

UNCERTAINTIES IN CLUSTER ENERGIES IN HOMOGENEOUS NUCLEATION THEORY

I. J. FORD,* J. C. BARRETT* and M. LAZARIDIS†

* Theoretical Studies Department, AEA Industrial Technology, B424.4, Harwell Laboratory, Didcot, Oxon OX11 0RA, U.K. and † Technical Research Centre of Finland, Aerosol Technology Group, Nuclear Engineering Laboratory, P.O. Box 208, SF-02150 Espoo, Finland

(First received 20 November 1992; and in final form 25 March 1993)

Abstract—A statistical mechanical theory of homogeneous nucleation is developed based on a cluster potential energy which is independent of the position of the molecules in the cluster. The way in which the potential energy vanishes for clusters consisting of single monomers is shown to have an appreciable effect on the nucleation rate. Various possible models are obtained which have similarities to several other models in the literature. By equating constants in the potential with bulk values for the latent heat and surface tension, predictions of the model can be obtained. The theory predicts a temperature dependent enhancement of the nucleation rate compared to classical theory and shows better agreement with experimental data for some, but not all substances.

1. INTRODUCTION

A phase transition is driven by a reduction in the free energy of the system, but there are circumstances close to the equilibrium conditions where the original phase is metastable. A thermal fluctuation is required to nucleate the new phase since there is a free energy barrier between the two phases. Nucleation is important in a variety of areas of science and technology. In materials science, the properties of films and castings can depend on the grain structure, which is determined by the nucleation mechanism. Cloud formation has implications in the atmosphere as well as in certain manufacturing processes.

In our special area of interest, an understanding of aerosol nucleation is necessary for the analysis of nuclear reactor accidents which lead to the overheating of the reactor core. Volatile fission products such as caesium or iodine, or control rod materials such as cadmium or silver, could be released in such circumstances, and the transport of radioactive substances out of the core and possibly into the environment is of great concern. Aerosol transport is the most effective mechanism for wide dispersal, and the nucleation of particles from the vapours as they cool is an important process. Since large temperature gradients are expected in an overheated core, high supersaturations are possible, and so homogeneous nucleation is likely to be an important mechanism for particle formation. Heterogeneous nucleation, where foreign particles act as condensation nuclei, may also occur.

The theory of liquid droplet formation from supersaturated, metastable vapours is, however, unable to account for the growing body of experimental measurements (Oxtoby, 1992). Some aspects, for instance the supersaturation dependence of the rate of homogeneous nucleation, can be explained successfully, but the temperature dependence of the predictions can be wildly inaccurate. For this reason, together with the practical importance of nucleation phenomena, much recent interest has been directed at the problem.

The potential energy of a cluster of interacting monomers enters into most theoretical treatments of the homogeneous nucleation of liquid droplets from a supersaturated vapour. Expressions for the potential energy should vanish for a cluster consisting of a single monomer. Since in most homogeneous nucleation theories (Volmer and Weber, 1926; Becker and Döring, 1935) it is the energy of the critical cluster, typically consisting of tens or hundreds of monomers, which is important, this detail is usually considered to be irrelevant. A recent paper (Girshick and Chiu, 1990), however, highlighted the fact that requiring the free energy change for monomers to vanish in a particular way, a property referred to as self-consistency or just consistency, could lead to substantial changes in predictions. The free energy expression is related to the cluster potential energy and the purpose of this paper

is to demonstrate the connection and show that consistent free energies rely on cluster potential energies which vanish for monomers. We also aim to place the theory on a firm statistical mechanical basis. There are uncertainties in the manner in which the potential energy goes to zero for small clusters, however, leading to a variety of models. These differ substantially from the usual classical theory (Becker and Döring, 1935) and include the model suggested by Girshick and Chiu (1990) and Girshick (1991), as a special case.

In the following section we review the classical theory and then present a statistical mechanical model which leads to a similar form. In section 3 we investigate various possible choices for the cluster potential energy and illustrate the consequences of each. In section 4 we compare the predictions of our model with experimental nucleation rates and in section 5 we draw conclusions.

