

## Instability of ionization equilibrium of a weakly ionized three-component plasma

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The general stability conditions of a three-component plasma lead, in addition to the usual critical phenomena, to the appearance of a chemical instability, connected with the multiple solution of the law of mass action. As a result of a first-order transition the system will separate into two phases with different degrees of ionization. As the fraction of highly ionized phase increases, the conductivity of the system becomes metallic. Such a phenomenon can explain the metal-dielectric transition and its connection with such critical phenomena in different systems as weak electrolytes, molten salts, metal-ammonia solutions, and solid-state plasmas.

### I. INTRODUCTION

In recent years the three-component plasma has been used for a description of different physical phenomena, such as, for example, properties of electrolytes, molten salts, metal-ammonia solutions, solid-state plasma (electrons, holes, and excitons in Ge and Si, as well as the electrons, ions, and donor centers in heavily doped semiconductors).

It is assumed that in all these cases ionization reaction of three components which takes place is



Here  $A$  might be, for example, molecules of halogenides of alkaline metals (NaCl, KCl, ...) which, as a result of the ionization reaction (1), are dissociated into ions  $I$  and  $e$ . For the electron-hole plasma in Ge and Si,  $A$  are excitons and  $I$  and  $e$  are holes and electrons, respectively. For the metallic vapor at high pressures the ionization reaction (1) means the partial ionization of atoms  $A$  and the appearance of ions  $I$  and electrons  $e$ , etc.

The metal-nonmetal transition has been observed experimentally in all indicated examples; this transition is often located near the critical points of these substances. Therefore, there arises a problem of mutual influence of these two transitions.

However, two independent models for a description of the metal-nonmetal transition and mechanical and/or diffusional instability are usually used. We shall be interested in the analysis of these two transitions as different thermodynamic instabilities of the same system, and we shall see that the metal-nonmetal transition is caused by the instability of the ionization of reaction (1). (We denote it later as a chemical instability.) In a previous

paper we have demonstrated an appearance of a chemical instability in the isomerization reaction.<sup>1</sup> The ionization reaction is another example of the same kind of instability.

One can easily understand the appearance of instability through the example of ionization of atoms. The ionization potential of an isolated atom decreases with the degree of ionization, due to the screening of the Coulomb interaction by free ions and electrons. Such an increase of the energy of a system may be compensated by the increase of the entropy so that weakly and strongly ionized phases will have the same value of chemical potential, i.e., they can coexist in equilibrium. Thus as temperature and/or pressure increase, instead of a gradual increase of the degree of ionization, the dielectric system will separate into two phases, "dielectric" and "metallic," each one in ionization equilibrium; this is a first-order phase transition ending in a critical point.

The law-of-mass action can have more than one solution for concentration of electrons in the conduction band of a semiconductor (indicative of a phase transition) at temperatures lower than the energy gap; this fact was apparently first noted by Adler and Brooks who studied the temperature dependence of the energy gap.<sup>2</sup> Later, the problem of stability of a three-component plasma (in the ideal-gas approximation for the neutral particles) has been discussed by Norman and Starostin<sup>3</sup> and Ebeling.<sup>4</sup> Because of the approximations used, these models do not allow the complete analysis of either the phase diagram or of the interdependence of different phase transitions.

Quantitatively, chemical instability is associated with an appearance of multiple solutions of the law-of-mass action. Let us recall the thermodynamic description of a chemical reaction.

Let the number of atoms at the beginning of a reaction be  $N_0$ . The change in the number of the reacting particles is determined by the stoichiometric coefficients of the given reaction ( $\nu_A = -1$ ,  $\nu_I = 1$ ,  $\nu_e = 1$ ) and the so-called extent of reaction  $\xi$ ,

$$N - N_0 = \nu_A \xi, \quad N_I = \nu_I \xi, \quad N_e = \nu_e \xi. \quad (2)$$

As one can see from Eq. (2) the parameter  $\xi$  is the number of elementary reactions (1) that occur in the system.

Thus, for a given initial number of particles  $N_0$ , the thermodynamic state of a system is determined by two thermodynamic variables (say, pressure  $P$  and temperature  $T$ ) and the chemical variable  $\xi$ . In other words, for the description of our system in a canonical ensemble we use the Gibbs free energy  $G$  determined in the following way:

$$\begin{aligned} dG &= -SdT + Vdp + \mu_A dN_A + \mu_I dN_I + \mu_e dN_e \\ &= -SdT + Vdp + (\mu_I + \mu_e - \mu_A) d\xi, \end{aligned} \quad (3)$$

where  $S$  is the entropy,  $V$  is the volume, and  $\mu_i$  is the chemical potential of the  $i$ th component. Equation (2) has been used in the last step in (3). The same conditions of stability are obtained if  $V$  and  $T$  are chosen as independent variables provided that the Helmholtz free energy  $F$  is used rather than  $G$ .

Let us introduce the affinity of the reaction  $A \equiv -\partial G / \partial \xi$  which is a combination of chemical potentials. As one can see from (2) and (3),  $A = -\sum \nu_i \mu_i$ . Thus in equilibrium  $(\partial G / \partial \xi)_{P, T} = -A = \sum \nu_i \mu_i = 0$ , and for ionization reaction (1), we obtain

$$\mu_A = \mu_I + \mu_e. \quad (4)$$

Equation (4) is called the law-of-mass action.

As one can see from Eq. (3) the reacting system becomes unstable when the second derivative of the Gibbs free energy  $G$  with respect to the extent of reaction  $\xi$  becomes negative,  $\partial^2 G / \partial \xi^2 < 0$ , i.e., the stability condition has the following form:

$$\left( \frac{\partial A}{\partial \xi} \right)_{T, P} < 0. \quad (5)$$

As was shown in Ref. 5 the stability condition for a system containing one additional component which does not take part in a chemical reaction

and has a chemical potential  $\mu$  is

$$\left( \frac{\partial A}{\partial \xi} \right)_{T, P, \mu} < 0. \quad (6)$$

The violation of Eqs. (5) and (6) is an indication of a phase transition. As is well known, the phase transition occurs when temperatures, pressures, and chemical potentials for the coexisting phases are equal. However, we have restricted ourselves to the analysis of the violation of the stability conditions (5) and (6), assuming, as is usually the case, that an instability indicates the existence of a phase transition, and that the instability curve (spinodal) is located sufficiently close to the coexistence curve (binodal). The spinodal and binodal intersect at the critical points which are determined by the simultaneous solution of the following equations for case (5):

$$\left( \frac{\partial A}{\partial \xi} \right)_{P, T} = \left( \frac{\partial^2 A}{\partial \xi^2} \right)_{P, T} = 0, \quad (7)$$

or with additional constraint,  $\mu = \text{const}$  for all non-reacting components for case (6).

