

IMPERFECT VAPOUR–GAS MIXTURES AND HOMOGENEOUS NUCLEATION

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Abstract—We study the imperfect behaviour of vapour–gas mixtures and the associated total pressure dependence of the homogeneous nucleation rate of liquid droplets from a vapour. A pressure dependent rate of homogeneous nucleation has an important bearing on the analysis of aerosol formation during a severe reactor accident. It is found from a statistical mechanical approach that interactions between gas molecules and vapour monomers or sub-critical clusters perturbs the equilibrium between vapour and condensate and thereby alters the nucleation rate. The effect can be expressed in terms of second virial coefficients. Estimates of the effect lead to a nucleation rate reduction with increasing pressure, the magnitude depending on the carrier gas used. The largest effect considered involves a six-fold reduction in rate for *n*-nonane nucleation in argon at 273 K and a supersaturation of 10, when the pressure is raised by 1 atm. The reduction is rather less significant in a carrier gas of helium.

1. INTRODUCTION

In nuclear safety, the potential for generating airborne particles, or aerosol, by overheating the reactor core during a possible accident, is of central importance in assessing the risks of dispersal of radioactive substances into the environment. The aerosol is formed by evaporation of materials from overheated fuel rods or other structures, and condensation of the vapour in the coolant channels. Particle nucleation can occur by homogeneous or heterogeneous processes, depending on the availability of foreign condensation nuclei, and the vapour supersaturations. Temperature gradients in the core are likely to be high, which favours the homogeneous process. The theory of homogeneous nucleation, however, is not completely successful in accounting for experimental data. Recently, attention has been given to the effect of other gases present in the system and whether their pressure affects the nucleation process. Since the pressure can vary widely depending on the reactor system, this is an important consideration.

This paper seeks to explore the effect of a carrier gas on the equilibrium between a vapour and its condensate. This equilibrium has an important bearing on the nucleation rate. The effect has been calculated previously from thermodynamics leading to the conclusion that, for ideal gas and vapour, the equilibrium vapour pressure p_{ve} behaves as

$$p_{ve} = p_{ve}^0 \exp \frac{v_0(p - p_{ve}^0)}{kT}, \quad (1)$$

where p is the total pressure, p_{ve}^0 is the equilibrium vapour pressure in the absence of the carrier gas, v_0 is the liquid volume per molecule of condensate and kT is Boltzmann's constant multiplied by absolute temperature. This is sometimes known as the Poynting correction (Poynting, 1881). When non-ideal behaviour is taken into account the new equilibrium is often expressed by (Beattie, 1949)

$$p x_v = p_{ve}^0 \exp \left[\frac{v_0(p - p_{ve}^0)}{kT} + \frac{(B_g - 2B_{gv})p}{RT} \right], \quad (2)$$

to first order in p , where x_v is the mole fraction of vapour in the mixture and B_g and B_{gv} are the gas and vapour–gas interaction second virial coefficients, which are defined according to the equation of state

$$\frac{p\tilde{V}}{RT} = 1 + \frac{B}{\tilde{V}} + O\left(\frac{1}{\tilde{V}^2}\right), \quad (3)$$

and

$$B = \sum_{\ell} x_{\ell} x_m B_{\ell m}, \quad (4)$$

which also involves the vapour second virial coefficient, B_v , with x_{ℓ} the mixture mole fractions ($\ell = v, g$) and where \bar{V} is the molar volume (Beattie, 1949).

Equations (1) and (2) state that the presence of a carrier gas alters the equilibrium between a vapour and its condensate. The significance as far as nucleation is concerned is that the supersaturation, the driving force for the phase transition, is affected by the carrier gas, so that there will appear a pressure dependence in the nucleation rate. Before estimating the appropriate virial coefficients and calculating the sensitivity of the nucleation rate to pressure, we seek to clarify equation (2) by approaching the problem through statistical mechanics. We work with a specific model of cluster interactions (the square well cluster potential) which serves as an illustration of the more abstract thermodynamic approach.