2. THE CLASSICAL THEORY AND A STATISTICAL MECHANICAL APPROACH

The classical theory treats nucleation in terms of the passage of clusters over a free energy barrier separating a metastable vapour state from a stable condensed state. The rate of passage can be written (Becker and Döring, 1935)

$$J = C n_{i^*}, \quad (1)$$

where n_{i^*} is the thermal equilibrium population of clusters containing i^* monomers, i^* being the critical size where the peak in free energy occurs. The parameter C is the product of the collision rate of monomers with the critical cluster and the "Zeldovich factor" which accounts for non-equilibrium effects (Zeldovich, 1943).

Cluster populations in thermal equilibrium are written

$$n_i = n_1 \exp(-\Delta G_i/kT), \quad (2)$$

where n_1 is the population of monomers, ΔG_i is the free energy change of cluster formation and kT is Boltzmann's constant multiplied by the absolute temperature. Classical theory is based upon the model:

$$\Delta G_i = \sigma A_1 i^{2/3} - ikT \ln S, \quad (3)$$

where $A_1 i^{2/3}$ is the surface area of the i -cluster, σ the bulk liquid surface tension and S the supersaturation, which is the ratio of actual vapour pressure to the vapour pressure which would be in equilibrium with a plane surface of condensate.

We see immediately that ΔG_1 is not zero, which is inconsistent with equation (2). The simplest means of imposing this is to write (Girshick and Chiu, 1990),

$$\Delta G_i = \sigma A_1 (i^{2/3} - 1) - (i - 1)kT \ln S, \quad (4)$$

which introduces large changes in the calculated cluster populations. We shall examine the assumptions implicit in choosing this form later in this paper.

A form similar to the classical result can be derived from a statistical mechanical model. Our starting point is the law of mass action (Abraham, 1974)

$$n_i = q_i \left(\frac{n_1}{q_1} \right)^i, \quad (5)$$

where q_i is the partition function for an i -cluster,

$$q_i = \frac{1}{i! h^{3i}} \int \prod_{j=1}^i d\mathbf{p}_j \int \prod_{v=1}^i d\mathbf{x}_j \exp \frac{-1}{kT} \left[\frac{1}{2m} \sum_{j=1}^i \mathbf{p}_j^2 + U_i(\{\mathbf{x}_j\}) \right], \quad (6)$$

which involves the monomer momenta and positions \mathbf{p}_j and \mathbf{x}_j , the monomer mass m and the i -cluster potential energy $U_i(\{\mathbf{x}_j\})$. h is Planck's constant. Also implicit is a cluster definition which provides a constraint over the integration of the $\{\mathbf{x}_j\}$. We assume that U_i is independent of the molecular positions within the cluster. This approximation was used by

Abraham (1968), who used a square well interaction to evaluate U_i , and by Huang and Seinfeld (1992) who found U_i using the cell model of liquids.

The importance of cluster definition in nucleation theory has been discussed recently by Ellerby *et al.* (1991). They note that, to avoid overcounting, the cluster volume should be defined with its centre at the centre of mass of the molecules in the cluster. Abraham (1968) used a cluster centred on one of the molecules of the cluster, but with this definition some arrangements are not counted. On the other hand, the cluster used by Huang and Seinfeld (1992) has boundaries fixed in space and so its centre of mass fluctuates. As noted by Reiss *et al.* (1968) these fluctuations should be compensated for by introducing a factor $P(0)$, equal to the probability density that the cluster centre is at the origin. This can be estimated as discussed by Reiss *et al.* (1968): a single molecule moving at random in a sphere of volume v_i centred on the origin has a probability distribution for its x -displacement with mean zero and variance $1/5(3v_i/4\pi)^{2/3}$. For i molecules moving independently in the sphere, the x -displacement of the centre of mass is the mean of the x -displacements of the individual molecules and, by the central limit theorem, this has a normal distribution with mean zero and variance $1/(5i)(3v_i/4\pi)^{2/3}$ for large i . The y - and z -displacements have the same distributions so $P(0)$ is given by the product of these distributions evaluated at $x=y=z=0$.

The partition function, λ_i , for a cluster of i molecules in a volume v_i , with boundaries fixed in space, is simply

$$\lambda_i = \frac{\gamma^i v_i^i}{i!} \exp(-U_i/kT), \quad (7)$$

where $\gamma = (2\pi mkT/h^2)^{3/2}$. The required partition function q_i is related to λ_i by Reiss *et al.* (1968)

$$q_i = \lambda_i V P(0) = \frac{5}{3} \left(\frac{10}{\pi} \right)^{1/2} \frac{\gamma^i V v_0^{i-1} i^{i+1/2}}{i!} \exp(-U_i/kT), \quad (8)$$

where $v_0 = v_i/i$ is the cluster volume per monomer and V is the total volume of the vapour-condensate system.

