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Classical binary nucleation theory applied to the real mixture *n*-nonane/methane at high pressures

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A thermodynamic model of the formation free energy of a droplet, based on a real equation of state, has been implemented in the binary classical nucleation theory to analyze homogeneous nucleation of mixtures of *n*-nonane and methane in the coexistence region at high pressures. The composition of the critical nucleus is computed by solving the Kelvin equations, the chemical potentials, and molar volumes being evaluated from the Redlich–Kwong–Soave equation of state. Real gas behavior appears to have a strong effect on nucleation due to mutual interactions between methane and nonane molecules. Numerical calculations show an increasing concentration of methane in critical clusters with increasing pressure at fixed temperature and supersaturation. As a consequence, the surface tension of the critical droplets, which is evaluated by means of the Parachor method, is lowered, having a strong increasing effect on the nucleation rate; a 10 bar increase of total pressure leads to an increase of the nucleation rate of several orders of magnitude. © 1995 American Institute of Physics.

I. INTRODUCTION

During handling and transport of natural gas, it is observed that large and sudden pressure drops may induce mist formation. Muijtens *et al.*¹ showed that the condensation in the gas mixture is a nonequilibrium phase change of the higher alkanes, such as nonane and decane, which are present in the mixture besides the main components methane and nitrogen. From the strong deviation from vapor–liquid phase equilibrium of the onset points of condensation measured in a Wilson cloud chamber, it was concluded that droplets were formed by a homogeneous nucleation process. The measured onset points were located inside the coexistence region of the gas mixture in the p – T phase diagram, above the critical temperature of the main component methane. This coexistence region is characterized by the appearance of real gas effects in condensation, when pressure is above a few bars. The real gas effects become visible in density dependent solubilities affecting partial equilibrium vapor pressures, and in so-called retrograde condensation, i.e., condensation induced by a decrease of pressure.

Up to now, no examples of application of nucleation theory to nucleation in the coexistence region at high pressures are known from literature. In this paper we present numerical calculations based on classical binary nucleation theory of the mixture *n*-nonane/methane. Since natural gas consists of many components, most of them being heavier hydrocarbons, we chose the *n*-nonane/methane mixture as a model mixture to study homogeneous nucleation. At pressures ranging from 10 to 200 bar corresponding to exploration pressures of natural gas, the coexistence regions of natural gas and of the mixture mentioned above with a molar *n*-nonane concentration of about 10^{-4} , largely coincide in

the p – T phase diagram and therefore are expected to exhibit similar real gas effects in condensation.

From now on, we shall consider the *n*-nonane/methane mixture. The real gas effects due to the mutual interactions of the nonane and methane molecules lead to a solubility of methane in liquid nonane that increases with pressure. Since the droplets will contain a significant amount of methane besides the nonane, the modeling of homogeneous nucleation requires a binary nucleation model.

The theory of homogeneous condensation goes back to the work of Volmer and Weber² and Becker and Döring.³ They developed the classical nucleation theory (CNT) of pure vapors which predicts the nucleation rate, i.e., the rate at which critical nuclei are formed. A major role in this theory is played by the capillary approximation; properties of microscopic droplets are taken as if the droplets were of macroscopic sizes. Reiss⁴ extended CNT to binary vapors. The calculation of the kinetic prefactor was improved by Stauffer.⁵ Later, the correctness of the implementation of the Gibbs–Duhem identity in binary nucleation theory was discussed by Renninger *et al.*,⁶ Doyle,⁷ and Wilemski.⁸ Wilemski^{8–10} introduced the model of a droplet consisting of a bulk and a surface layer with excess molecules,^{11,12} and at the same time pointed out the shortcomings of this model. Because of the rather unsatisfactory assumption of the capillarity approximation for droplets that consist of typically 10–100 molecules, several attempts have been made to improve CNT (Refs. 13–16) with varying success.

Numerical studies of binary homogeneous condensation with CNT performed so far mainly refer to aqueous solutions and mixtures of alcohols. Nucleation rates were determined as a function of activities of the species present in the mixture, and attention was paid to the composition of the critical cluster.¹⁷ In the following sections we will present an extension of CNT allowing calculation of nucleation rates in mixtures showing real gas effects. Results obtained with the model are presented.