As we shall see later, the violation of Eqs. (5) and (6) determines all types of phase transitions in systems with chemical reactions; liquid-liquid, liquid-gas, and chemical instability. Nevertheless, different authors have used other criteria of instability which are not general and, at best, determine some types of instability (nonuniqueness of the isotherms  $p = p(V)$ ,<sup>6</sup> the inequalities  $(\partial N_A / \partial N_I)_T > -1$ ,<sup>7</sup>  $(\partial N_A / \partial N_I)_T > 0$ ,<sup>3,4</sup>  $(\partial P / \partial V)_T < 0$ ,<sup>8</sup>  $(\partial P / \partial V)_{T, A=0} < 0$ ,<sup>9</sup> etc.).

In order to analyze the stability conditions the different versions of the nonideal system of neutral particles and the Debye-Hückel system of charged particles will be considered in the remaining part of this paper.

## II. THREE-COMPONENT IONIC PLASMA (MOLTEN SALTS AND WEAK ELECTROLYTES)

The Van der Waals model for the neutral particles is the simplest one for the description of nonideal systems. We shall use the approximation of charged rigid spheres with Debye-Hückel interaction for the ions. Thus the Helmholtz free energy  $F$  has the following form:

$$\begin{aligned} F &= (N - N_I) T \ln \left[ \frac{N - N_I}{eV} \left( \frac{2\pi\hbar^2}{m_A T} \right)^{3/2} \right] + N_I T \ln \left[ \frac{N_I}{eV} \left( \frac{2\pi\hbar^2}{m_I T} \right)^{3/2} \right] + N_I T \ln \left[ \frac{N_I}{2eV} \left( \frac{2\pi\hbar^2}{m_e T} \right)^{3/2} \right] \\ &+ \frac{(N - N_I)^2 T}{V} \left( b - \frac{a}{T} \right) - VT \kappa^3 \left( \frac{\ln(1 + c\kappa)}{(c\kappa)^3} + \frac{1}{2c\kappa} - \frac{1}{(c\kappa)^2} \right) + N_I I; \quad \kappa = \left( \frac{8\pi e^2 N_I}{\epsilon TV} \right)^{1/2}. \end{aligned} \quad (8)$$

The first three terms in Eq. (8) describe the ideal gases of the neutral particles, positive, and negative ions, respectively. Here we have used the condition of electroneutrality  $N_I = N_e$ . The fourth term is the

Van der Waals correction to the equation of state of neutral particles. [We shall return to the discussion of the form of this correction later, after Eq. (12).] The fifth term is the Debye-Hückel correction for an ideal system when "c" approaches zero. The appearance of dielectric constant  $\epsilon$  in this term is due to the screening of the Coulomb interaction by neutral particles. Finally, the last term in Eq. (8) contains the dissociation energy  $I$ .

Performing the differentiation of Eq. (8) with respect to  $N_I$  [as is clear from comparison of (2), (5), and (8),  $N_I \equiv \xi$ ] one finds the law-of-mass action (4) for the model under consideration:

$$A(N_I) \equiv T \ln \left[ \frac{2(N - N_I) V e}{N_I^2} \left( \frac{m_I m_e}{m_A} \frac{T}{2\pi\hbar^2} \right)^{3/2} \right] + \frac{2(N - N_I) T}{V} \left( b - \frac{a}{T} \right) + \frac{\kappa^3 V}{2(1 + c\kappa) N_I} - I = 0. \quad (9)$$

According to (5) the boundary of stability is determined by the derivatives of the Helmholtz free energy (8) in the following manner:

$$\left( \frac{\partial A}{\partial N_I} \right)_{T, P} = \frac{(\partial A / \partial N_I)_{T, V} (\partial P / \partial V)_{T, N_I} - (\partial A / \partial V)_{N_I, T} (\partial P / \partial N_I)_{T, V}}{(\partial P / \partial V)_{T, N_I}} = 0. \quad (10)$$

Performing the appropriate calculations one can see that Eq. (10) reduces to a form

$$\left[ 1 + 2 \left( b - \frac{a}{T} \right) \frac{N - N_I}{V} \right] \left( 1 - \frac{V \kappa^3}{32\pi N_I (1 + c\kappa)^2} \right) = 0. \quad (11)$$

Thus, in this case, two instability curves appear, each of which has a clear physical meaning. In fact, one of them is the Van der Waals instability of neutral particles, and the other one is the chemical instability of the ionization equilibrium.

The instability curve,  $(\partial P / \partial V)_T = 0$ , has the following form in the Van der Waals model:

$$-2a \frac{N}{V} + \frac{T}{(1 - bN/V)^2} = 0. \quad (12)$$

It is easy to see that the first factor in Eq. (11) coincides with Eq. (12), if one expands (12) into a series in  $N/V$  and simultaneously neglects in Eq. (11) a shift of the boundary of stability for neutral particles due to the presence of charges ( $N_I \ll N$ ). Such a coincidence of stability conditions in the first factor in (11) and in (12), only after an expansion in  $N/V$ , is connected with the form of non-ideal corrections in Eq. (8). This correction has a form of a virial expansion and does not take into consideration the finite size of the particles. This effect can be also found by consideration of the term

$$-(N - N_I) T \ln [1 - (N - N_I) b/V],$$

rather than the first term of its series expansion, as it has been done in Eq. (8). The mutual influence of the two phase transitions thus obtained would be greater. Such an improvement of the model could be important when two transitions are close to one another.