Using equations (5), (7) and (2) we now have

$$\Delta G_i = U_i - (i-1)kT \ln \frac{n_1 v_0}{V} + kT \ln \left(\frac{i!}{i^{i+1/2}} \frac{3}{5} \left(\frac{\pi}{10} \right)^{1/2} \right), \quad (9)$$

where we have used $q_1 = \gamma V$.

Now we write the potential energy as the sum of surface and volume terms:

$$U_i = b i^{2/3} g_s(i) - a i g_v(i), \quad (10)$$

which is of the usual form except for the introduction of two functions g_s and g_v , which have the properties:

$$g_s(1) = 0, \quad g_v(1) = 0, \quad (11)$$

and also

$$\lim [i^{2/3} g_s(i)] \rightarrow i^{2/3}, \quad \lim [i g_v(i)] \rightarrow i, \quad (12)$$

for large i , so that both U_1 is zero and the large i behaviour for U_i involves just volume and surface terms, proportional to i and $i^{2/3}$, respectively. We then have

$$\Delta G_i = b i^{2/3} g_s - a i g_v - (i-1)kT \ln \frac{n_1 v_0}{V} + kT \left(\ln \left[\frac{3\pi}{5^{3/2}} \left(1 + \frac{1}{12i} \right) \right] - i \right). \quad (13)$$

where we have used Stirling's formula:

$$i! \simeq (2\pi i)^{1/2} i^i e^{-i} \left(1 + \frac{1}{12i} \right) \quad (14)$$

to approximate the final term in square brackets in equation (9). It should be noted that the last term in equation (13) does not vanish when $i = 1$. This is due to the approximations used

to derive this term (namely, Stirling's formula and the central limit theorem). For $i=1$, $P(0)=1/v_1$ so the factor $3/5(\pi/10)^{1/2}$ in equation (9) is replaced by 1. Then ΔG_i does vanish for $i=1$.

For $n_1=n_{1e}$, the monomer population in equilibrium with a plane surface of condensate, we now impose the condition

$$\lim_{i \rightarrow \infty} \left[\frac{d\Delta G_i}{di} \right] = 0. \quad (15)$$

This is equivalent to demanding that the critical cluster for saturated conditions is the bulk liquid with a plane surface. No nucleation is permitted in such circumstances: Inserting equation (13) in equation (15) we find

$$p_{ve} = n_{1e} \frac{kT}{V} = \frac{kT}{ev_0} \exp\left(-\frac{a}{kT}\right). \quad (16)$$

Equation (16) has the same form as the Clausius–Clapeyron equation, if we identify a with L_1 , the molecular latent heat of condensation. Now ΔG_i becomes

$$\Delta G_i = bi^{2/3}g_s(i) - (i-1)kT \ln S - a(ig_v(i) - i + 1) + kT \left(\ln \frac{3\pi}{5^{3/2}} - 1 \right). \quad (17)$$

where we have introduced the supersaturation $S = n_1/n_{1e}$ and ignored the $1/12i$ term in equation (13). We see emerging the surface term and the $\ln S$ term expected from the thermodynamic approach (equations (3) and (4)) together with some extra contributions. To obtain the correct surface energy for large clusters, we identify b in equation (17) with the surface energy per molecule, $A_1\sigma$. The form of the g functions is addressed in the next section.

The introduction of the equilibrium condition equation (15) is the important step which links the statistical mechanical approach to the more usual thermodynamic treatments, and as far as we are aware, has not been made before. The relationship between terms in the free energy and the underlying cluster model is now explicit.