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II. BINARY HOMOGENEOUS NUCLEATION THEORY

Since the introduction of binary nucleation theory, different models and interpretations have been published in the literature. Therefore we shall give a brief outline of the theory as it is implemented in our calculations.

The nucleation rate is the number of droplets formed per unit time and space. It is expressed in the following form:

$$J = K \cdot e^{-\Delta G/k_B T}. \quad (1)$$

K is a kinetic prefactor, ΔG in the exponential is the free reversible energy of formation of a critical droplet, k_B is Boltzmann's constant, and T the temperature. The energy of formation $\Delta G(n_1, n_2)$ is a function of the numbers of particles of species 1 and 2 in the droplet. When the gas–vapor mixture is in a supersaturated state, the $\Delta G(n_1, n_2)$ plane exhibits a saddle point. The position of this saddle point is considered to represent the critical nucleus. The critical nucleus is in unstable equilibrium with the surrounding vapor, and the saddle point forms the lowest passage over an energy barrier. Clusters passing over this barrier will grow to macroscopic droplets. Different models have been employed to calculate ΔG . In CNT, Gibbs' capillarity approximation is used to describe the clusters on the basis of classical thermodynamics.

A. Classical droplet model

We adopt the binary classical theory as described by Wilemski. In this macroscopic model of a droplet and surrounding vapor, the droplet consists of bulk liquid with numbers of bulk molecules n_1^l and n_2^l and a surface layer with numbers of surface molecules n_1^s and n_2^s . Bulk and surface are considered to be in thermodynamic equilibrium and the droplet is assumed to be incompressible. The number of surface molecules is an excess number, defined as $n^s = n - n^l - n^v$, where n is the total number of molecules in the system, and n^v is the number of molecules in the vapor. The excess molecules n_i^s do not contribute to the droplet volume. The presence of the surface layer in the droplet model implicitly takes into account the effect of surface enrichment; the concentration of species 1 and 2 near the surface can differ from the interior composition. According to this droplet model, the free formation energy is⁸

$$\begin{aligned} \Delta G = & (p - p^l)V^l + \sigma A + \sum_{i=1,2} (\mu_i^l - \mu_i^v)n_i^l \\ & + \sum_{i=1,2} (\mu_i^s - \mu_i^v)n_i^s. \end{aligned} \quad (2)$$

Chemical potentials μ_i^l and μ_i^v are evaluated at pressures p^l in the droplet and p^v of the vapor, respectively. V^l is the droplet volume, A is the surface area, and σ the surface tension. Because bulk liquid and surface are assumed to be in equilibrium, $\mu_i^s = \mu_i^l$, bulk and surface molecules can be taken together in Eq. (2); $n_i^l = n_i^l + n_i^s$. If we define the difference in chemical potential between droplet and vapor as $\Delta\mu_i = \mu_i^l(p^l, T) - \mu_i^v(p^v, T)$, and furthermore assume that the formation of clusters does not lead to a change of vapor pressure p (i.e., $p^v = p$), then ΔG can be written as

$$\Delta G = (p^v - p^l)V^l + \sigma A + \sum_{i=1,2} \Delta\mu_i n_i^l. \quad (3)$$

The saddle point of this ΔG plane is determined by

$$\left. \frac{\partial \Delta G}{\partial n_i^l} \right|_{\text{sp}} = 0, \quad i = 1, 2. \quad (4)$$

Combining Eqs. (3) and (4) together with the Gibbs–Duhem relation for the bulk,

$$S^l dT - V^l dp^l + \sum_{i=1,2} n_i^l d\mu_i^l(p^l, T) = 0, \quad (5)$$

and the Gibbs adsorption equation for the surface,

$$S^s dT + A d\sigma + \sum_{i=1,2} n_i^s d\mu_i^s = 0, \quad (6)$$

we arrive at

$$\Delta\mu_i = 0. \quad (7)$$

In deriving the last result, we used the Laplace relation $p^l = p^v + 2\sigma/r$, and the expressions for the volume and surface area of a spherical droplet, $V^l = \sum_i n_i^l v_i = \frac{4}{3}\pi r^3$ and $A = 4\pi r^2$.