It is enough for us to know that the Van der Waals parameters  $a$  and  $b$  are connected with the critical parameters

$$b = \frac{1}{3} v_{cr}, \quad a = \frac{9}{8} T_{cr} v_{cr}. \quad (13)$$

We shall see later, due to the approximations of this model, the critical temperature of the chemical instability is unchanged by the existence of the second branch of instability which influences, however, the critical volume and pressure.

By equating the second factor in Eq. (11) to zero, one obtains the following equation for the number density  $N_I/V \equiv x^2$ :

$$x = \frac{T/T_c}{(32\pi c^3)^{1/2}} \left[ 1 - \frac{T}{2T_c} \pm \left( 1 - \frac{T}{T_c} \right)^{1/2} \right], \quad T_c = \frac{e^2}{16\epsilon c}. \quad (14)$$

Two signs in Eq. (14) correspond to two phases with different degrees of ionization. The critical point is determined by the temperature for which the two solutions of Eq. (14) are the same. Of course, the latter definition of the critical point is equivalent to (7). It follows from (14) that the critical temperature and the critical concentration of ions for the chemical instability are

$$T_c = \frac{e^2}{16\epsilon c}, \quad N_{I, c} = \frac{V_c}{v_0}, \quad v_0 \equiv 128\pi c^3. \quad (15)$$

To find the critical specific volume  $v_c = V_c/N$  one must use the law-of-mass action (9) and then find the critical pressure from the equation of state  $p = -(\partial F / \partial V)_{T, N_I}$ . After some calculations and using definitions (13) and (15), the appropriate equations become

$$y = M \exp(I/T_c - Ly - 8),$$

$$P_c = (T_c/v_0)(0, 18 + y + \frac{1}{2}Ly^2),$$

where  $(16)$

$$y = (v_0 - v_c)/v_c, \quad M = (1/2e v_0) [(m_A/m_I m_e) 2\pi\hbar^2/T_c]^{3/2},$$

$$L = (2v_{cr}/3v_0)(1 - \frac{27}{8}T_{cr}/T_c).$$

Let us perform the numerical calculations for the molten salts NaCl and CsCl. The critical pa-

TABLE I. Critical parameters, dissociation energies, and effective ionic radii of the salts.

	$T_{cr}$ (°K)	$P_{cr}$ (atm)	$\rho_{cr}$ (g/cm <sup>3</sup> )	$n_{cr}=(\rho_{cr}/m_{mol})$ (cm <sup>-3</sup> )	$I$ (eV)	$C$ (Å)	$T_c$ (°K)	$n_c$ (cm <sup>-3</sup> )	$P_c$ (atm)
NaCl	3400	350	0.22	$2.2 \times 10^{21}$	4.2	1.4	7450	$0.95 \times 10^{21}$	194
CsCl	3040	110	0.3	$1.05 \times 10^{21}$	4.4	1.8	5800	$0.5 \times 10^{21}$	120

rameters of these salts,<sup>10</sup> the dissociation energies,<sup>10</sup> and the effective ionic radii<sup>11</sup> are given in Table I. Dielectric constants are assumed to be equal to unity. The dielectric constant for halogenides is equal to unity at high temperatures. However, one can find in the literature the value  $\epsilon = 3$ , as well (Ref. 12, p. 356), without references to the temperature interval. The critical temperatures  $T_c$ , pressures  $p_c$ , and number densities  $n_c$  for the chemical instability are obtained from Eqs. (15) and (16) and also shown in Table I.

The  $p$ - $T$  and  $n$ - $T$  phase diagrams for the molten salts NaCl and CsCl are depicted in Figs. 1 and 2. Dashed lines in Figs. 1 and 2 show schematically the form of the coexistence curves for the chemical instability which have not been calculated in the present work. Some portions of these curves obtained from different models can be found in Ref. 13.

The model under consideration could also be applied to the weak electrolytes. Let us consider the dilute solutions of alkaline salts in different solvents. For example, solubility of CsCl in NH<sub>3</sub> is equal to 0.038%.<sup>11</sup> Therefore, one can study the chemical instability of this system assuming that the salt does not change the critical parameters

of NH<sub>3</sub> [ $T_{cr} = 406$  °K;  $P_{cr} = 112$  atm (Ref. 14)]. Ionic radius, as is shown in Table I, is equal 1.8 Å, while the dielectric constant of the medium is high,  $\epsilon = 15$ . (We neglect the possible solvation of ions as well as the additional chemical reactions.) According to (15) we obtain  $T_c \approx 390$  °K, i.e., very close to the critical temperature,  $T_{cr} = 406$  °K. It is possible, therefore, that the liquid-vapor and metal-nonmetal transitions coincide, i.e., the dielectric vapor-metallic liquid-phase transition exists. Note that Eq. (16) has no solution for the critical density if the dissociation energy for CsCl is taken as 4.4 eV, as is shown in Table I. The highly polarized medium significantly lowers the dissociation energy. We do not know of any optical measurements of the absorption edge for this system which would allow one to find the effective dissociation energy and then, from (16), the critical parameters of the phase transition connected with the chemical instability.

### III. THREE-COMPONENT ELECTRON-IONIC PLASMA (METALLIC VAPORS)

As distinct from the ionic plasma, here one of the components (electrons) is considerably lighter than the other components. This circumstance can

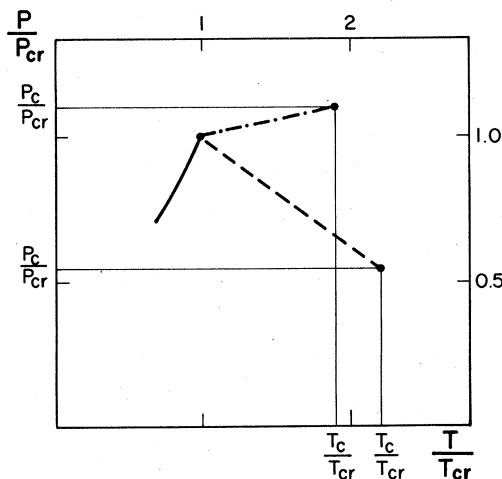


FIG. 1. Schematic form of pressure-temperature phase diagram for molten salts NaCl (-----) and CsCl (- - - -).  $T_{cr}$  and  $T_c$  are the critical points of the liquid-gas and the chemical instability, respectively.

