IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

The ideal law of mass action and first-order phase transition

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1983 J. Phys. A: Math. Gen. 16 L435

(http://iopscience.iop.org/0305-4470/16/12/008)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 129.252.86.83
The article was downloaded on 30/05/2010 at 16:46

Please note that terms and conditions apply.

J. Phys. A: Math. Gen. **16** (1983) L435–L437. Printed in Great Britain

LETTER TO THE EDITOR

The ideal law of mass action and first-order phase transition

M Elwenspoek

Institut für Atom- und Festkörperphysik, Freie Universität Berlin, Arnimallee 14, D-1000 Berlin 33, Federal Republic of Germany

Received 28 April 1983

Abstract. We show that the ideal law of mass action for a chemical reaction $\mu A \leftrightarrows A_\mu$ predicts a first-order phase transition if we allow μ to become large.

Recently multiple solutions of the law of mass action (LMA) have been obtained for a variety of situations (Gittermann and Steinberg 1978a, b, 1979). This gives rise to a first-order phase transition. The LMA has several solutions if it is applied to the case of non-ideal mixtures, if the energy of formation of molecules is in the same range as the interaction of unbound atoms. It can be shown that also Sommer's association model for binary alloys (Sommer 1982a, b) predicts a phase transition of first order in certain circumstances (Elwenspoek 1983).

We focus on the fact that even the ideal LMA predicts a phase transition, if the number of atoms constituting the molecule becomes very large. Consider the chemical reaction

$$\mu A \leftrightarrows A_\mu.$$

The system composed of A-atoms and A_μ-molecules may be described by the Gibbs function

$$G = N_A G_A + N_{A_\mu} G_{A_\mu}. \tag{1}$$

Here N_A is the number of moles of unbound A-atoms and N_{A_μ} is the number of molecules which contain μ A-atoms. Suppose the total number of A-atoms (bound + unbound) is N; then

$$N_A = N - \mu N_{A_\mu}. \tag{2}$$

Defining concentrations $n = N_{A_\mu}/N$, $X_1 = N_A/(N_A + N_{A_\mu})$ and $X_2 = N_{A_\mu}/(N_A + N_{A_\mu})$, we have for the Gibbs function per mole A

$$G = (1 - \mu n) G_A + n G_{A_\mu}. \tag{3}$$

We consider now n as an order parameter and minimise G with respect to n, i.e. $(\partial G/\partial n)_{T,p} = 0$ (p and T being pressure and temperature, respectively). This results in

$$G_{A_\mu} = \mu G_A. \tag{4}$$

If we adopt the usual definitions G_A^0 and $G_{A_\mu}^0$ which refer to the chemical potentials of pure A and pure A_μ in the standard states at given p and T, and neglect interactions

© 1983 The Institute of Physics

between A-atoms and A_μ-molecules—hence considering an ideal mixture—we have

$$G_A = G_A^0 + RT \ln pX_1, \qquad G_{A_\mu} = G_{A_\mu}^0 + RT \ln pX_2. \tag{5a, b}$$

The combination of (4) and (5) gives the LMA

$$\ln\{n[1-(\mu-1)n]^{\mu-1}/(1-\mu n)^\mu\} = -g^0/RT + (\mu-1)\ln p \tag{6}$$

where

$$g^0 = G_{A_\mu}^0 - \mu G_A^0. \tag{7}$$

g^0 as defined in (7) is a function of μ; this is a (quasi) extensive quantity with respect to μ, $g^0 \propto \mu$. We decompose g^0 into an enthalpy and an entropy term,

$$g^0 = \mu g_0' = \mu(h_0 - Ts_0), \tag{8}$$

and neglect temperature dependence of h_0 and s_0. h_0 and s_0 (enthalpy and entropy, respectively) refer to the enthalpy and entropy *per atom* in the A_μ-molecule. If we allow different specific heats of pure A and pure A_μ, g_0 contains also a $\ln T$ term.

Combination of (8) and (6), replacing n by n'/μ, so that n' varies between 0 and 1, and looking at $\mu \gg 1$, gives for the LMA

$$\ln\left(\frac{n'}{\mu(1-n')}\right)^{1/\mu} + \ln\left(1+\frac{n'}{\mu(1-n')}\right) = \frac{s_0}{R} - \frac{h_0}{RT} + \ln p. \tag{9}$$

It is easily seen that the first term of the left-hand side is a step function with respect to n' if μ becomes large: at $n' \to 0$ and $n' \to 1$ it diverges to $-\infty$ and $+\infty$ for fixed but arbitrary μ and for $n' \neq 0$ and $n' \neq 1$, it approaches 0 for $\mu \to \infty$. The second term of the left-hand side is only important for $n' \to 1$, so the total left-hand side approaches a step function for $\mu \to \infty$.

Therefore (9) has two solutions for n' for large μ: n' may be either nearly 0 or 1, corresponding to the two cases: few A are bound in an A_μ-'molecule' or many A are bound. Obviously, the phase transition occurs when the right-hand side of (9) vanishes, i.e. when p increases or T decreases we come from very small portions of A condensed in A_μ-'molecules' to nearly all A condensed in A_μ-'molecules'. At the standard pressure,

$$T_c = h_0/s_0 \tag{10}$$

where h_0 and s_0 represent the latent heat and entropy of transition.

We note that the same consideration may be applied for mixtures. As an example, consider a binary, where the chemical reaction is

$$\mu A + \nu B \leftrightarrows A_\mu B_\nu$$

which results for $\mu = \nu \to \infty$ and at a concentration $X_A = X_B = 50$ at % in

$$R \ln 2 = s_0 - h_0/T_c \tag{11}$$

at standard pressure. Clearly, $R \ln 2$ arises from the statistical distribution of A and B atoms in the unbound state. Indeed, if one compares the values for ΔS_M, the entropy of fusion, in alcali-halogenides with those of simple metals and rare gases, one finds a distinct trend to larger ΔS_M-values in the two compound systems, which however does not reach the predicted value of $R \ln 2$, because of the chemical short-range order in the liquid salts near the melting temperature.

It seems to be worth noting that for two-component systems a phase transition occurs also for $s_0 = 0$ at finite temperatures, in contrast to the one-component systems. One should also note that the phase transition temperature T_c for two-component systems is lowered if h_0 and s_0 have the same values (same ratios) as in one-component systems.

Our considerations might cast some new light upon first-order phase transitions. A phase transition is possible if molecules or atoms can interact energetically in different ways in either state which is necessarily connected with differences in entropy. Though the description of a condensation by an ideal mixture of the two phases is a hopelessly crude approach—a more unrealistic one is not imaginable—a most important feature is nevertheless described: the first-order phase transition.

The cooperative phenomena are hidden in the requirement that $\mu \to \infty$; for finite μ, the transition becomes broad. This corresponds to the well known fact that a phase transition is sharp only in infinite systems. Cooperative phenomena are necessary to build up the infinitely large 'molecule'.

References

Elwenspoek M 1983 *Thesis, Freie Universität Berlin* (unpublished)
Gittermann M and Steinberg V 1978a *Chem. Phys. Lett.* **57** 455
—— 1978b *J. Chem. Phys.* **69** 2763
—— 1979 *Phys. Rev.* A **20** 1236
Sommer F 1982a *Z. Metallkunde* **73** 72
—— 1982b *Z. Metallkunde* **73** 77