Using the incompressible fluid approximation $\mu_i^l(p^l, T) = \mu_i^l(p^v, T) + v_i(p^l - p^v)$ in which v_i is the partial molecular volume of species i , one arrives at the so-called Gibbs–Thomson or Kelvin equations,

$$\Delta^* \mu_i + \frac{2\sigma v_i}{r} = 0. \quad (8)$$

In this equation $\Delta^* \mu_i = \mu_i^l(p^v, T) - \mu_i^v(p^v, T)$.

As stated by Wilemski,⁹ all variables in these equations are functions of bulk composition only. Therefore, at the saddlepoint only the bulk composition can be obtained from these equations. The method described by Laaksonen *et al.*¹⁷ to calculate n_i^s and n_i^l cannot be applied here because the surface molecules do not contribute to the droplet volume in this model. The free energy of formation of a critical cluster at the saddle point follows from Eq. (3), with $\Delta\mu_i = 0$, because the critical cluster is in unstable equilibrium with the surrounding vapor,

$$\Delta G_{\text{sp}} = \frac{1}{3} \sigma A. \quad (9)$$

B. Kinetics

The kinetic prefactor K of Eq. (1) was first derived by Reiss⁴ and later modified by Stauffer.⁵ The result obtained by Stauffer is given by the following equations:

$$K = N R_{\text{av}} Z, \quad (10)$$

where K is the product of the number density N of monomers in the gas, an average growth rate R_{av} and the Zeldovich factor Z . R_{av} is given by

$$R_{av} = \frac{\det(\mathbf{R})}{(R_{11} \sin^2 \phi + R_{22} \cos^2 \phi - 2R_{12} \sin \phi \cos \phi)}; \quad (11)$$

R_{av} depends on the growth rate tensor $\mathbf{R}$ and on the angle ϕ of the direction of the current of clusters in the saddle point. We shall assume that no cluster-cluster interactions take place, but only monomers collide with the critical cluster, then the elements of $\mathbf{R}$ are given by⁵

$$\begin{aligned} \mathbf{R} &= \begin{pmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{pmatrix}, \\ R_{11} &= A(n_1, n_2) \beta_1, \\ R_{12} &= R_{21} = 0, \\ R_{22} &= A(n_1, n_2) \beta_2, \end{aligned} \quad (12)$$

where $A(n_1, n_2)$ is the cluster surface area, and β_1 and β_2 are the impingement rates of molecules of substance 1 and 2. The expression for the Zeldovich factor reads

$$Z = -\frac{1}{2} \frac{\partial^2 \Delta G(x, y)}{\partial x^2} \bigg/ (-\det \mathbf{D})^{1/2}. \quad (13)$$

The tensor $\mathbf{D}$ consists of the derivatives of ΔG with respect to the total number of molecules in the cluster. In combination with CNT, a problem arises in the calculation of R_{av} and Z , because ΔG is not known as a function of the overall cluster composition, but only as a function of bulk composition. Therefore $\mathbf{D}$ can not be determined exactly from this model. However, as already remarked by Wilemski,⁹ this will not play a crucial role since the influence of $\mathbf{D}$ is limited to the relatively unimportant kinetic prefactor.

III. A REAL GAS MODEL FOR ΔG

Calculation of the nucleation rate according to CNT requires a thermodynamic description for the gas and liquid mixture taking into account all real gas effects involved in the nucleation process.

First, the bulk composition of the critical droplet can be found by solving an equation that follows from a linear combination of the Kelvin equations:

$$v_2 \Delta^* \mu_1 - v_1 \Delta^* \mu_2 = 0. \quad (14)$$

For given p and T , all quantities in this equation are known functions of droplet bulk composition only, which follow from the EOS.

Second, it is not possible to evaluate mixture properties from the properties of the pure substances; methane is in a state in which no pure liquid methane can exist. Surface tension, which is a very important parameter determining the height of the energy barrier ΔG in Eq. (1), will thus be estimated by using an empirical correlation (Parachor method).