Previous attempts to include monomer-cluster interactions include the IMC model (Kobraei and Anderson, 1988, 1991) though this has not included the effect of a carrier gas. Also, the pressure effect resulting from the Poynting correction has been recognised and estimated (Mirabel, 1991). The significance of the virial coefficient corrections in equation (2), however, has not been addressed within nucleation theory.

2. STATISTICAL MECHANICS APPROACH

Previous work derived equilibrium cluster populations for an ideal vapour neglecting excluded volume effects (Barrett *et al.*, 1991). The partition function is

$$Z = \sum_{\{n_i\}} \left(\prod_{i \geq 2} \frac{q_i^{n_i} (V\gamma)^{n_i}}{n_i! n_1!} \right), \quad (5)$$

where $\{n_i\}$ denotes a set of cluster populations where there are n_i clusters of size i , subject to the constraint $\sum_i i n_i = N$, with N the total number of vapour molecules in the system. V is the system volume and $\gamma = (2\pi mkT/h^2)^{3/2}$, where m is the vapour molecular mass and h is Planck's constant. The i -cluster partition function q_i is given, in the square well cluster potential model, by

$$q_i = \frac{\gamma^i V v_0^{i-1} i^{i+2}}{i!} \exp(-U_i/kT), \quad (6)$$

with v_0 the liquid volume per molecule and U_i the i -cluster potential energy, which we take here to be of the form

$$U_i = bi^{2/3} - ai. \quad (7)$$

Note that this is the cluster potential energy and not the Gibbs energy of cluster formation (Ford and Barrett, 1991). We assume here the centre of mass coordinate system definition of a cluster (Reiss *et al.*, 1990). Other cluster definitions slightly alter the result for q_i given above, as has been examined elsewhere (Ford and Barrett, 1991), but we use this definition here as it is the most widely used and does not affect the pressure dependence we seek to illustrate. Also, the cluster potential equation (7) we use is not consistent at $i=1$. The consequences of ensuring that $U_1=0$ have been studied (Ford and Barrett, 1991), but for simplicity this matter is neglected, again because the pressure effect does not depend on such considerations.

The partition function Z is given, to a good approximation, by the largest term in the sum over sets of $\{n_i\}$: this leads to

$$Z \approx \prod_{i \geq 2} \frac{q_i^{n_i} (V\gamma)^{n_i}}{n_i! n_1!}, \quad (8)$$

with the n_i given by the law of mass action

$$n_i = q_i \left(\frac{n_1}{q_1} \right)^i. \quad (9)$$

This development leads to a nucleation rate independent of carrier gas pressure: in other words the n_i are independent of the number of carrier gas molecules, n_g . We shall now introduce such a dependence.

Interactions between all species present in a mixture of vapour monomers, clusters and carrier gas molecules, appear in the development when the phase space integrals over particle positions are done more carefully. Previously, particle positions were allowed throughout the whole system volume, neglecting the effect of interactions. This led to the factors of V in equations (5) and (6). The phase space integral to be evaluated is

$$Q = \int \exp(-\beta H_{\text{int}}) \prod_j d^3 \mathbf{r}_j^v \prod_k d^3 \mathbf{r}_k^g \prod_i \left(\prod_{\ell} d^3 \mathbf{r}_\ell^i \right), \quad (10)$$

where $\beta = (kT)^{-1}$ and H_{int} specifies a set of two-body potentials depending on the positions of vapour monomers $\{\mathbf{r}_j^v\}$, gas molecules $\{\mathbf{r}_k^g\}$ and i -cluster centres of mass $\{\mathbf{r}_\ell^i\}$. If $H_{\text{int}} = 0$ then this yields $V^{n_1} \prod_{i \geq 2} V^{n_i} V^{n_g}$. The inclusion of a carrier gas into the system without considering interactions would produce a gas partition function as an extra factor in equation (5), which would have had no effect on the cluster populations. This was implicitly neglected in the derivation of equation (5).