3. CLUSTER SURFACE AND VOLUME ENERGIES

Example g -functions can now help in illustrating the development. We consider the following simple forms:

$$g_s(i) = 1 - i^{-x}, \quad g_v(i) = 1 - i^{-y}. \quad (18)$$

For $x \geq 2/3$ and $y \geq 1$ these satisfy the conditions (11) and (12) and their use in equation (17) yields

$$\Delta G_i = b(i^{2/3} - i^{2/3-x}) - (i-1)kT \ln S - a(1 - i^{1-y}) + kT \ln \left(\frac{3\pi}{5^{3/2}e} \right). \quad (19)$$

With $x = 2/3$ and $y = 1$ we obtain the following expression for the free energy change on the formation of the critical cluster:

$$\Delta G_{i^*} = b(i^{*2/3} - 1) - (i^* - 1)kT \ln S + kT \ln \left(\frac{3\pi}{5^{3/2}e} \right), \quad (20)$$

which is the same as equation (4) (with $i = i^*$), apart from the small additional constant term. However, if instead we choose larger values of x and y , so that $(i^*)^{2/3-x}$ and $(i^*)^{1-y}$ are negligible compared to 1, we obtain from equation (19)

$$\Delta G_{i^*} \simeq bi^{*2/3} - (i^* - 1)kT \ln S - a + kT \ln \left(\frac{3\pi}{5^{3/2}e} \right). \quad (21)$$

Two more possibilities exist, not considered further here, corresponding to the choices $x = 2/3$, $y > 1$ and $x > 2/3$, $y = 1$. The classical theory uses equation (3) for ΔG_{i^*} in equa-

tions (1) and (2) to obtain the nucleation rate. Using equations (20) or (21) instead therefore leads to an enhancement of the classical nucleation rate by a factor $5^{3/2}e/(3\pi)\exp(b/kT)/S$ and $5^{3/2}e/(3\pi)\exp(a/kT)/S$, respectively. The former is similar to the correction factor suggested by Girshick and Chiu (1990). Taking $b = A_1\sigma$ and $a = L_1$ we have $b/kT \approx 12$ and $a/kT \approx 20$ for *n*-nonane at 273 K so these enhancements are significant; furthermore, it is clearly necessary to decide which choices of x and y are the most reasonable. Clearly, only a detailed model of cluster binding could provide this: in any case, the forms in equation (18) are not offered as unique choices: they simply contain the extremes of behaviour as special cases and help to classify the possibilities for ΔG_i^* listed above. Recent work by Dillmann and Meier (1989, 1990) involves a surface term with an assumed functional form, fixed by demanding the correct prediction of virial coefficients. This might be a procedure for establishing the g -functions experimentally.

We recall that additional approximations have been made in the development of equation (21), including use of the central limit theorem and Stirling's formula, so that corrections would be necessary for small i .

The basic uncertainty in the theory, corresponding to the form of the g -functions, lies in whether we expect the asymptotic form of the cluster energy to apply at the critical size, or only for very large i . That is to say, whether the large i limit of U_i :

$$U_i^L = bi^{2/3} - ai \quad (22)$$

applies close to i^* , which would correspond to the capillarity approximation, or whether $b(i^{2/3} - 1) - a(i - 1)$ (or some other form) is more appropriate. If we are to adhere to the capillarity approximation, which assumes that the critical cluster has the properties of a bulk liquid droplet, then we are required to choose $x > 2/3$ and $y > 1$ in which case equation (22) is a good approximation to the potential energy at the critical size and equation (21) is the appropriate free energy expression.

Model values of x and y could be provided by calculations of cluster energies using particular intermolecular forces. An analytic model, which is essentially a mean field approach, using a square well potential between monomers with depth ε and range η , yields (Abraham, 1974)

$$U_i = -\frac{\varepsilon}{2} \left(\frac{\eta}{r_0} \right)^3 \left(i - \frac{9}{16} \frac{\eta}{r_0} i^{2/3} \right), \quad (23)$$

where $r_0 = (3v_0/4\pi)^{1/3}$. Equation (23) has been used previously, arbitrarily multiplied by $(1 - i^{-1})$ to ensure that it vanishes at $i = 1$ (Abraham, 1968). In the light of our discussion, however, this factor is not necessary since equation (23) would not be expected to hold for all i down to $i = 1$.

We also mention in passing that the procedure employed by Abraham (1968) to determine the value of r_0 in equation (23) using second virial coefficient data is extremely sensitive to the small i behaviour of U_i and therefore to the forms of $g_s(i)$ and $g_v(i)$ used.

We shall concentrate in the next section on the predictions of the model when ΔG_i^* is given by equation (21), since an equation similar to equation (20) has previously been considered by Girshick and Chiu (1990).