From several available equations of state we selected the Redlich-Kwong-Soave (RKS) and the Lee-Kesler-Plöcker (LKP) equations, because they proved to be well applicable to alkanes.¹⁸ The RKS equation is of the cubic type and therefore relatively simple from a calculational point of view. The LKP equation of state is a transcendental one, thus com-

putationally more complex. It is applicable, however, over a wider range of reduced temperatures. To compare both EOS to test their suitability to our application, we calculated the equilibrium molar volume of the liquid as a function of temperature and pressure. The molar volume is a very important parameter in our model because of its appearance in the Kelvin equations and in the surface tension correlation. The results obtained were compared with experimental data of Shipman *et al.*¹⁹ Although RKS is known for its poor prediction of liquid molar volume, results obtained by RKS when Peneloux' correction¹⁸ was included turned out to be far better than LKP results in predicting the molar volumes (RKS, less than 0.8% deviation from experimental data; LKP, up to 6% deviation). For this reason, the RKS equation of state was used for all thermodynamic calculations throughout this work.

The RKS equation has the following form:

$$p = \frac{RT}{V_{RKS} - a} - \frac{b}{V_{RKS}(V_{RKS} + a)}, \quad (15)$$

where

$$a = \frac{0.086 \ 64 RT_c}{p_c}$$

and

$$b = \frac{0.427 \ 48 R^2 T_c}{p_c} \left[1 + f(\omega) \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2,$$

with

$$f(\omega) = 0.48 + 1.574 \omega - 0.176 \omega^2.$$

In these equations, R is the universal gas constant, V_{RKS} is the molar volume (subscript m is left out to avoid confusion with mixture properties in the remainder of this text), ω is Pitzer's acentric factor, and the subscript c refers to the critical point. For a mixture, a and b are evaluated from the pure component values using the mixing rules

$$a_m = \sum_i y_i a_i,$$

$$b_m = \sum_i \sum_j y_i y_j (b_i b_j)^{1/2} (1 - k_{ij}).$$

The quantities y_i in the above expressions denote the molar fractions of the components, both in the vapor and liquid phases. From now on, however, we will use x_i for the liquid molar fractions. In the last mixing rule, the interaction parameter k_{ij} is introduced. Its value is determined by a fit to experiments.²⁰

The RKS equation is known to yield too large values for the liquid molar volume V . The correction term proposed by Peneloux¹⁸ reads

$$V = V_{RKS} - c, \quad (16)$$

where V is the corrected molar volume and

$$c = 0.407 \ 68 (0.294 \ 41 - Z_{RA}) \frac{RT_c}{p_c}$$

Z_{RA} is the Rackett compressibility factor of the substance under consideration. For a mixture, the correction term is obtained by using the conventional mixing rule

$$c_m = \sum_i x_i c_i.$$

From the above equations, an expression for the chemical potential can be derived in analytical form in a standard way by integration of pressure with respect to volume (obtaining the free energy F as a result) and then taking the derivative with respect to n_i . In this way an expression of the form $\mu = f(T, V, y_i)$ is obtained. For the liquid, of course, y_i is replaced by x_i .

The partial molecular volumes are found by substituting the mixing rules into the RKS equation and applying standard expressions from thermodynamics for the partial volumes (N_A denotes Avogadro's number),

$$N_A v_1 = V_{\text{RKS}} - x_2 \frac{\partial V_{\text{RKS}}}{\partial x_2} - c_1, \quad (17)$$

$$N_A v_2 = V_{\text{RKS}} + x_1 \frac{\partial V_{\text{RKS}}}{\partial x_2} - c_2. \quad (18)$$

In these equations the Peneloux correction has been used. Because of the use of the incompressible fluid approximation in deriving the Kelvin equations (8), the molecular liquid volume has to be calculated at pressure p_v outside the droplet. Using chemical potentials and molecular volumes obtained from Eqs. (15)–(18) in Eq. (14), a solution for the droplet bulk composition is found, and $\Delta^* \mu_i$ and v_i are known.