Equation (10) can be evaluated, leading to

$$\begin{aligned} Q \approx V^{n_1} \prod_{i \geq 2} V^{n_i} V^{n_g} & \left(1 + \frac{1}{2} n_g(n_g - 1) I_g/V + \frac{1}{2} n_1(n_1 - 1) I_v/V \right. \\ & + \sum_{i \geq 2} \frac{1}{2} n_i(n_i - 1) I_i/V + n_1 n_g I_{gv}/V \\ & \left. + \sum_{i \geq 2} n_1 n_i I_{1i}/V + \sum_{i \geq 2} n_g n_i I_{gi}/V + \sum_{i \neq j \geq 2} n_i n_j I_{ij}/V \right), \end{aligned} \quad (11)$$

where

$$I_{k\ell} = \int (\exp(-\beta \phi_{k\ell}) - 1) d^3 r, \quad (12)$$

and $\phi_{k\ell}$ denotes the interaction potential between species k and species ℓ . I_{kk} is denoted I_k and the suffix k can be g or i ($i \geq 1$). (The label v will be used interchangeably with 1 to denote vapour monomers.) The extra terms in equation (11) correspond to contributions to equation (10) from all possible pairwise combinations of the available species.

In passing, it should be mentioned that Kobraei and Anderson have suggested the IMC model which includes monomer-monomer and monomer-cluster interactions (Kobraei and Anderson, 1991) but not interactions with a carrier gas. We shall see that the latter are much more important, indeed the IMC model shows sizeable deviations from the interaction-free theory only for very low temperatures (Kobraei and Anderson, 1988).

We now consider a situation where the interactions between clusters and both monomers and gas molecules are simply due to excluded volume effects. That is to say $\phi_{gi} \rightarrow \infty$ within the cluster volume iv_0 and zero outside, and similarly for ϕ_{1i} . Then

$$I_{1i} = I_{gi} = -iv_0. \quad (13)$$

We also drop cross-terms in equation (11) between clusters with two or more atoms in each. Then we have

$$Z = \sum_{\{n_i\}} \left(\prod_{i \geq 2} \frac{q_i^{n_i} (V\gamma)^{n_i}}{n_i!} \frac{(V\gamma_g)^{n_g}}{n_g!} Z_i \right), \quad (14)$$

where

$$Z_i = 1 + \frac{1}{2} n_g(n_g - 1) I_g/V + \frac{1}{2} n_1(n_1 - 1) I_v/V + n_1 n_g I_{gv}/V - \sum_{i \geq 2} (n_1 + n_g) n_i iv_0/V. \quad (15)$$

As before, the set $\{n_i\}$ is chosen by extremizing the logarithm of the general term in the sum in equation (14), again subject to $\sum_{i=1}^{\infty} in_i = N$. Using the method of Lagrange multipliers

this leads to a corrected form of the law of mass action. In detail, we have, for $i \geq 2$

$$\ln q_i - \ln n_i - (n_1 + n_g)i v_0/V - i\lambda = 0, \quad (16)$$

and

$$\ln \gamma V - \ln n_1 + \frac{1}{2}(2n_1 - 1)I_v/V + n_g I_{gv}/V - \sum_{i \geq 2} i n_i v_0/V - \lambda = 0, \quad (17)$$

where we have expanded $\ln Z_i$ to first order and λ is the Lagrange multiplier for the given constraint. Neglecting the sum of cluster terms in equation (17) we have

$$n_i = q_i \left(\frac{n_1}{\gamma V} \right)^i \exp \left(\frac{1}{2} i(2n_1 - 1)I_v/V - i n_g I_{gv}/V - \frac{i p v_0}{kT} \right), \quad (18)$$

where we have used $pV = (n_1 + n_g)kT$, neglecting a term in p^2 . Note that the last term in the exponent, which corresponds to Poynting's correction in equation (1) as we shall find shortly, arises from the exclusion of vapour monomers and gas molecules from the cluster volumes.