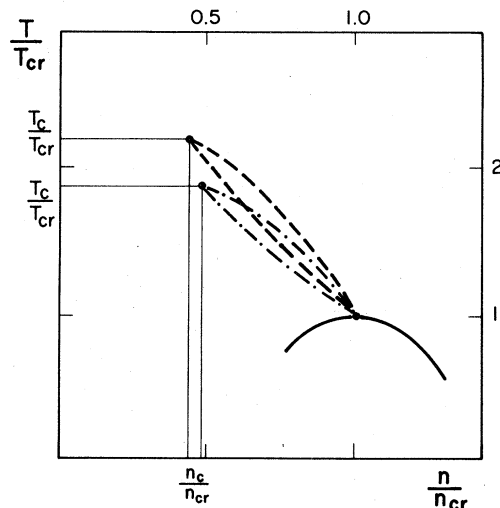


FIG. 2. Schematic form of temperature-density phase diagram for the molten salts.  $T_{cr}$  and  $T_c$  as in Fig. 1.

be taken into account in a model assuming that the heavy particles (atoms and ions) are located at the crystal lattice sites while the light electrons are free to move throughout this lattice. Furthermore, we assume that the sum  $N_0 = N_A + N_I$  of the numbers of atoms ( $N_A$ ) and of ions ( $N_I$ ) is less than the whole number of lattice sites  $N, N_0 < N$ . There are two

order parameters in such a system; the density  $\rho = N_0/N$  and the fraction  $N_I/N_0$ . Corresponding to these order parameters the two types of instabilities (liquid-vapor and the chemical instability) are possible.

The Helmholtz free energy of a system has the following form:

$$F = \frac{Z\epsilon_A}{2N} (N_0 - N_I)^2 - 2T \left( \frac{\pi n_0}{N} \right)^{1/2} \left( \frac{2e^2}{\epsilon T} \right)^{3/2} \left( \frac{\ln(1+c\kappa)}{(c\kappa)^3} + \frac{1}{2c\kappa} - \frac{1}{(c\kappa)^2} \right) + N_I T \ln \left[ \frac{n_0 N_I}{2eN} \left( \frac{2\pi\hbar^2}{m_e T} \right)^{3/2} \right] + T \left( (N - N_0) \ln \frac{N - N_0}{N} + N_I \ln \frac{N_I}{N} + (N_0 - N_I) \ln \frac{N_0 - N_I}{N} - N \ln 2 \right) + N_I I, \quad (17)$$

where  $\epsilon_A$  is the interaction energy between atoms (ions) located at the nearest-neighbor sites,  $I$  is the atomic potential, and  $Z$  is the coordination number of a crystal lattice.

The first two terms in Eq. (17) are the interaction energies between the atoms and charged particles. The third term is the free energy of an electron gas. The next (entropy) term relates to the localized atoms and ions. The final term is due to the formation of the ions and electrons as a result of the ionization of atoms.

In the second and third terms in Eq. (17) we passed from the dimensionless density  $\rho$  to the dimensional one according to the formula  $n = n_0 \rho$ . But the critical point in the lattice-gas model is characterized by a critical density  $\rho_c = \frac{1}{2}$ . Therefore, the value  $n_0$  is equal to double the critical density,  $n_0 = 2n_{cr}$ .

Analogously to the previous paragraph, let us find the law-of-mass action (4) for the model (17):

$$A = - \left( \frac{\partial F}{\partial N_I} \right)_{N, T} = T \ln \left[ \frac{(N_0 - N_I) 2N}{N_I^2 n_0} \left( \frac{m_e T}{2\pi\hbar^2} \right)^{3/2} \right] - Z\epsilon_A \frac{N_0 - N_I}{N} + 2r \frac{(N_I/N)^{1/2}}{1 + \alpha(N_I/N)^{1/2}} - I = 0, \quad (18)$$

$$r = \frac{(\pi n_0)^{1/2}}{2} \left( \frac{2e^2}{\epsilon T} \right)^{3/2}, \quad \alpha = c \left( \frac{8\pi e^2 n_0}{\epsilon T} \right)^{1/2}.$$

According to (10), the boundary of stability is determined by the derivatives of the free energy (17), where the number of sites (cells) of a crystal lattice  $N$  plays a role of volume  $V$ . Performing the appropriate calculations one can transform the condition  $(\partial A / \partial N_I)_{P, T} = 0$  to the following form:

$$\frac{Z\epsilon_A}{T} \frac{2(N - N_0) + N_I}{N} - \frac{2N - N_I}{N_0 - N_I} + r \frac{N - N_I}{N_0 - N_I} \left( \frac{N_I}{N} \right)^{1/2} \times \frac{1}{[1 + \alpha(N_I/N)^{1/2}]^2} - \frac{Z\epsilon_A r N_I^{1/2} (N - N_0)}{TN^{3/2} [1 + \alpha(N_I/N)^{1/2}]^2} = 0. \quad (19)$$

In contrast to (11), Eq. (19) is not expressed as

a product of simple terms. However, after an expansion to order of  $(N_I/N)^{1/2}$ , Eq. (19) can be rewritten

$$\left( 1 - \frac{Z\epsilon_A \rho (1 - \rho)}{T} \right) \left( 1 - \frac{r(N_I/N)^{1/2}}{2[1 + \alpha(N_I/N)^{1/2}]^2} \right) = 0. \quad (20)$$

Vanishing of the first factor in Eq. (20) determines the usual stability condition of a crystal lattice and leads to the critical parameters  $\rho_{cr} = \frac{1}{2}$ ,  $T_{cr} = \frac{1}{4} Z\epsilon_A$ . Hence, to the first approximation in  $(N_I/N)^{1/2}$ , the charged particles do not shift the liquid-gas critical point, while to the second approximation in  $(N_I/N)^{1/2}$  the nonsymmetry of the metallic side of the coexistence curve appears, which agrees with experiment.