With this result, it is possible to calculate the droplet radius from either one of the Kelvin equations written in the form

$$r = - \frac{2\sigma v_i}{\Delta^* \mu_i}. \quad (19)$$

The critical free energy barrier, ΔG_{sp} , is now obtained from Eq. (9), provided that the surface tension is known.

Several correlations exist for the surface tension, most of which need the pure component values as their input. Since relevant temperatures are above the critical temperature of methane, these correlations can not be used for the mixture under consideration. A relation that can be used for our purposes is the Macleod–Sugden correlation,¹⁸ an expression obtained by the best fit to experiments. It reads

$$\sigma^{1/4} = \sum_i (P_i) \left(\frac{x_i}{V^l} - \frac{y_i}{V^v} \right) \quad (20)$$

in which superscripts l and v refer to liquid and vapor, respectively. The parameters P_i are the so-called parachors of the components. Originally, Macleod suggested to calculate these from molecular structures; however, better agreement with experiments can be obtained by empirically fitting the parachor values to measurements. For our calculations, the values obtained by Deam and Maddox²¹ are used. We note that the parachor method is a fit on bulk composition. This is consistent with the fact that, as a solution of the Kelvin equa-

tions, bulk compositions are obtained which are substituted into Eq. (20) in order to find the surface tension of the droplet. A limitation of this method is the lack of a proper correction for the curvature of the droplet surface which is still subject of discussion in literature.^{22–24}

What remains to be calculated, is the kinetic prefactor K of expression (1) in which the second derivatives of ΔG at the saddle point position with respect to the total numbers of molecules, n_1^l and n_2^l are present. As was already pointed out in Sec. II B, we have no information concerning the excess numbers n_1^s and n_2^s . According to Wilemski,⁹ the best one can do is using Reiss' original expression for ΔG , i.e.,

$$\Delta G(n_1^l, n_2^l) = \sum_{i=1,2} n_i^l \Delta^* \mu_i + \sigma A \quad (21)$$

keeping σ constant at the value of the critical droplet. The shape of the ΔG surface obtained in this way is approximately correct in the neighborhood of the saddle point.

For the impingement rates β_i present in the growth rate tensor $\mathbf{R}$ [Eq. (12)], the ideal expression $\beta_i = \rho_i / \sqrt{k_B T / 2 \pi m_i}$ is used, where ρ_i is the number density of monomers of species i and m_i is the molecular mass. It is expected that the values of β_i only have a slight effect on the nucleation rate.

No special attention has been paid to the limiting case to unary nucleation. It may be expected that a small overestimate of the nucleation rate appears, when the position of the saddlepoint is too close to the n_1 -axis. This might occur in the low pressure limit, in which only a little methane will be dissolved in the droplets. A more extensive treatment of this matter is given by Wilemski.²⁵

Finally, we introduce a supersaturation S , which will be used in presenting results of our calculations

$$S = \frac{y_1}{y_{1,\text{eq}}}, \quad (22)$$

where y_1 and $y_{1,\text{eq}}$ are the molar vapor fractions of nonane in the supersaturated state and at equilibrium, respectively. The equilibrium molar fraction is calculated by equating the

FIG. 1. Contourplot of the free energy surface in the vicinity of the saddle point. $T = 240$ K, $p = 40$ bar, and $y_1 = 1 \times 10^{-4}$ ($S \approx 8$). The value of ΔG at the saddle point is $65.5 k_B T$; contours correspond to increment steps of $1 k_B T$.

FIG. 2. Nucleation rate in the mixture *n*-nonane/methane as a function of supersaturation with the total pressure as a parameter, $T = 240$ K.

chemical potentials in the vapor and the liquid for both components at given p and T . We emphasize that this definition is not used in the calculation of nucleation rates. The reason for using the supersaturation ratio in representing the results is that S is considered to be the driving force behind the condensation process.

The calculations described are implemented in a FORTRAN numerical code. Calculations can be performed for *n*-alkanes (up to *n*-dodecane) with several carrier gases. The numerical values of the mixture *n*-nonane/methane, used in the present calculations, are listed in the Appendix. The program code is available upon request.