Combining equations (6) and (18) we now have

$$n_i = \exp \left[-\beta U_i + \ln(\gamma^i V i^{i+2}/i!) + (i-1) \ln v_0 + i \ln(n_1/(\gamma V)) - \frac{1}{2} i(2n_1 - 1)I_v/V - i n_g I_{gv}/V - i p v_0/(kT) \right]. \quad (19)$$

This expression allows us to study the equilibrium between monomer and condensate, and the effect on this due to the carrier gas. For $n_1 = n_1^e$, the monomer population in equilibrium with a plane surface of condensate, the derivative of the exponent must vanish as $i \rightarrow \infty$. If we consider equilibrium in the absence of carrier gas and use equation (7) then this results in

$$a\beta + 1 + \ln v_0 + \ln n_1^e - \ln V - \frac{1}{2}(2n_1^e - 1)I_v/V - p_{ve}^0 v_0/(kT) = 0, \quad (20)$$

where we have made use of Stirling's formula. On substituting back into equation (19) this yields

$$n_i = \exp \left[-\beta b i^{2/3} + \frac{3}{2} \ln i - \ln(2\pi)^{1/2} - \ln(v_0/V) + i \ln(n_1/n_1^e) - i(n_1 - n_1^e)I_v/V - i n_g I_{gv}/V - i(p - p_{ve}^0)v_0/(kT) \right]. \quad (21)$$

Using

$$\frac{n_1}{V} \approx \frac{p_v}{kT} \left(1 - \frac{p_v I_v}{2kT} \right) \quad (22)$$

and a similar expression for n_g , we then obtain

$$n_i = n_1 \exp \left[-\beta b i^{2/3} + \frac{3}{2} \ln i - \ln(2\pi)^{1/2} - \ln(v_0/V) + (i-1) \ln S - (i-1)(p_v - p_{ve}^0)I_v/(2kT) - \ln n_1^e - i(p_v - p_{ve}^0)I_v/(kT) - i(p - p_v)I_{gv}/(kT) - i(p - p_{ve}^0)v_0/(kT) \right], \quad (23)$$

where the supersaturation $S = p_v/p_{ve}^0$ and terms in p_v^2 , etc. have been dropped. We have written the populations with the standard prefactor of n_1 . This can be rewritten

$$n_i = n_1 \exp \left[-b i^{2/3}/(kT) + \frac{3}{2} \ln i - \ln(2\pi)^{1/2} + (i-1) \ln S \right]$$

$$\begin{aligned} & -\ln(p_{ve}^0 v_0/(kT) - 3i(p_v - p_{ve}^0)I_v/(2kT) \\ & + p_v I_v/(2kT)) - i(p - p_v)I_{gv}/(kT) - i(p - p_{ve}^0)v_0/(kT) \end{aligned} \quad (24)$$

or, by introducing second virial coefficients, as

$$\begin{aligned} n_i = n_1 \exp \left[-bi^{2/3}/(kT) + \frac{3}{2} \ln i - \ln(2\pi)^{1/2} + i \ln S - \ln(p_v v_0/(kT)) \right. \\ \left. + 3i(S-1)p_{ve}^0 B_v/(RT) - p_v B_v/(RT) + 2i(p - p_v)B_{gv}/(RT) - i(p - p_{ve}^0)v_0/(kT) \right], \end{aligned} \quad (25)$$

where R is the gas constant and

$$B_v = -I_v N_A/2 \quad (26)$$

is the usual definition of a second virial coefficient in terms of the intermolecular potential, where N_A is Avogadro's number (Hirschfelder *et al.*, 1964). We now see how a carrier gas alters the vapour-plane condensate equilibrium: the supersaturation corresponding to the new equilibrium is given by

$$\ln S = (p - p_{ve}^0)v_0/(kT) - 3(S-1)p_{ve}^0 B_v/(RT) - 2(p - Sp_{ve}^0)B_{gv}/(RT). \quad (27)$$

This equation describes in a form suitable for nucleation theory the change in equilibrium between vapour and liquid brought about by non-ideal effects and the presence of a carrier gas. Equation (2) is not suitable, though it can easily be generated from equations (14), (15) and (21). The difference between equations (2) and (27), apart from small terms, is the term involving B_g .