Vanishing of the second factor in Eq. (20) determines the boundary of the chemical instability. Performing the analysis analogous to (14) and (15), one can find the critical temperature and concentration for the chemical instability which resemble results (15):

$$T_c = \frac{e^2}{16\epsilon c}, \quad N_{I,c} = \frac{N_c}{v_0 n_0}, \quad v_0 = 128\pi c^3. \quad (21)$$

To find the critical density  $\rho_c$  and the critical pressure  $p_c$  one must use the law-of-mass action (18) and the equation of state  $p = -(\partial F / \partial N)_{T, N_I}$ , which can be rewritten in the following form:

$$y = M \exp [I/T_c + (4T_{cr}/T_c)y - 8], \quad (22)$$

$$p_c = (T_c/v_0) \{ -0.82 - n_0 v_0 \ln [1 - (n_0 v_0)^{-1} y] - (Z\epsilon_A n_0 v_0 / 2T_c) y^2 \},$$

where

$$y = \rho_c - (n_0 v_0)^{-1}, \quad M = \frac{1}{2n_0 v_0^2} \left( \frac{2\pi\hbar^2}{m_e T_0} \right)^{3/2}.$$

The model under consideration could be applied to the metallic vapor at high densities where a sharp increase of conductivity, at the temperatures and the densities near the critical point, has been

found experimentally. [We have considered<sup>15</sup> the metal-nonmetal transition using a model slightly different from (17), without analyzing the full stability conditions.] Let us perform numerical calculations for cesium. The critical parameters for cesium are  $T_{cr}=2020$  °K,  $p_{cr}=110$  atm,  $\rho_{cr}=0.45$ (g/cm<sup>3</sup>).<sup>16</sup> The value of  $n_0$  entering (21) and (22) is equal, as was mentioned above, to the double critical density, i.e.,  $n_0=2n_{cr}=2\rho_{cr}/m=4\times 10^{21}$  cm<sup>-3</sup>. Unfortunately, there exist neither experimental nor theoretical information about the effective ionization potential  $I$ , dielectric constant  $\epsilon$ , and the effective radius of charged particles  $c$ . Therefore, let us assume a likely order of magnitude value,  $I=3.89$  eV (the ionization potential of an isolated cesium atom,<sup>14</sup>)  $\epsilon=1$  and  $c=1$  Å. From (21) and (22) it turns out that  $T_c=10\,000$  °K,  $p_c=2800$  atm,  $\rho_c=0.630$ , i.e.,  $n_c=2.52\times 10^{21}$  cm<sup>-3</sup>. The schematic form of the  $T$ - $n$  phase diagram is depicted in Fig. 3.

Comparing the phase diagrams of the ionic and electron-ionic plasma, one can see that in the latter system the critical parameters of the chemical instability are higher than in the former one as can be expected. It is probable that the metal-nonmetal transition observed experimentally is indeed the lower part of the coexistence curve corresponding to chemical instability.

#### IV. IONIZATION REACTION IN A REGULAR SOLUTION (SOLUTIONS OF METAL IN THEIR SALTS)

So far we have considered different types of ionization of the neutral particles (atoms, molecules).

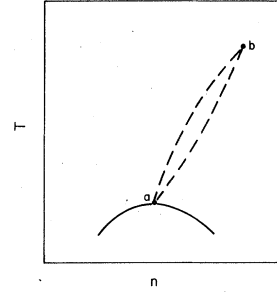


FIG. 3. Schematic form of temperature-density phase diagram for the metallic vapor of cesium.  $a$  and  $b$  are the critical points of the liquid-gas and the chemical instabilities, respectively.

Such systems are characterized by instability with respect to the liquid-vapor separation as well as by the chemical instability. However, the situation is common when the dissociating system is located in a solution. The solvent does not participate in a chemical reaction even if it could be a catalyst for it. Such a solution could be unstable with respect to diffusion, as well as chemically unstable. Let us assume that the solvent and neutral particles make up a strictly regular solution which, as is well known, allows an order-disorder phase transition. Solutions of metals in their fusion salts are the typical examples of such systems.

The Gibbs free energy has the following form:

$$\Phi = NT \ln \left[ \frac{N}{N_0 + N_I} \frac{P}{T} \left( \frac{2\pi\hbar^2}{mT} \right)^{3/2} \right] + (N_0 - N - N_I) T \ln \left[ \frac{N_0 - N - N_I}{N_0 + N_I} \frac{P}{T} \left( \frac{2\pi\hbar^2}{m_A T} \right)^{3/2} \right] + \frac{UN(N_0 - N - N_I)}{N_0 - N_I} + 2N_I T \ln \left[ \frac{P}{\sqrt{2}T} \left( \frac{4\pi^2\hbar^4}{T^2 m_I m_e} \right)^{3/4} \right] - 2 \left( \frac{\pi P T}{N_0 + N_I} \right)^{1/2} \left( \frac{2e^2 N_I}{\epsilon T} \right)^{3/2} \left( \frac{\ln(1+c\kappa)}{(c\kappa)^3} + \frac{1}{2c\kappa} - \frac{1}{(c\kappa)^2} \right) + N_I I, \quad (23)$$

where  $m$  and  $N$  are the mass and the number of particles of the solvent. To get Eq. (23) we used the condition of electroneutrality  $N_I = N_e$  and the conservation of number of the heavy particles in the ionization reaction:  $N + N_A + N_I = N_0 = \text{const}$ .

The first three terms in Eq. (23) have a standard form for the so-called strictly regular solutions. The next two terms describe a system of charged particles, and, finally, the last term is responsible for dissociation.

The law-of-mass action  $(\partial\Phi/\partial N_I)_{P, T, N} = 0$  takes the form

$$\ln \left[ \frac{P}{2T} \frac{N_I^2}{(N_0 + N_I)(N_0 - N - N_I)} \left( \frac{m_A}{m_I m_e} \frac{2\pi\hbar^2}{T} \right)^{3/2} \right] + \frac{I}{T} - \frac{U}{T} \left( \frac{N}{N_0 - N_I} \right)^2 - 2 \left( \frac{\pi P}{T} \right)^{1/2} \left( \frac{2e^2}{\epsilon T} \right)^{3/2} \left( \frac{N_I}{N_0 + N_I} \right)^{3/2} \left[ \frac{\ln(1+c\kappa)}{(c\kappa)^3} - \left( \frac{1}{2c\kappa} + \frac{1}{(c\kappa)^2} - \frac{N_0 + N_I}{2N_I} \right) (1+c\kappa)^{-1} \right] = 0. \quad (24)$$