IV. RESULTS AND DISCUSSION

A plot of a typical free energy surface according to Eq. (21) for the *n*-nonane/methane mixture is shown in Fig. 1. The conditions are $T = 240$ K, $p = 40$ bar, and the molar fraction of *n*-nonane in the gas $y_1 = 1 \times 10^{-4}$ corresponding to a saturation ratio $S \approx 8$. The critical cluster consists of 66 nonane molecules and 11 methane molecules. During nucleation, the saddle point is passed in the direction φ indicated by the arrow.

Figures 2 and 3 show the nucleation rate as a function of

FIG. 3. Nucleation rate in the mixture *n*-nonane/methane as a function of supersaturation with the total pressure as a parameter, $T = 260$ K.

FIG. 4. Methane liquid fraction as a function of total pressure. The solid curve represents the composition of the critical droplet at supersaturation $S = 20$. The dashed curve refers to equilibrium liquid; $T = 240$ K.

supersaturation with the pressure as a parameter for two different temperatures. The model predicts a large effect of total pressure on the nucleation rate. At fixed supersaturation, increasing pressure induces an increase of nucleation rate by several orders of magnitude demonstrating real gas effects in homogeneous nucleation. Apart from this phenomenon, the generally observed exponential dependence of nucleation rate on supersaturation at given total pressure and temperature can also be seen in the figures.

The interaction of nonane and methane in the nucleation process also comes forward when the composition of the critical cluster is considered. The saddle point of Fig. 1 already indicated the presence of methane in the critical cluster. In Fig. 4 the molar fractions of methane in the critical cluster and in the corresponding equilibrium liquid state are plotted as a function of pressure at fixed supersaturation and temperature. The methane molar fraction increases from approximately 0 at low pressure to 0.11 at 40 bar. This is less than the equilibrium molar fraction, but, as can be seen from Fig. 5, it has significant consequence for the surface tension. The increasing amount of methane in the critical cluster lowers the surface tension from 2.7×10^{-2} N/m to 1.9×10^{-2} N/m at 40 bar. The decrease of surface tension has a direct

FIG. 5. Surface tension as a function of pressure for fixed values of supersaturation and temperature. The solid curve corresponds to the critical droplet composition, the dashed curve refers to the equilibrium composition.

FIG. 6. Pressure dependence of the equilibrium gas composition of the mixture *n*-nonane/methane. Dashed curve, nonane molar fraction in the gas phase at vapor–liquid equilibrium at 240 K as a function of the mixture total pressure. Solid curve corresponding equilibrium *n*-nonane vapor density.

consequence for the energy barrier ΔG [Eq. (9)], which is also reduced. This largely explains the enhanced nucleation rate with pressure.

In Figs. 2 and 3 the nucleation rate was plotted as a function of supersaturation S . It has to be realized here that the saturated nonane vapor density itself depends on the mixture total pressure, as is shown in Fig. 6. Due to real gas effects, the solubility of nonane in the gas phase increases, resulting in an increase of equilibrium nonane concentration $y_{1,\text{eq}}$ and therefore an even stronger increase of equilibrium nonane vapor density $\rho_{1,\text{eq}}$, at pressures above 20 bar. So, S is not a measure for the actual nonane vapor density when nucleation rate curves at different pressures are compared.

In Fig. 7 the nucleation rate is plotted as a function of nonane vapor density ρ_1 which is obtained from the relation $\rho_1 = y_1/V^v$, where V^v is the molar volume of the vapor mixture. An increase of total pressure above 10 bar at fixed nonane vapor density and temperature appears to reduce the nucleation rate. This can also be observed in Fig. 8. In this plot the nucleation rate is given as a function of pressure (solid curve) with a fixed nonane vapor density of $\rho_1 = 0.25 \text{ mol m}^{-3}$. The dashed curve shows the nucleation rate if not

FIG. 7. Nucleation rate in the mixture *n*-nonane/methane as a function of nonane vapor density for different total pressures at $T=240 \text{ K}$.