We now drop terms in the exponent in equations (25) which are proportional to p_{ve}^0 since these are small, and write

$$\begin{aligned} n_i = n_1 \exp \left[-\frac{1}{kT} \left(bi^{2/3} - kT \ln \left(\frac{i^{3/2}}{(2\pi)^{1/2}} \right) - ikT \ln S \right. \right. \\ \left. \left. + kT \ln \left(\frac{p_v v_0}{kT} \right) + ip(v_0 - 2B_{gv}/N_A) \right) \right]. \end{aligned} \quad (28)$$

This form is valid for clusters with $i \gg 1$.

3. PRESSURE DEPENDENCE OF NUCLEATION RATE

The nucleation rate of droplets can now be obtained by standard methods (Hung *et al.*, 1989):

$$J = \left(\frac{2\sigma_0}{\pi m} \right)^{1/2} \frac{Sp_{ve}^0 q}{kT} \frac{q}{(2\pi)^{1/2}} \left(1 - \frac{27kT}{4bi^{*2/3}} \right) \exp \left[\frac{3}{2} \ln i^* - \frac{3}{2} \frac{bi^{*2/3}}{3kT} \right] \quad (29)$$

with

$$\ln S = \frac{2b}{3kTi^{*1/3}} - \frac{3}{2i^*} + \frac{p(v_0 - 2B_{gv}/N_A)}{kT}, \quad (30)$$

and where we have used the capillarity approximation, i.e. $b = A_1 \sigma_0$ with $A_1 i^{2/3}$ the surface area of an i -cluster and σ_0 the bulk liquid surface tension. i^* is the critical size corresponding to the maximum of the exponent in equation (28), and q is the sticking coefficient. It is possible to examine the pressure dependence of J analytically by neglecting the $\ln i^*$ term in the exponent in equation (29) and the $3/(2i^*)$ term in equation (30). Then

$$\begin{aligned} \frac{d \ln J}{dp} &= \frac{-8}{27kT} \left(\frac{b}{kT} \right)^3 \frac{(v_0 - 2B_{gv}/N_A)}{(\ln S - p(v_0 - 2B_{gv}/N_A)/(kT))^3} \\ &= \frac{-32\pi v_0^2}{3kT} \left(\frac{\sigma_0}{kT} \right)^3 \frac{(v_0 - 2B_{gv}/N_A)}{(\ln S - p(v_0 - 2B_{gv}/N_A)/(kT))^3}, \end{aligned} \quad (31)$$

where we have used $b = \sigma_0(36\pi v_0^2)^{1/3}$ (Hung *et al.*, 1989).

Now, for *n*-nonane at 273 K, $v_0 \approx 2.8 \times 10^{-28} \text{ m}^3$ (Hung *et al.*, 1989) and so $pv_0/(kT) \approx 7.34 \times 10^{-3}$ at 10^5 Pa and 273 K. This is small compared to $\ln S$ if $S \approx 10$, and taking $2B_{gv}/N_A$ to be of the same order of magnitude, we can then write

$$\frac{d \ln J}{d p} \approx \frac{-32\pi v_0^2}{3kT} \left(\frac{\sigma_0}{kT} \right)^3 \frac{(v_0 - 2B_{gv}/N_A)}{(\ln S)^3}. \quad (32)$$

Using $\sigma_0 = 2.472 \times 10^{-2} \text{ Nm}^{-1}$ and $S = 10$ this gives

$$\frac{d \ln J}{d p} \approx -4.37 \times 10^{-6} (1 - 2B_{gv}/(N_A v_0)). \quad (33)$$

Neglecting B_{gv} , the p dependence of J is small, as has been noted before (Mirabel, 1991).