According to (6) the boundary of stability is determined by vanishing of the derivative  $(\partial A/\partial N_I)_{P, T, \mu}$ . This condition could be rewritten

$$\left( \frac{\partial A}{\partial N_I} \right)_{P, T, \mu} = \frac{(\partial A/\partial N_I)_{P, T, N} (\partial \mu/\partial N)_{P, T, N_I} - (\partial A/\partial N)_{P, T, N_I} (\partial \mu/\partial N_I)_{P, T, N}}{(\partial \mu/\partial N)_{P, T, N_I}}. \quad (25)$$

Performing all the necessary differentiations and taking into account that  $\mu = (\partial\phi/\partial N)_{P, T, N_I}$ , one can find the boundary of stability which has the following factorized form:

$$\left(T - \frac{2UN(N_0 - N - N_I)}{(N_0 - N_I)^2}\right) \left[T - \frac{(\pi P)^{1/2}}{4T} \times \left(\frac{2e^2}{\epsilon}\right)^{3/2} \left(\frac{N_I}{N_0 + N_I}\right)^{1/2} \times \frac{N_0 - N_I}{(N_0 + N_I)(1 + c\kappa)^2}\right] = 0. \quad (26)$$

Two factors in (26) determine the two types of instability, namely, diffusional and chemical. The difference between (26) and the instability conditions discussed previously is that here we obtain lines of critical points rather than isolated points. This difference is obvious by virtue of an additional degree of freedom associated with the presence

$$T_0 \ln \left( \frac{P_c [(m_A/m_I m_e) 2\pi h^2 / T_0]^{3/2}}{2T_0(1 + p_c v_0 / T_0) [(N_0 - N_c) p_c v_0 / T_0 N_0 - 1]} \right) + I - \frac{UN_c^2 P_c^2 v_0^2}{N_0^2 T_0^2 (p_c v_0 / T_0 - 1)^2} - \frac{8T_0^2(4 \ln 2 - 2 + P_c v_0 / T_0)}{P_c v_0} = 0. \quad (29)$$

As an example, let us apply this model to the solution of Na in NaCl. The critical parameters of this system are  $T_{cr} = 1350$  K;  $N_{cr} = 0.5N_0$ ,<sup>17</sup> the dielectric constant  $\epsilon = 1.7$ ,<sup>12</sup> and the effective ionization potential  $I = 1.90$  eV. Unfortunately, we do not know any experimental data concerning the effective ionic radius  $c$ ; therefore, we choose the likely value  $c = 3.5$  Å. Then, one obtains from (28),  $T_c = 1750$  K. Let us find the projection of the boundary stability on the plane  $p = \text{const}$ , say  $p = 150$  atm. From Eq. (29) we can find a location of the critical point on this plane, namely,  $N_c = 0.7N_0$ , and the  $T-N$  phase diagram has the form depicted in Fig. 3.

#### V. IONIZATION IN A REGULAR SOLUTION WITH SIGNIFICANTLY DIFFERENT MOLAR VOLUMES OF COMPONENTS (METAL-AMMONIA SOLUTIONS)

Regular solutions of metals in their fusion salts which have been considered in Sec. IV, have the critical points at about (50–50)% solutions. This experimental situation is adequately described by the model of regular solution [see (27)]. On the other hand, critical phenomena in the comprehensively studied metal-ammonia solutions have been observed in systems of which metal constitute a few molar fractions. Nevertheless as it was noted in Ref. 18, one can describe the phase separation in metal-ammonia solutions using the

of a solvent.

We shall not analyze the full phase diagram here. Let us find the location of critical points for the case of weak ionization, to first order in the parameter  $[N_I/(N_0 + N_I)]^{1/2}$ . As one would expect, a vanishing of the first factor in Eq. (26) will give, in the approximation used, the critical point of a binary mixture

$$T_{cr} = \frac{1}{2}U, \quad N_{cr} = \frac{1}{2}(N_0 - N_{I,cr}). \quad (27)$$

Vanishing of the second factor in (26) determines the chemical instability. As a first approximation ( $N_I/N_0 \ll 1$ ), the analyses similar to (14) and (15), leads to the critical parameters for the chemical instability

$$T_0 = \frac{e^2}{16\epsilon c}, \quad N_{I,c} = \frac{N_0 T_0}{v_0 P}, \quad v_0 \equiv 128\pi c^3. \quad (28)$$

Substituting (28) in the law-of-mass action (24) one can find the  $N_c - P_c$  line of critical points for the chemical instability

model of regular solution for volume rather than molar fractions (the Flory model).

Let  $V$  be the molar volume of one of the components (in our case, solvent), and  $V_A$  the molar volume of the second component (neutral atoms). The volume fractions  $\phi$  and  $\phi_A$  are connected with the number of particles of the solvent  $N$  and those of the neutral atoms  $N_0 - N - N_I$  in the following obvious way:

$$\phi = \frac{NV}{NV + (N_0 - N - N_I)V_A}, \quad (30)$$

$$\phi_A = \frac{(N_0 - N - N_I)V_A}{NV + (N_0 - N - N_I)V_A}.$$

The Gibbs free energy has the form (23) where  $N$ ,  $N_0 - N - N_I$ , and  $N + (N_0 - N - N_I) = N_0 - N_I$  are replaced by  $VN$ ,  $V_A(N_0 - N - N_I)$ , and  $VN + V_A(N_0 - N - N_I)$ , respectively. Let us introduce the ratio of the molar volumes  $q = V_A/V$  (degree of polymerization or solvation) which is now an important parameter. When  $q \neq 1$ , the Gibbs free energy (23) has to be changed in the entropy part (first two terms) as well as in the energy [third term in (23)]. One can show that the entropy part is a monotonic function of  $q$ , and the energy term has a maximum. Therefore, for some  $q$  both these parts can be equally important.

