The Solubility of Gas Bubbles

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The solubility of a gas is usually defined in terms of its concentration in a semi-infinite material in equilibrium with the gas phase at a pressure of one atmosphere at a specified temperature. Since bubbles have a finite radius of curvature, it is important to extend this definition to describe their solubility in a way which is analogous to the equation relating the increase in solubility and decrease in radius of solid precipitates.

A thermodynamic analysis is presented which evaluates the gas solubility in equilibrium with a bubble and shows it to be independent of bubble radius except in so far as this radius is related to the pressure. The analysis is also applicable to bubbles having crystallographic faces and to bubbles whose shape is modified by intersection with grain-boundaries.

1. Introduction

It has long been established [1] that small water droplets evaporate at an enhanced rate because of the higher vapour pressure associated with a convex surface of small radius of curvature. Conversely it has been shown that the vapour pressure is reduced over a concave surface. In condensed systems, where precipitates are dispersed in a second phase, an analogous situation arises such that small precipitates have a higher solubility and on prolonged heat-treatment they dissolve in favour of the growth of larger precipitates [2, 3]. In all these situations the driving force is derived from the reduction in total interfacial energy of the system.

When a gas bubble dissolves in a solid matrix, the energy changes are more complex. If the gas pressure p is restrained by surface tension forces [4], then $p = 2\gamma/r$, where γ is the surface energy per unit area and r is the bubble radius. It follows that a reduction in bubble-size is accompanied by a loss of vacancies [5] and a consequent increase in the contained gas pressure. Entirely contrary to the case of solid precipitates, if a small bubble should dissolve and contribute to the growth of a larger one, there is no overall change in surface energy [6]. This is readily illustrated by considering two bubbles such that the smaller one of radius r_1 dissolves and the bubble of radius r_2 increases to a radius r_3. Since the amount of gas and temperature are both constant,

$$(2\gamma/r_1)(4\pi r_1^3/3) + (2\gamma/r_2)(4\pi r_2^3/3) = (2\gamma/r_3)(4\pi r_3^3/3),$$

and so $r_1^2 + r_2^2 = r_3^2$ which implies that there is no change in total surface area or energy.

It follows from the above relation, however, that $r_1^3 + r_2^3 < r_3^3$, hence there is an increase in the total volume occupied by the gas. This immediately leads to an increase in its entropy and to a driving force for bubble growth which is effective if the gas solubility is not negligibly small.

2. Thermodynamic Approach to the Equilibrium of a Gas Bubble

We consider the change in free energy of the system where the gas is sparingly soluble and when a bubble containing n atoms of a monatomic gas decreases in size as δn atoms dissolve in the infinite matrix in which the bubble is situated. Except for very small bubbles, the elastic strain energy in the region surrounding the bubble is negligible and need not be considered. Since the change takes place isothermally, work is done against the surface tension of the material γ and it is not necessary to invoke the value of the bound energy. In formulating the equation describing this process we must take into account the heat of solution ΔH of the gas, the change in entropy of the matrix and of the

bubble, the work done as the bubble shrinks and the decrease in its surface energy. Hence we can write

$$\delta n \Delta G = \delta n(\Delta H - T\Delta S) + \delta nkT\ln c - \\ \delta(nkT\ln p) + \delta(pv) - \gamma \delta A \quad (1)$$

where ΔG is the free energy change per atom entering solution; ΔS is the associated entropy change; c is the gas atom concentration in the matrix; p is the gas pressure in the bubble; v is the bubble volume; A is the surface area of the bubble; k is the Boltzmann's Constant and T is temperature in °K. When the bubble is in equilibrium with the matrix such that it is tending neither to grow nor to dissolve, $\Delta G = 0$ and so:

$$O = \Delta H - T\Delta S + kT\ln c - kT\ln p - \\ nkT\delta p/p\delta n + \delta(pv)/\delta n - \gamma\delta A/\delta n \;. \quad (2)$$

Equation 2 now gives the gas concentration c in terms of the pressure p in the bubble, but to obtain an explicit relationship we must assume a law of gas behaviour and recall that $p = 2\gamma/r$ since, otherwise, there would be a flux of vacancies into or out of the bubble and equilibrium conditions would not be achieved [5]. Providing the gas pressure is not too high, it is simplest to take as an approximation that the perfect gas laws are obeyed, though it can be shown that a similar result is obtained in the more general case. Thus we can write

$$pv = (2\gamma/r)(4\pi r^3/3) = 8\pi\gamma r^2/3 = nkT$$

and on differentiating

$$\delta(pv) = 16\pi\gamma r \, dr/3 = kT\delta n \;.$$

We also readily deduce that

$$nkT\delta p/p = -nkT\delta r/r = -\delta nkT/2$$

and $\quad \gamma\delta A = \gamma 8\pi r\delta r = 3\delta nkT/2 \;.$

Substituting these values, equation 2 reduces to the form

$$O = \Delta H - T\Delta S + kT\ln c - kT\ln p$$

or $\quad c = p \exp(\Delta S/k) \exp(-\Delta H/kT) \;. \quad (3)$

A small extension of the argument leads to the corresponding equation for a diatomic gas which dissociates on entering solution, namely,

$$C = p^{\frac{1}{2}} \exp(\Delta S_d/2k) \exp(-\Delta H_d/2kT) \quad (4)$$

where the suffixes d refer to the diatomic gas.