Second virial coefficients have been measured for many pure substances and correlated in terms of an assumed Lennard-Jones intermolecular potential, involving depth and range parameters ε and σ , respectively. Interaction second virial coefficients can be calculated using effective Lennard-Jones parameters given by

$$\begin{aligned} \varepsilon_{12} &= (\varepsilon_1 \varepsilon_2)^{1/2} \\ \sigma_{12} &= \frac{1}{2}(\sigma_1 + \sigma_2), \end{aligned} \quad (34)$$

where the single suffix parameters refer to the pure substances (Hirschfelder *et al.*, 1964). Tables of measured values are also available for some mixtures (Dymond and Smith, 1980). Table 1 gives the calculated values of B_{gv} at 273 K for mixtures of *n*-nonane with various carrier gases. Data are available for *n*-nonane in argon at 323 K and 353 K (Dymond and Smith, 1980; Vigdergauz and Semkin, 1971), which is described well by the parametrization in Table 1. The Table also gives the nucleation rate reduction factor per 10^5 Pa pressure increment, calculated according to equation (33) with $S = 10$ and $T = 273 \text{ K}$. The most sensitive mixture considered is *n*-nonane/argon, with a six-fold reduction in nucleation rate due to an increase in the carrier gas pressure by 10^5 Pa . The other carrier gases lead to rather smaller corrections. Non-isothermal effects (Barrett *et al.*, 1991; Feder *et al.*, 1966) in the theory of nucleation lead to an increase in rate with total pressure, strongest at low p_v/p . Both pressure effects are shown in Fig. 1, for *n*-nonane in argon.

Various measurements of the pressure dependence of the nucleation rate have been made. Katz *et al.* (1988) observed a reduction in J by nine orders of magnitude over a pressure interval of about 3 atm in diffusion chamber experiments using *n*-nonane in H_2 or He. The pressure effect described here would be small and cannot account for this behaviour. Wagner and Strey (1984), however, used argon as the carrier gas in their expansion chamber experiments, but for *n*-nonane operated at higher supersaturations ($S \geq 100$) and lower temperatures compared with our reference case. Referring to equation (32), we see that the slope of $\ln J$ against p is a factor of 8 smaller of $S = 100$ instead of 10. The effect is therefore

Table 1. Lennard-Jones parameters for pure substances, calculated from measured second virial coefficients (Hirschfelder *et al.*, 1964) and estimated parameters and interaction virial coefficients for various mixtures, at 273 K. Also shown is the correction factor to the pressure independent nucleation rate expression, arising from imperfect gas behaviour at $p = 10^5 \text{ Pa}$, $S = 10$ and $T = 273 \text{ K}$

	$\varepsilon/k \text{ (K)}$	$\sigma \text{ (\AA)}$	$B_{gv} \text{ (cm}^3 \text{ mol}^{-1}\text{)}$	$\frac{J(p = 10^5 \text{ Pa})}{J_{p\text{-independent}}}$
<i>n</i> -nonane	240	8.45	—	—
He	10.24	2.56	—	—
H_2	29.2	2.87	—	—
Ar	120	3.405	—	—
<i>n</i> -nonane/He	49.6	5.53	60	0.89
<i>n</i> -nonane/ H_2	83.7	5.66	-6.6	0.62
<i>n</i> -nonane/Ar	170	5.92	-276	0.15

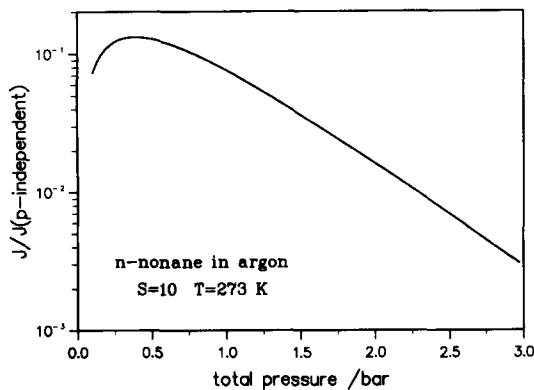


Fig. 1. Dependence of nucleation rate on total pressure: an increase at low pressures due to non-isothermal effects and a decrease at high pressures due to imperfect vapour/carrier gas properties.

