

## References

- 1 S. P. Gubin, *Koord. Khim.*, 1994, **20**, 403 (*Russ. J. Coord. Chem.*, 1994, **20**, 379).
- 2 S. P. Gubin, T. V. Galuzina, P. A. Kozmin, M. D. Surajskay and T. B. Larina, *Koord. Khim.*, 1994, **20**, 665 (*Russ. J. Coord. Chem.*, 1994, **20**, 627).
- 3 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard and D. G. Watson, *J. Chem. Soc., Dalton Trans.*, 1989, S1.

- 4 B. F. G. Jonson, D. A. Kaner, J. Lewis, P. R. Raithby and M. J. Rosales, *Organometallic Chem.*, 1982, **231**, 59.

Received: Moscow, 14th November 1994  
 Cambridge, 31st January 1995; Com. 4/07163H

## On the Phase Approach in the Thermodynamics of Aggregative Systems

Anatoly I. Rusanov,\* Fedor M. Kuni and Alexander K. Shchekin

Department of Chemistry, St. Petersburg State University, 199034 St. Petersburg, Russian Federation. Fax: +7 812 218 1346; e-mail: rusanov@coll.chem.lgu.spb.su

The conditions of phase equilibrium for particles of an aggregative polydisperse system are considered. It is shown that only stationary points in the equilibrium distribution curve satisfy simultaneously the conditions of aggregative equilibrium and phase equilibrium. At other points, the curve shape determines the change of the chemical potential corresponding to the phase equilibrium.

Two types of polydisperse aggregative systems are the most widely known: the population of nuclei of a new phase in the process of phase transition and associated solutions including micellar ones. The analysis of the equilibrium distribution of particles in an aggregative system plays a key role in the thermodynamics and kinetics of phase transitions and micellization. The analysis is based on the aggregative equilibrium condition:

$$\mu_n = n\mu \quad (1)$$

where  $\mu_n$  is the chemical potential of an aggregate consisting of  $n$  molecules,  $\mu$  is the chemical potential of the monomeric form of matter and  $n$  is the aggregation number. The equilibrium distribution itself is derived from equation (1),<sup>1</sup> as well as the mass action law used especially when considering micellization in surfactant solutions.<sup>2</sup> The approach based on the mass action law is often opposed to the phase approach where every particle of aggregative system is treated as a region of a certain phase  $\alpha$  surrounded by a phase  $\beta$ , *i.e.* a polydisperse system is considered as a heterogeneous one. Herewith, the ordinary phase equilibrium condition is used:

$$\mu^\alpha = \mu^\beta \quad (2)$$

In reality, the aggregative equilibrium and phase equilibrium are independent to a certain extent. These are not alternative approaches to the description of something the same, but different phenomena which may be combined or, the reverse, realized separately. The delicate problem of the relation between the aggregative equilibrium and phase equilibrium was touched upon earlier,<sup>3,4</sup> but mainly only extreme points in the equilibrium distribution curve were analysed. This presentation considers the whole run of the distribution curve from the phase equilibrium standpoint.

Statistical mechanics gives the following expression for the chemical potential:<sup>1</sup>

$$\mu_n = G_n^0 + kT \ln(\Lambda_n^3 c_n f_n) \quad (3)$$

where  $G_n^0$  is the Gibbs energy for a separately taken aggregate of  $n$  molecules with resting centre of mass in a pure solvent (in the absence of other aggregates),  $k$  is the Boltzmann constant,  $T$  is temperature,  $\Lambda_n = h(2\pi m_n/kT)^{1/2}$  is the mean de Broglie wavelength for a given aggregate ( $h$  is the Planck constant,  $m_n$  is the aggregate mass) and  $c_n$  and  $f_n$  are its concentration and activity coefficient, respectively. The quantity  $\Lambda_n^{-3}$  is the partition function for the aggregate translational motion.

Correspondingly,  $kT \ln \Lambda_n^3$  is the contribution to free energy from the translational motion. Similarly,  $kT \ln f$  represents the contribution from the interaction between aggregates including monomers. Uniting  $kT \ln(\Lambda_n^3 f_n)$  and  $G_n^0$ , we write equation (3) as:

$$\mu_n = G_n + kT \ln c_n \quad (4)$$

where  $G_n$  is the Gibbs energy already related to a moving and interacting aggregate.

