0999 % and the AAD of saturated liquid enthalpies fall in range of 1.0643 % to 6.2984 % for the corresponding 319 literature data point of saturated vapor and saturated liquid enthalpies. It is indicates also that the over all AAD of saturated vapor and saturated liquid enthalpies of these points are 1.3022 % and 3.1670 % respectively.

For mixtures, the AAD of saturated vapor and saturated liquid enthalpies fall in range of 0.9807 % to 6.8912 % and 1.5767 % to 6.9085 % respectively, for the corresponding 165 literature data point of saturated vapor and saturated liquid enthalpies, and that the overall AAD of saturated vapor and saturated liquid enthalpies of these points are 3.5574 % and 3.4979 % respectively.

The relationship of eq.(4) that resulted from the general fitting of literature saturated vapor and saturated liquid enthalpies values at different temperatures is linear relation. This makes it possible to obtain one of the relations that relates the two constants *A* and *B* for each pure compound which are defined in term of the corresponding critical temperature and normal boiling point temperature representing at the following equation:

$$A = T_{rb} - B\left(1 - T_{rb}\right) \tag{9}$$

Another relation has been presented that relates the two constants *A* and *B* by the fitting of the literature values representing at the following equation:

$$A = 0.601206 - 0.412371\,B - 0.0133827\,B^2 \tag{10}$$

This relation together with relation of eq.(9) represent the most accurate relations that correlate the two constants *A* and *B*. Only twenty (methane, ethane, propane, n-butane, i-butane, nitrogen, oxygen, argon, chlorine, freon-11, freon-12, freon-13, freon-21, freon-22, methyl chloride, benzene, octaflouro cyclobutane, 1,3-butadiene, water and ammonia) out of thirty were used to obtain the constants *A* and *B*. the resulted absolute average deviation indicate that, these relations represent a generalized correlations for saturated coexisting vapor and liquid enthalpies.

The reason for using the dimensionless term DH is to obtain as much as possible a linearized simple relation (eq.(4)), from which the constants *A* and *B* were obtained when applied it at the normal boiling point.

Accuracy of The Developed Correlations

The correlation of the enthalpies of saturated vapor and liquid coexisting phases that developed which are represented by the eq.(4) and eq.(11) have been applied for various pure compounds and mixtures.

Experimental data of enthalpies of saturated vapor and liquid for these pure components and mixtures were obtained from literature.

The overall percent average absolute deviations of saturated vapor and saturated liquid enthalpies for 83 literature data point of these seven pure components are 1.5929 % and 3.1058 % respectively for the present work, and using the equation of state for example that for Lee and Kesler [7] method are 21.7782 % and 50.9913 % respectively.

The overall percent average absolute deviations of saturated vapor and saturated liquid enthalpies for 58 literature data points of these six binary mixtures are 2.9795 % and 3.2412 % respectively, and that for Lee and Kesler method are 24.8202 % and 39.7035 % respectively.

These comparisons indicate that the present method of calculating the saturated vapor and saturated liquid enthalpies is straight forward, easy, and simple as compares with that of equation of state which involves complexity and less accuracy.

Conclusion

New simple relations are developed for the prediction of the saturated vapor and saturated liquid enthalpies of pure substances and mixtures. These relations are based on the rectilinear diameter principle and the law of corresponding states. They are:

For Pure Compounds

$$DH = A + B\,\tau \tag{4}$$

For Mixtures

$$DH_m = A_m + B_m\,\tau_m \tag{11}$$

Where DH represents the average reduced saturated enthalpies at any temperatures divided by the average reduced saturated enthalpies at the normal boiling point. The terms DH and τ are defined as follows:

$$DH = \frac{\left[\dfrac{(H_{sv}+H_{sl})_T}{2RT_C}\right]}{\left[\dfrac{(H_{sv}+H_{sl})_b}{2RT_b}\right]} \tag{5}$$

$$\tau = 1 - \frac{T}{T_c} \tag{6}$$

And the constants A and B are defined in terms of critical temperature and normal boiling point temperature, using the following relations:

$$A = (T_b/T_c) - B\left[1-(T_b/T_c)\right] = T_{rb} - B(1-T_{rb}) \tag{9}$$

$$A = 0.601206 - 0.412371\,B - 0.0133827\,B^2 \tag{10}$$

The average absolute deviations when using the above correlation in range from 1.0643 % to 6.2984 % for saturated liquid enthalpies and range from 0.3292 % to 3.0999 % for saturated vapor enthalpies for 319 data points of 23 pure substance. For mixtures the average percent absolute deviations range from 1.5767 % to 6.9085 % for saturated liquid enthalpies, and in the range of 0.9807 % to 6.8912 % for saturated vapor enthalpies of 165 data points of 13 binary mixtures and 1 ternary mixture.