unlikely to be large for these experiments. Strey *et al.* (1991) studied nucleation of *n*-hexanol in argon at $S \approx 10$, and $T \approx 273$ K and found no apparent difference in rates at 1.3 bar and 0.65 bar. Using $\sigma_0 = 0.02784 \text{ Nm}^{-1}$, and $v_0 = 2.04 \times 10^{-28} \text{ m}^2$ (Strey and Schmeling, 1983) we obtain from equation (32)

$$\frac{d \ln J}{dp} \approx -2.49 \times 10^{-6} \left(1 - \frac{2B_{gv}}{v_0 N_A} \right) \quad (35)$$

for the *n*-hexanol/argon mixture. Lennard-Jones parameters for *n*-hexanol could not be found in the literature, but using those for *n*-hexane (Hirschfelder *et al.*, 1964) leads to the estimate $B_{gv} \approx -229 \text{ cm}^3 \text{ mol}^{-1}$ at 273 K. In actual fact, the Lennard-Jones parameters for hexane do not provide a good description of the data for this substance (Dymond and Smith, 1980; Cruikshank *et al.*, 1966), so it is preferable to make an estimate based upon the available experiments in the range 293–323 K (Cruikshank *et al.*, 1966). This leads to the approximate value $B_{gv} \approx -150 \text{ cm}^3 \text{ mol}^{-1}$ at 273 K for *n*-hexane. The use of *n*-hexane data to provide the virial coefficient for *n*-hexanol in argon is supported by the similarity of interaction virial coefficients for butanol and *n*-butane in argon, and *n*-propanol and propane in argon (Dymond and Smith, 1980). The value of $-150 \text{ cm}^3 \text{ mol}^{-1}$ leads to a reduction in J by a factor of 0.57 on increasing the pressure from 0.65 bar to 1.3 bar. Non-isothermal effects leads to an increase in J by a factor of 1.19 due to this change of pressure, which partially offsets the above reduction, but still a reduction of the nucleation rate by about a third, under the given conditions, is expected on the basis of the above approximations. The null result of Strey *et al.* (1991) may indicate that the interaction virial coefficient for *n*-hexanol is not well approximated by that of *n*-hexane, or perhaps the effect described here is below the level of sensitivity of the experiment.

In general, the pressure dependence of the nucleation rate due to gas molecule/cluster and gas molecule/monomer interactions is strongest when the supersaturation is low (~ 10) and the carrier gas molecule concentration large.

Let us briefly consider whether the changes in equilibrium vapour pressure described above affect the interpretation of data from various experimental techniques. In expansion chambers, the initial vapour pressure is not necessarily saturated. After the expansion, the vapour pressure can be calculated based on an adiabatic expansion. The nucleation rate is then given by equations (29) and (30). However, with diffusion chambers, the vapour pressure profile is determined by the equilibrium vapour pressure at the pool surface. Thus not only p_{ve} but also p_v is dependent on the total pressure, though the dependence of p_v is weaker. At the nucleation position in the chamber, we can write $p_{ve} \approx p_{ve}^0 \exp(\alpha p/T_n)$ with $\alpha = v_0/k - 2B_{gv}/R$ and T_n the nucleation temperature. Assuming the vapour pressure profile in the chamber is linear and $p_{ve} \approx 0$ at the roof, the local vapour pressure p_v is changed by an amount related to the pressure dependent elevation of the equilibrium vapour pressure at

the pool surface: $p_v = p_v^0 \exp(\alpha p/T_p)$, where p_v^0 is the unperturbed vapour pressure and T_p the pool temperature. The supersaturation at the nucleation position is therefore given by

$$S = S^0 \exp \left[-\frac{\alpha p}{T_n} \left(1 - \frac{T_n}{T_p} \right) \right], \quad (36)$$

where S^0 is the unadjusted supersaturation. Using, for example, $T_p = 330$ K and $T_n = 270$ K (Hung *et al.*, 1989) the factor in round brackets in equation (36) is about 0.18. The pressure effect on the nucleation rate calculated earlier would therefore be very much suppressed when the measurements are made with a diffusion chamber.