4. DISCUSSION

Using a simple model of the cluster potential energy U_i , we have obtained expressions for the cluster formation free energy ΔG_i which differ from the classical expression, equation (3). Comparing equations (21) and (3), we see that equation (21) contains a $(i - 1)kT \ln S$ term, rather than $ikT \ln S$, and an additional term $-a$ which we have provisionally identified with $-L_1$, the molecular latent heat. This additional term also appears in a version of the theory of Reiss *et al.* (1968), which we refer to as RKC II. This theory uses,

$$\Delta G_i = bi^{2/3} - (i - 1)kT \ln S - kT \ln \left[\left(\frac{12}{\pi} \right)^{3/2} i^{1/2} \right] + kT \ln \frac{p_{ve} v_0}{kT} \quad (24)$$

with the final term equal to $-a-kT$ when equation (16) is used. The main difference between equations (24) and (21) lies in the appearance of the $-1/2kT \ln i$ term.

The free energy in an alternative version of the theory suggested by Reiss *et al.* (1968), which we refer to as RKCI, is given by

$$\Delta G_i = hi^{2/3} - ikT \ln S - kT \ln \left[\left(\frac{6}{\pi} \right)^{3/2} i^{3/2} \right], \quad (25)$$

which has no term corresponding to a , and has a different coefficient of the $\ln i$ term.

To illustrate the above discussion, we show in Fig. 1 a comparison between J_{exp} , the nucleation rate data for toluene (Schmitt *et al.*, 1983) and J_{th} , the theoretical rates arising from equations (1), (2) and (21). A similar comparison was made by Girshick and Chiu (1990), using equation (20) neglecting the small final term, and their predictions gave $J_{\text{th}}/J_{\text{exp}} \approx 10$. The figure also shows the RKCI and II predictions. The enhancement over classical theory due to the additional term $-a$ leads to better agreement with experiment in this case. However, for other substances, such as propanol (Strey *et al.*, 1986), classical theory gives the best agreement as shown in Fig. 2.

To obtain numerical results shown in Figs 1 and 2, we have used equation (16) to express a in terms of the equilibrium vapour pressure. It should be mentioned that the values of a obtained are somewhat less than the molecular latent heat, L_1 . This is because our square well model is too crude to give accurate quantitative predictions of the equilibrium vapour pressure. Using $a = L_1$ in Figs 1 and 2 leads to a greater enhancement of the nucleation rate (and therefore worse agreement with experiment).

Since i^* increases with temperature, it is possible that the $(i^*)^{2/3-x}$ and $(i^*)^{1-y}$ terms in ΔG_i^* , appearing in section 3 but subsequently ignored, may be more important at low temperatures than at higher temperatures. Certain choices of x and y could possibly improve agreement between theory and experiment further. However, such a development is beyond the simple picture that has been formulated here.

5. CONCLUSIONS

Nucleation phenomena are important in a variety of areas of science and technology, and yet no theory to date has been fully successful in accounting for all the experimental aspects of one particular example, the formation of aerosol droplets from supersaturated vapours. In order to make progress, we believe a proper statistical mechanical treatment of clusters must be developed. Technically, this avoids the problems associated in the past with

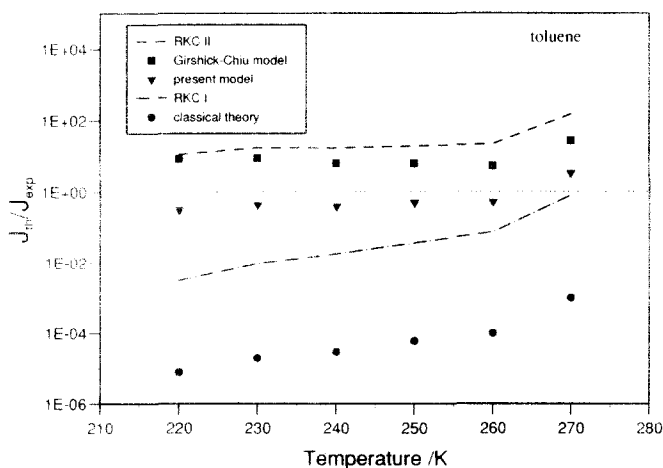


Fig. 1. Comparison of experimental nucleation rates for toluene (Schmitt *et al.*, 1983) against predictions of various models: Reiss *et al.* (1968), Girshick and Chiu (1990), classical theory (Becker and Döring, 1935) and the present model.