FIG. 8. Nucleation rate as a function of pressure for a fixed nonane vapor density $\rho_1 = 0.25 \text{ mol m}^{-3}$. Solid curve, *n*-nonane/methane mixture calculated with binary nucleation theory. Dashed curve, CNT for *n*-nonane with an inert carrier gas; $T=240 \text{ K}$.

methane, but an inert carrier gas is added. The pronounced difference between binary nucleation under real gas conditions and unary nucleation with an inert carrier gas is clear. Adding methane to nonane first shows a strong increase of nucleation rate, due to the lowering of surface tension caused by the presence of methane in the critical cluster. So, initially this effect dominates the effect of decreasing supersaturation with pressure. At higher pressures, the situation is reversed and finally, when pressure is high enough, thermodynamic equilibrium is attained again. Adding an inert component to a nonane vapor of fixed density shows a monotonically decreasing nucleation rate with (inert) gas pressure, this being a result of a higher energy barrier due to the increase of liquid chemical potential, while vapor chemical potential is not changed much. Recently, a reduction of the nucleation rate with increasing total pressure of 1-propanol in helium and in hydrogen, was experimentally found by Heist *et al.*²⁶ in a special high pressure diffusion cloud chamber.

Finally, in Fig. 9 a p – T phase diagram is shown of a

FIG. 9. p – T diagram with lines of constant nucleation rate for a gas mixture with molar fraction *n*-nonane $y_1 = 1 \times 10^{-4}$. The outer curve corresponds to vapor–liquid equilibrium for given nonane fraction. The labels denote the nucleation rate in $\text{cm}^{-3} \text{ s}^{-1}$.

n-nonane/methane mixture with a nonane molar fraction of 1×10^{-4} . The outer curve, on which the gas mixture with given nonane concentration is in equilibrium with the liquid phase, forms the boundary of the two-phase coexistence region. Inside this envelope, lines of constant nucleation rate are drawn, lines representing higher nucleation rates are found further inwards the coexistence region. Furthermore, lines of given nucleation rate form “retrograde curves,” and they all appear to converge to the critical point of the mixture.

V. CONCLUSIONS

The classical binary nucleation theory has been extended with a thermodynamic model taking into account real gas effects. For calculating chemical potentials and molar volumes the RKS equation of state was applied, surface tension was modeled with the Parachor method. This model enables the theoretical study of homogeneous nucleation of real gas mixtures in the coexistence region, such as the *n*-nonane/methane mixture, subject of the calculations performed in this paper. The model predicts for this mixture an increase of nucleation rate with pressure when supersaturation and temperature are fixed. Due to real gas effects, an increasing amount of methane is present in the critical droplet with increasing pressure, as also occurs in equilibrium condensation. The presence of methane in the critical cluster lowers the surface tension, and therefore the free energy of formation is lowered, leading to an enhanced nucleation rate.

We have only presented calculations for the *n*-nonane/methane mixture. However, it is to be expected that similar results are found in other mixtures at high pressures, when interactions between the mixture components are present. An example is the *n*-nonane/nitrogen mixture.

Up to now no experimental data of homogeneous nucleation in the coexistence region at high pressures have been published in literature. Experimental work with a nucleation pulse expansion wave tube is in progress.^{27,28} Results will be published separately.

APPENDIX

Numerical values of the *n*-nonane/methane mixture used in the calculations are listed below.

n-Nonane: critical pressure $p_c = 22.9$ bar, critical temperature $T_c = 594.6$ K, Pitzer's acentric factor $\omega = 0.445$, Rackett compressibility factor $Z_{RA} = 0.2543$, molar mass

$M = 128.259$ g/mol, and parachor $P = 387.6$ $\text{g}^{1/4} \text{cm}^3 \text{s}^{-1/2} \text{mol}^{-1}$.

Methane: critical pressure $p_c = 46.0$ bar, critical temperature $T_c = 190.4$ K, Pitzer's acentric factor $\omega = 0.011$, Rackett compressibility factor $Z_{RA} = 0.2892$, Molar mass $M = 16.043$ g/mol, and parachor $P = 81.0$ $\text{g}^{1/4} \text{cm}^3 \text{s}^{-1/2} \text{mol}^{-1}$.

The interaction parameter for the mixture $k_{ij} = 0.0448$. All listed data can be found in the book of Reid, Prausnitz, and Poling,¹⁸ except for the binary interaction parameter which comes from Knapp *et al.*²⁰

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