These equations are identical with the equations [7] for the gas concentration in a semi-infinite solid in contact with a gas at a pressure p.

Thus no additional terms need to be included because of the curvature of the surface in the case of a bubble. Since, however, $p = 2\gamma/r$ it follows that small bubbles have a higher solubility than larger ones. Before considering this aspect in further detail, we next deal with the influence of bubble shape.

3. The Effect of Bubble Shape on Solubility

Bubble shape is affected principally in two ways, by intersection with grain-boundaries and/or by a limited number of low energy surfaces of the matrix which surrounds it.

Bubbles are frequently situated on grain-boundaries since there is then a decrease in free energy due to the change in size and shape of the bubbles [8]. An otherwise spherical bubble takes the form of two equal sections of spherical caps, symmetrically placed with regard to the plane of the grain-boundary [3]. If the surface of the bubble did not have constant curvature everywhere, except at the grain-boundary, there would be local differences of chemical potential which is contrary to the condition for equilibrium. The angle θ between the grain-boundary plane and tangent plane to either cap at a point of intersection is determined by the relative values of the surface energy γ and grain-boundary energy γ_g since to maintain equilibrium $2\gamma \cos\theta = \gamma_g$. Thus the lenticular shape of the bubble is precisely defined. It can readily be shown that its volume $V = 2\pi r^3(\frac{2}{3} - \cos\theta + \frac{1}{3}\cos^3\theta)$, its total surface area $A_s = 4\pi r^2(1 - \cos\theta)$ and the area A_g of grain-boundary removed by the bubble is given by $A_g = \pi r^2 \sin^2\theta \;.$

In establishing conditions of equilibrium, we evaluate the work done when the gas at pressure p expands the volume of the bubble by δV. This increases the area of the bubble surface by δA_s and the area of grain-boundary removed by δA_g. For a small departure from equilibrium we can write

$$p\delta V = \gamma\delta A_s - \gamma_g \, \delta A_g$$

so that

$$p\frac{dV}{dr} = \gamma\frac{dA_s}{dr} - 2\gamma\frac{dA_g}{dr}\cos\theta$$

and making appropriate substitutions

$$p\left[6\pi r^2\left(\frac{2}{3} + \frac{\cos^3\theta}{3} - \cos\theta\right)\right] = \\ \gamma[8\pi r(1 - \cos\theta) - 4\pi r \sin^2\theta\cos\theta]$$

which reduces to $pr = 2\gamma$.

We conclude that the gas concentration adjacent to a bubble on a grain-boundary is determined entirely by the gas pressure contained which is related only to the surface energy of the matrix and the radius of curvature of the faces. Thus equation 3 is again applicable in describing gas solubility adjacent to a bubble.

The analysis has so far assumed that bubbles are spheres or are described by sections of spherical surfaces. It is often observed that bubbles have plane faces which correspond to planes of lowest surface energy in the matrix material [9]. This feature however does not introduce a major complication since, when equilibrium shape is reached, it has been established [10] that the perpendicular distance of a surface from the centre of a bubble is proportional to the energy of that surface. Thus, if surfaces of energy $\gamma_1, \gamma_2 \ldots \gamma_i \ldots$ are respectively at distances $x_1, x_2 \ldots x_i \ldots$ from the bubble centre, $2\gamma_1/x_1 = 2\gamma_2/x_2 = \ldots = 2\gamma_i/x_i = \ldots$ and this ratio can be equated to the gas pressure contained so that equation 3 still applies in evaluating the solubility of the bubble.

4. Conclusions

Equation 3 is shown to be valid irrespective of bubble size and shape and the increased solubility of smaller bubbles arises only because at equilibrium they enclose gas at a higher pressure. It is important however to avoid apparent paradoxes which may arise from this conclusion. If one considers a bubble situated within a semi-infinite medium in contact with gas at a pressure equal to that of the gas within the bubble, then it might be assumed that this would be a stable situation because there would be no concentration gradient of gas within the material. Such a result, though, is clearly incorrect since there would be a net decrease in free energy of the

system if the bubble were to dissolve. The apparent paradox arises since it is unrealistic to consider the bubble unaffected by the external pressure and the semi-infinite medium concept is inapplicable in this case. The paradox is removed when the bubble is situated in a matrix which is hydrostatically compressed by the external gas. The bubble is then compressed to a smaller size with consequent increase in the pressure of gas it contains. A higher gas concentration thus exists in the matrix near the bubble and as a result the bubble dissolves.

Acknowledgements

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