Finally, we consider in more detail the gas molecule/cluster interaction potential which was assumed earlier to be infinite for gas molecule positions within the cluster and zero outside. This led to an excluded volume interaction and the ipv_0 term in equation (28). If the interaction extended outside the cluster then an additional term would appear in equation (15), which would lead to the following term in the exponent in equation (28)

$$\Sigma = \frac{p}{kT} \int (\exp(-\phi_{gi}/(kT)) - 1) d^3r, \quad (37)$$

where ϕ_{gi} is the cluster-gas molecule interaction potential and the integral is taken to be over the volume outside the cluster sphere of volume iv_0 . In order to proceed, let us assume that ϕ_{gi} is a constant, ϕ_0 , out to a range d from the surface. Then

$$\Sigma \approx \frac{-p \phi_0}{kT} A_1 i^{2/3} d, \quad (38)$$

so that the model has a pressure dependent surface tension

$$\sigma' = \sigma + \frac{p \phi_0 d}{kT}. \quad (39)$$

However, this effect is almost certainly small, since even for $\phi_0 \approx kT$, $d \approx 5$ Å, $p = 10^5$ Pa the change in surface tension is only about 0.2%.

4. CONCLUSIONS

A pressure dependence of the rate of homogeneous nucleation of a radioactive aerosol within a reactor core during a severe accident would have to be taken into account in the modelling of the system. Such a dependence has been observed experimentally and we here attempt to formulate a possible explanation involving imperfect gas properties.

The effect of an imperfect carrier gas on the phase equilibrium between an imperfect vapour and its condensate has been studied, within a statistical mechanical approach. Corrections to the equilibrium vapour pressure arise due to interactions between the gas molecule, vapour monomer and cluster species in the mixture. These are represented in equations (2) and (27) by second virial coefficients. Interaction between monomers and gas molecules alters the monomer concentration, as shown in equations (17) and (26) involving the interaction virial coefficient B_{gv} . Interaction between clusters and gas molecules introduces, in our model, the Poynting correction in equations (16) and (27) as well as a pressure dependent cluster surface tension, equation (39), but more generally can be treated in terms of a cluster-gas molecule interaction virial coefficient. Together, these corrections lead to a dependence of the equilibrium populations of clusters on the total system pressure. This introduces a pressure dependence for the droplet nucleation rate. The dependence, however, is sensitive to the carrier gas used. For helium and hydrogen the effect is small, but for a carrier gas of argon, the nucleation of *n*-nonane droplets from vapour shows an appreciable pressure dependence at 273 K and a supersaturation of 10. Whichever gas is used, the effect is strongest at low supersaturations. The effect is more pronounced in expansion chamber experiments rather than in diffusion chambers.

Unless the estimates made of interaction virial coefficients are very inaccurate the effect cannot explain the strong pressure dependence of *n*-nonane nucleation rates in diffusion chamber experiments with H₂ and He carrier gases (Katz *et al.*, 1988). Nevertheless, other experiments with other substances and techniques show little or no pressure dependence (Strey *et al.*, 1991), so the situation is unclear. For *n*-hexanol nucleation in argon at 273 K and a supersaturation of 10 we predict a 30% reduction in the rate as the pressure is raised from 0.65 bar to 1.3 bar. The null result for these conditions experimentally (Strey *et al.*, 1991) suggests that the estimate is either inaccurate, below experimental sensitivity, or that additional effects are operating.

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