Following the usual formalism of the thermodynamics of a small spherical particle,<sup>5</sup> we may write:

$$G_n = \sigma A/3 + \mu^\alpha n \quad (5)$$

where  $\sigma$  is the surface tension of an aggregate,  $A$  is its surface area (to be more exact, the area of the surface of tension) and  $\mu^\alpha$  is the chemical potential of the molecules in the internal phase  $\alpha$  of the aggregate. We emphasize that all the quantities in equation (5) refer to a real moving and interacting aggregate (a similar expression may be written for an aggregate with resting centre of mass:<sup>5</sup> it will be of the same form but with different values of the quantities). The Gibbs–Duhem equation for a spherical and equilibrium (inside it) disperse particle will also be needed:<sup>6</sup>

$$d(\sigma A/3) + n d\mu^\alpha = 0 \quad (6)$$

Now, differentiating equation (4) with respect to  $n$  with equations (5) and (6) in mind, we obtain:

$$d\mu_n/dn = \mu^\alpha + kT d \ln c_n/dn \quad (7)$$

On the other hand, differentiating equation (1) along the distribution curve (*i.e.* at constant  $\mu$ ), we find:

$$d\mu_n/dn = \mu = \mu^\beta \quad (8)$$

where the self-evident condition  $\mu = \mu^\beta$  has been used since the monomers are situated automatically in outer phase  $\beta$ . Comparing equations (7) and (8), we arrive at a remarkable relationship:

$$\mu^\alpha + kT d \ln c_n/dn = \mu^\beta \quad (9)$$

which shows that the condition of phase equilibrium (2) is realized only at those points in the equilibrium distribution

curve where the condition  $d \ln c_n / dn = 0$  is satisfied. These may be extreme points for concentration or inflection points in the  $c_n(n)$  curve with a horizontal tangent. A maximum of  $c_n$ , for example, corresponds to micelles. A minimum of  $c_n$  corresponds to equilibrium Gibbs-Volmer nuclei in the population of nuclei of a new phase. An inflection point corresponds to the boundary state, for example, to the critical micelle concentration.<sup>7</sup>

Since  $\mu^B = \mu$ , this quantity remains constant on moving along the distribution curve at a given physical state of a system. Then, differentiating equation (9) along the distribution curve, we obtain the condition:

$$d\mu^\alpha / dn = -kTd^2 \ln c_n / dn^2 \quad (10)$$

from which it is seen that the shape of the distribution curve determines completely the change of chemical potential  $\mu^\alpha$  at each point of the curve. If the curve is plotted as  $\ln c_n$  vs.  $n$ , then  $\mu^\alpha$  increases at convex parts and decreases at concave parts of the curve with increasing aggregation number  $n$ . Inflection points correspond to extremes of chemical potential. If the curve is plotted as  $c_n$  vs.  $n$ , then  $\mu^\alpha$  increases by necessity with  $n$  at convex parts of the curve: the transition from increasing to decreasing can occur only at a concave part.

Thus, we arrive at the following conclusion. The conditions of aggregative equilibrium and phase equilibrium are realized simultaneously only at stationary points in the equilibrium

size distribution curve for particles in a polydisperse aggregative system. Only the aggregative equilibrium condition holds at all other points, and the change of the chemical potential corresponding to phase equilibrium is completely determined by the shape of the distribution curve.

## References

- 1 F. M. Kuni and A. I. Rusanov, *Teor. Mat. Fiz.*, 1970, **2**, 265 (in Russian).
- 2 A. I. Rusanov, *Mitselloobrazovanie v rastvorakh poverchnostno-aktivnykh veshchestv (Micellization in Surfactant Solutions)*, Khimiya, St. Petersburg, 1992 (in Russian).
- 3 A. I. Rusanov, *Kolloidn. Zh.*, 1987, **49**, 932 [*Colloid J. USSR (Engl. Transl.)*, 1987, **49**, 816].
- 4 A. I. Rusanov, *Adv. Colloid Interface Sci.*, 1992, **38**, 271.
- 5 A. I. Rusanov, *Phasengleichgewichte und Grenzflächenercheinungen*, Akademie-Verlag, Berlin, 1978 (in German).
- 6 A. I. Rusanov, *Kolloidn. Zh.*, 1981, **43**, 890 [*Colloid J. USSR (Engl. Transl.)*, 1981, **43**, 723].
- 7 E. Ruckenstein and R. Nagarajan, *J. Phys. Chem.*, 1975, **79**, 2622.