At first, let us restrict ourselves to the consideration of the  $q$  dependence of the energy term,

as has been done in Ref. 18. Thus one can use Eq. (23) replacing only the third term in (23) by  $U'[NV\phi_A^2 + (N_0 - N - N_I)V_A\phi^2]$ . Performing all calculations in the same manner as in the previous section, we find that the instability condition  $(\partial A/\partial N_I)_{P,T,\mu}$  reduces again to the product of two terms. The condition of the chemical instability is the same as in Eq. (26), but the condition of the liquid-liquid separation becomes

$$T = \frac{2U'V^2V_A^2N(N_0 - N - N_I)(N_0 - N_I)}{[NV + (N_0 - N - N_I)V_A]^3}. \quad (31)$$

Then, from the analyses similar to (14) and (15), one obtains, for the critical point of a binary mixture,

$$N_{cr} = (N_0 - N_{I,cr})t, \quad t = q/[(1 - q + q^2)^{1/2} + 1], \quad (32)$$

$$T_{cr} = 2U'V_Aqt(1 - t)/[t + (1 - t)q]^3.$$

It follows from Eq. (32) that at  $q = 1$  we return to Eq. (27) (with redefined constant  $U'V_A = U$ ), while as  $q \rightarrow \infty$   $N_{cr, q \rightarrow \infty} \rightarrow -1$  and  $T_{cr, q \rightarrow \infty} \rightarrow \frac{2}{3}U'V_A = \frac{4}{3}T_{cr, q=1}$ .

Metal-ammonia solutions have been studied experimentally in great detail. An analysis of the vapor-pressure-concentration curves is a direct method for obtaining the chemical potentials.<sup>18</sup> It was found,<sup>19</sup> that  $U' = 6.45$  cal/cm<sup>3</sup>, and the sodium is solvated and surrounded by about 6.5 NH<sub>3</sub> molecules. Therefore,  $V \equiv V_{NH_3} = 25$  cm<sup>3</sup>/mol and  $V_A = V_{Na} + 6.5V_{NH_3} = (65 + 6.5 \times 25)$  cm<sup>3</sup>/mol = 227.5 cm<sup>3</sup>/mol. Then  $q \equiv V_A/V \approx 9$  and, according to (32),  $N_{cr} = 0.04$  and  $T_{cr} = 230$  °K which is in agreement with experimental data.

Directing our attention to the chemical instability, we note that the corresponding critical temperature,  $T_c = e^2/16\epsilon c$  is quite low due both to the large dielectric constant and large effective ionic radius of this medium. Taking  $c \approx 4$  Å, which is of order of the size of potential well for the solvated ions, then  $T_c = 520$  °K. As before, the  $N_c - p_c$  curve of critical points is given by Eq. (29), where  $I$  can be found from the absorption edge measurements. Thus, for example,  $I = 0.85$  eV for Li-NH<sub>3</sub>.<sup>20</sup>

It is easy to take into account the difference between molar volumes in the entropy terms in Eq. (23), as well. Then, however, the stability condition does not factorize into the product of two terms, so that in order to determine the critical parameters it is necessary to solve equations  $A = (\partial A/\partial N_I)_{T,P,\mu} = (\partial^2 A/\partial N_I^2)_{P,T,\mu} = 0$  numerically.

## VI. CONCLUSIONS

Let us clarify the physical reasons for the instability under consideration. For the fluids, the chemical potentials can be written in the form  $\mu_i = \mu_{i,0}(P, T) + T \ln(\gamma_i X_i)$ , where the activities  $\gamma_i$

determine the deviation of the fluid ideality; in the latter case  $\gamma_i = 1$ . Then one can write the law-of-mass action (4) in the following form:

$$X_A/X_I X_e = K_{id}(T, P) \gamma_I \gamma_e / \gamma_A \equiv K \quad (33)$$

The chemical equilibrium constant for the ideal system  $K_{id}(T, P)$  is determined by the functions  $\mu_{i,0}(P, T)$ , i.e., by the properties of the single components, while for the nonideal system,  $K$  depends also on the interactions between components. The activities  $\gamma_i$  depend on the  $X_i$ ; therefore, for certain values of  $P$  and  $T$ , Eq. (33) can have more than one solution for the number density of the reacting species. This means that the given chemical reaction is "unstable" and phase separation can occur.

From these arguments it is clear that a system has to be considerably nonideal for the existence of the chemical instability, i.e., the interaction energy must be of order of the characteristic energy of a single particle. The chemical instability could appear in nonexotic conditions if the interaction energy between particles is high, as, for example, in a gas consisting of charged particles (plasma, electrolytes, molten salts, metal-ammonium solution, solid-state plasma). Another possibility is when the characteristic energies of single particles are small, as is the case of isomers. The latter case has been discussed previously<sup>1</sup>; here we considered a system of neutral and ionized particles in ionization equilibrium.

The chemical instability for the ionization reaction (1) means a separation of a system into two phases with different degrees of ionization. Increase of the volume occupied by the strongly ionized ("metallic") phase results in appearance of a metallic conductivity of the system as a whole.<sup>21</sup>

Let us note that the appearance of "metallic clusters" in the dielectric phase has been discussed, for example, for the metal-ammonia solutions. Different models have been used such as a liquid-vapor phase separation of the metal within the ammonia solvent,<sup>22</sup> appearance of aggregates of metal atoms,<sup>14</sup> charged "clouds" near metal atoms,<sup>23</sup> etc. In our consideration an inhomogeneity is a result of the chemical instability of the ionization reaction. This is a completely general criterion of the metal-nonmetal transition. At temperatures lower than the critical one, the Coulomb interaction between ions which is, on average, an attractive interaction, leads to a violation of stability as the density increases. On the other hand, the repulsion of the hard spheres at high densities restores the stability. If the radius of hard cores  $c$  approaches zero, the critical temperature  $T_c$  goes to infinity ac-



ording to (17). Of course, hard core is only one example of repulsion between particles at short distances. Qualitatively, the same results might be obtained with, for example, quantum-repulsion forces. Let us note that the hard-core approximation is equivalent to including the bound states in the statistical sum.<sup>4</sup>

As is well known, there exists another general criterion of metal-nonmetal transition, namely, the Mott criterion, according to which the transition occurs at high densities when the charged particles cannot create bound states because of the screening. The Mott transition does not take place if the density  $n$  is not too high, namely,<sup>24</sup>

$$n^{1/3} < 1/4a_0, \quad (34)$$

where  $a_0 = \epsilon \hbar^2 / m^* (Ze)^2$  is Bohr radius containing, in principle, the dielectric constant  $\epsilon$ , the total charge  $Ze$ , and the effective mass  $m^*$ .