These correlations are applied successfully at the saturated region up to the critical temperature. They compare favorably with any equation of state.

Nomenclature

AAD	Average Absolute Deviation	
A,B	Constants of equation 3 and 4	
DH	average reduced saturated enthalpies at any temperatures divided by the average reduced saturated enthalpies at the normal boiling point	-
H	Enthalpy	J/gm
Mt	Molecular Weight	gm/gmol
P	Pressure	bar
R	Gas Constants	
T	Temperature	K
U	Internal Energy	J/gm
V	Molar Volume	cm^3/mol
z	Compressibilty factor	

Greek Letters

τ	Defined by equation 6
ω	Acentric factor

SUBSCRIPTS

b	Normal boiling point
c	Critical point
i	Component i
j	Component j
r	Reduced value
AV	Average value
sl	Saturated liquid
sv	Saturated Vapor
m	Mixture

Superscripts

*	Ideal gas state

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Appendix

Statistical Measurement And Analysis of Dispersion

To know the applicability and accuracy of any proposed correlation it is very important to know how this correlation fits the experimental data which is done by comparing the obtained results from the proposed correlation with the experimental data.

The various measurement of dispersion or variation are available, the most common being the *Average Absolute Deviation*. “*AAD*”

$$\boxed{AAD = \frac{\sum_{i=1}^{n} \left| M_i^{obsd} - M_i^{calcd} \right|}{n}}$$

Where M is an intensive property and n is the number of data point.

علاقات مطورة للتنبؤ بالأنثالبيات المشبعة في منطقة البخار والسائل المتاخمة

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الخلاصة

تظمنت هذه الدراسة استخدام مبدأ نصف القطر الخطي للتعبير عن الأنثالبيات المشبعة في منطقة البخار والسائل المتاخمة ، وهذا قد تطلب استعمال علاقة مناسبة لحساب حرارة التبخر الكامنة.

أن العلاقات بين أنثالبية البخار المشبع مع أنثالبية السائل المشبع مع الضغط قد تم التحقق فيها بأستخدام بعض المواد النقية ، وقد بينت تلك الدراسات إن الضغط لا يمكن استخدامه لوصف الأنثالبيات المشبعة البخارية والسائلة بعلاقات عامة مبسطة.

تم في هذا البحث تطوير علاقات جديدة مبسطة للمواد النقية والخلائط ، وقد استعمل مبدأ نصف القطر الخطي وقانون الحالات المتناظرة كأساس في تطوير وتبسيط هذه العلاقات حيث ادخل المتغير *DH* كمصطلح جديد متظمناً المعدل المختزل للأنثالبيات الغازية و السائلة المشبعة ، وتلك العلاقات هي :

$$DH = A + B\tau$$ للمواد النقية

$$DH_m = A_m + B_m\ \tau$$ للخلائط

أن الثوابت A و B أمكن ربطهما بعلاقات مبسطة كما مبين ادناه:

$$A = \left(\frac{T_b}{T_c}\right) - B\left[1 - \left(\frac{T_b}{T_c}\right)\right]$$

$$A = 0.601206 - 0.412371\,B - 0.013378\,B^2$$

أن العلاقة الثانية استحدثت باستخدام طريقة (*Maximum Likelihood Principle*) باستخدام القيم في الأدبيات لعشرين مادة نقية ، وقد طبقت هذه العلاقة على بقية المواد المستخدمة مما يدل على عمومية هذه العلاقة. لا يتطلب استعمال هذه الطريقة لحساب الأنثالبيات المشبعة سوى معرفة درجة الحرارة الحرجة و درجة الغليان. هذه العلاقات يمكن تطبيقها بنجاح إلى حد المنطقة الحرجة.

تم مقارنة الطريقة الجديدة باستخدام معادلة الحالة مثل معادلة Lee- Kesler. وقد أظهرت المقارنات ان الدقة المتوخاة من الطريقة الجديدة اكبر بكثير منها في طريقة Lee- Kesler.

إن العلاقات المطورة يمكن تطويرها اكثر ليتسنى استخدامها بصورة مباشرة في الأغراض التصميمية لعمليات التقطير والعمليات الأخرى التي تتضمن وجود ظواهر التبخير والتكثيف.