Received: Moscow, 30th January 1995

Cambridge, 28th February 1995; Com. 5/00855G

## Cubic Solid-solution $Ti_xSi_yN_z(O)$ Films: Synthesis, Structure and Electronic Properties

Mikhail V. Kuznetsov,\* Elizaveta V. Shalaeva\*, Sergei V. Borisov, Boris V. Mitrofanov, Alexander L. Ivanovsky and Gennady P. Shveikin

Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 620219 Ekaterinburg, Russian Federation. Fax: +7 3432 444495

Monophase films of the metastable cubic phase  $Ti_xSi_yN_z(O)$  with the B1 structure have been synthesized; introduction of silicon atoms into the non-metallic sublattice of titanium oxynitride has been proved experimentally and theoretically.

Carbides, nitrides and oxides of IV-V group d-transition metals with the B1 structure and their solid solutions possess a unique set of properties combining high melting temperatures, hardness, radiation stability and a number of intriguing electromagnetic and spectral characteristics.<sup>1,2</sup> A new direction developed over the last few years in the modification of the composition and properties of these metal-like phases, which are characterized by a covalent-ionic-metallic type of chemical interaction, is the introduction of 3p-elements (Al, Si), whose nitrides (carbides) are non-isostructural with d-metal nitrides and which have a predominantly covalent type of chemical bonding, into the B1-lattice. According to experimental data available and theoretical quantum chemical calculations performed, the solid solutions  $Ti_xAl_{1-x}N$ ,  $Ti_xSi_yN_z$  (B1 structure type) are metastable and, therefore, can only be realized under non-equilibrium synthesis conditions, for instance, in the form of films in ion-plasma vapour deposition. A great number of works are now devoted to the synthesis, structure and properties of  $Ti_xAl_{1-x}N$  solid solution films.<sup>3-7</sup> The problems of the possibility and conditions of formation, the structure and stability of the cubic phases  $Ti_xSi_yN_z$  and  $Ti_xSi_yN_z(O)$  remain to be explored.

Ti-Si-N(O) films have been made by an arc-method<sup>8,9</sup> using the  $Ti_{0.7}Si_{0.3}$  target. The working gas ( $N_2$ ) pressure, substrate temperature and negative potential on the substrate were varied in the process of deposition. The films were examined by X-ray photoelectron (XPS) and Auger-spectroscopy (VG ESCALAB MKII), by X-ray probe microanalysis

(JCA-733) and by transmission electron microscopy (JEM-200C).

As a result it has been shown that within a narrow range of nitrogen pressure  $P(N_2) = 6 \times 10^{-2} - 1 \times 10^{-1}$  Pa the  $Ti_xSi_yN_z(O)$  films deposited by an arc-method at substrate temperature  $T = 470$  K have a monophase cubic structure of the B1 type [Fig. 1(a)]. X-ray probe microanalysis has given support to the uniform distribution of silicon atoms in the

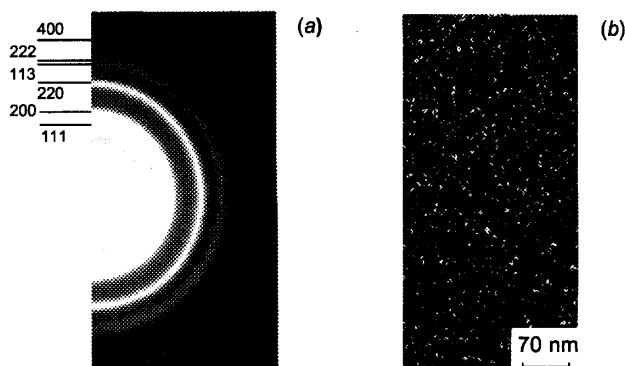


Fig. 1 The structure of Ti-Si-N(O) films deposited at  $T = 470$  K and  $P(N_2) = 1 \times 10^{-2}$  Pa.  $Ti_xSi_yN_z(O)$  phase (B1 structure type): micro-diffraction pattern (a) and dark-field electron-microscopy image in (111) and (200) reflections (b).