Common to all cases discussed above is the Debye-Hückel form of the interaction energy between the charged particles. It is assumed, therefore, that the gas of charged particles deviates slightly from the perfect gas, i.e., the mean energy of the Coulomb interaction of two particles ( $\sim Ze^2 / \epsilon r$ ) must be small compared to their kinetic energy ( $\sim T$ ). The average distance between particles  $r$  is determined by their number density and equal to  $n^{-1/3}$ . Thus we must have

$$n^{1/3} < T \epsilon / (Ze)^2. \quad (35)$$

Let us note that the fulfillment of these two conditions (34) and (35), means the absence of degeneracy and a possibility of a classical description of plasma. In fact, the criterion of an absence of degeneracy  $T > (\hbar^2 / m^*) n^{2/3}$  is the product of criteria (34) and (35).

In all cases discussed above and for all values of the parameters which have been used the chemical instability occurs before the criteria (34) and (35) are violated. However, the results of our calculations are crucially dependent on the dielectric constant  $\epsilon$ , the ionic radius  $c$ , and the dissociation energy  $I$  which, in turn, are functions of density. Further development of the model would involve taking into account the dependence of the Van der Waals parameters  $a$  and  $b$  as well as that of the dielectric constant  $\epsilon$  on the degree of ionization. Our treatment enables one to take into account the dependence of the dielectric constant on the degree of ionization and density. According to the Clausius-Mossotti relation a correction term appears which is linear in the density of particles. However, the inclusion of such a term requires simultaneously the inclusion of the next approximation in the Debye-Hückel energy. All these correction terms do not change, however, the general results derived above.

The dielectric constant increases near the critical points of pure fluids and binary mixtures. Dielectric constant and refractive-index measurements show<sup>25-27</sup> that the anomaly of the dielectric constant reaches a magnitude of about (0.01–0.1)% of the background in the narrow region of a few mK near the critical point. These experimental data agree with the theoretical analysis, showing that the dielectric constant belongs to the quantities with "weak" singularities at the critical points. On the other hand, our treatment does not attempt to describe the immediate vicinity of the critical points where the critical phenomena take place. To do this one would have to include the fluctuation terms in the free energies (8), (17), and (23).

<sup>1</sup>M. Gitterman and V. Steinberg, *J. Chem. Phys.* **69**, 2763 (1978).

<sup>2</sup>D. Adler and H. Brooks, *Phys. Rev.* **155**, 826 (1967).

<sup>3</sup>G. E. Norman and A. N. Starostin, *Teplofiz. Vys. Temp.* **8**, 413 (1970) [*High Temp. USSR* **8**, 381 (1970)].

<sup>4</sup>W. Eberling, *Ann. Phys. (Leipzig)* **19**, 104 (1967); **22**, 383 (1969); **22**, 392 (1969); *Physics* **38**, 378 (1968); **43**, 293 (1969).

<sup>5</sup>M. Gitterman and V. Steinberg, *J. Chem. Phys.* (to be published).

<sup>6</sup>K. H. Schramm, *Z. Phys.* **165**, 336 (1961).

<sup>7</sup>V. A. Alekseev, E. P. Velichoff, and G. W. Lopantzeva, *Electricity from M. H. D.* (IAEA, Vienna, 1966), p. 617.

<sup>8</sup>K. I. Serjakoff, *Teplofiz. Vys. Temp.* **6**, 749 (1968) [*High Temp. USSR* **6**, 735 (1968)].

<sup>9</sup>N. I. Klyuchnikov, S. A. Triger, *Zh. Eksp. Teor. Fiz.* **55**, 1248 (1968) [*Sov. Phys. JETP* **28**, 653 (1969)].

<sup>10</sup>A. D. Kirshenbaum, *J. Inorg. Nucl. Chem.* **24**, 1287 (1962).

<sup>11</sup>S. Petrucci, *Ionic Interactions*, Vol. 1. (Academic, New York-London, 1971).

<sup>12</sup>*Molten Salts Handbook*, edited by George J. Janz (Academic, New York-London, 1967).

<sup>13</sup>B. A. Zeigarnik, G. A. Kobzev, U. K. Kurilenkoff, and G. E. Norman, *Teplofiz. Vys. Temp.* **10**, 693 (1972) [*High Temp. USSR*, **10**, 658 (1972)].

<sup>14</sup>*Metal-Ammonia Solutions*, Colloq. Weyl, I. edited by G. Lepoutre and M. J. Sienko (Benjamin, New York, 1964).

<sup>15</sup>M. Gitterman and V. Steinberg, *Phys. Rev. Lett.* **35**, 1588 (1975).

- <sup>16</sup>U. Even and J. Jortner, Phys. Rev. B 8, 2536 (1973).
- <sup>17</sup>*Molten Salt Chemistry*, edited by M. Blander (Interscience, New York-London-Sydney, 1964).
- <sup>18</sup>U. Schindewolf and M. Werner, Ber Bunsenges. Phys. Chem. 81, 1008 (1977).
- <sup>19</sup>P. Demay, in *Electrons in Fluids*, edited by J. Jortner and N. R. Kestner (Springer-Verlag, New York-Heidelberg-Berlin, 1973), p. 195.
- <sup>20</sup>M. Cohen and J. Thompson, Adv. Phys. 17, 70 (1968); 17, 857 (1968).
- <sup>21</sup>M. Cohen and J. Jortner, Phys. Rev. B 8, 2556 (1973).
- <sup>22</sup>K. S. Pitzer, J. Am. Chem. Soc. 80, 5046 (1958).
- <sup>23</sup>J. C. Thompson, Rev. Mod. Phys. 40, 704 (1968).
- <sup>24</sup>N. F. Mott, Philos. Mag. 6, 287 (1961).
- <sup>25</sup>R. Hocken, M. A. Horowitz, and S. C. Greer, Phys. Rev. Lett. 37, 964 (1976).
- <sup>26</sup>R. Hocken and L. R. Wilcox, Bull. Am. Phys. Soc. 17, 614 (1972).
- <sup>27</sup>C. L. Hartley, D. T. Jacobs, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. 33, 1129 (1974).