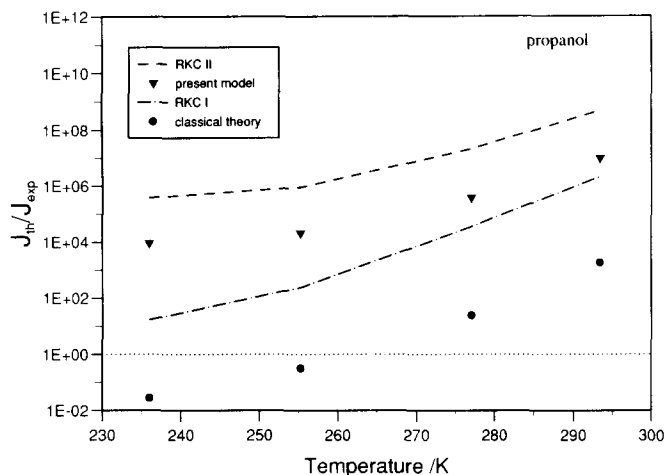


Fig. 2. Comparison of experimental nucleation rates for propanol (Strey *et al.*, 1986) against predictions of various models, as in Fig. 1.

replacement terms. The need for such terms arises when a droplet free energy expression is used which is assumed to represent $3i$ degrees of freedom, based on bulk continuum ideas. This then leads to too many degrees of freedom when cluster translation and rotation are included. Replacement terms correct for this overcounting. However, evaluating the underlying partition function of a cluster, as we have done, involves performing the spatial and momentum integrals which include all translational and rotational modes, a point made by Reiss *et al.* (1968). There is no need to add extra factors which then have to be corrected for.

We have constructed a homogeneous nucleation theory based on statistical mechanics and a model cluster potential which correctly goes to zero for a single monomer, and which also has the expected surface and volume behaviour for larger cluster sizes. However, there exist uncertainties in the cluster potential at the critical size. In order to resolve these uncertainties we make an appeal to the capillarity approximation to ensure that the potential energy of the critical cluster is appropriate to that of a macroscopic droplet. This leads to a model which is similar to but does not correspond exactly to classical theory, which is also based on the capillarity approximation but within a continuum thermodynamics approach. The model is similar in some aspects to RKC II theory but with a modification to the $kT \ln i$ term in the free energy, which alters the numerical predictions. The model is simple, and predicts a temperature dependent enhancement of the nucleation rate compared with classical theory. Further developments of the model, such as relaxing the position independence of the cluster potential, could improve agreement with experiment.

Acknowledgement—This work was undertaken for the U.K. Department of Trade and Industry as part of the General Nuclear Safety Research Programme.

REFERENCES

- Abraham, F. F. (1968) *J. appl. Phys.* **39**, 3287, 4791.
 Abraham, F. F. (1974) *Homogeneous Nucleation Theory*. Academic Press, New York.
 Becker, R. and Döring, W. (1935) *Ann. Physik (Leipzig)* **24**, 719.
 Dillmann, A. and Meier, G. E. A. (1989) *Chem. Phys. Lett.* **160**, 71.
 Dillmann, A. and Meier, G. E. A. (1990) *J. Chem. Phys.* **94**, 3872.
 Ellerby, H. M., Weakliem, C. L. and Reiss, H. (1991) *J. Chem. Phys.* **95**, 9209.
 Girshick, S. L. (1991) *J. Chem. Phys.* **94**, 826.
 Girshick, S. L. and Chiu, C.-P. (1990) *J. Chem. Phys.* **93**, 1273.
 Huang, D. D. and Seinfeld, J. H. (1992) *J. Coll. Interface Sc.* **151**, 258.

- Oxtoby, D. W. (1992) *J. Phys.: Condens. Matter* **4**, 7627.
- Reiss, H., Katz, J. L. and Cohen, E. R. (1968) *J. Chem. Phys.* **48**, 5553.
- Schmitt, J. L., Zalabsky, R. A. and Adams, G. W. (1983) *J. Chem. Phys.* **79**, 4496.
- Strey, R., Wagner, P. E. and Schmeling, T. (1986) *J. Chem. Phys.* **84**, 2325.
- Volmer, M. and Weber, A. (1926) *Z. Phys. Chem. (Leipzig)* **119**, 277.
- Zeldovich, J. B. (1943) *Acta. Physicochim. (U.R.S.S.)* **18**, 1.