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PHASE EQUILIBRIA FOR HIGHLY UNSYMMETRICAL PLASMAS AND ELECTROLYTES

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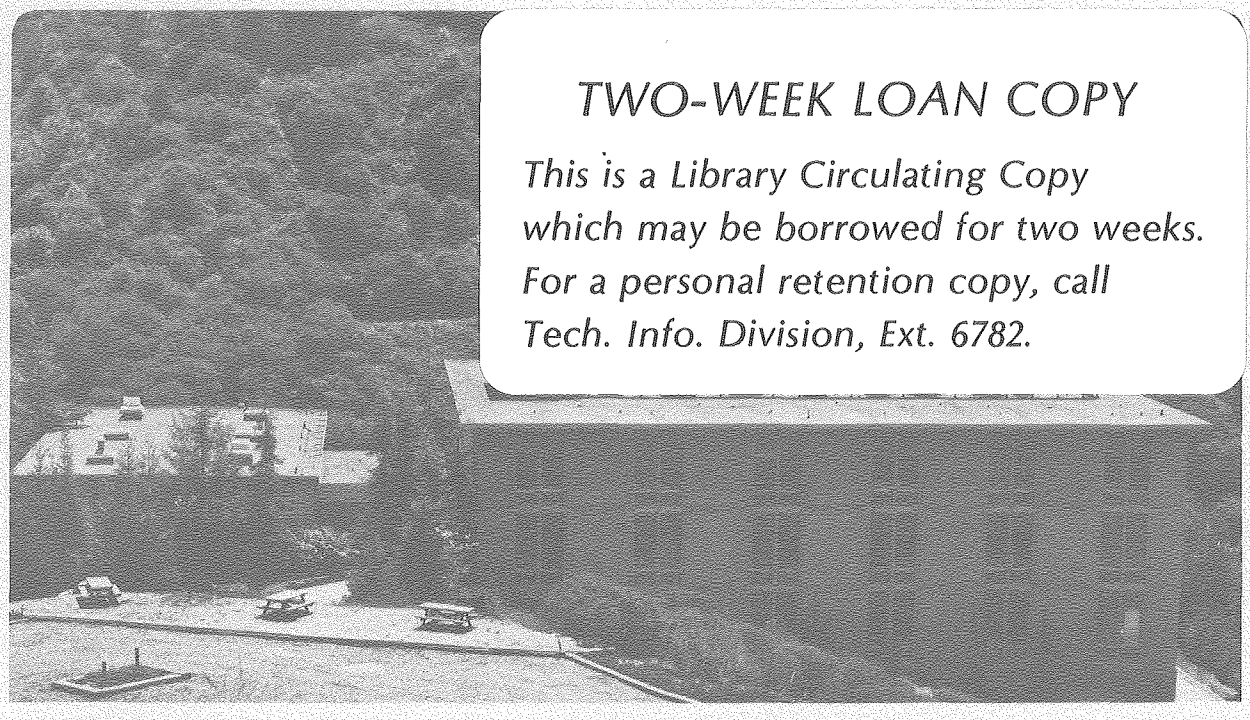

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Chemistry

Phase equilibria for highly unsymmetrical plasmas and electrolytes

(Debye-Hückel theory/critical phenomena)

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ABSTRACT. The conclusion of classical Debye-Hückel theory that a phase separation may occur in highly unsymmetrical plasmas or electrolytes is shown to be false and to arise from a serious error in the treatment of the interaction of pairs of the most highly charged ions. After an approximate correction for this error, no phase separation is predicted. Specific application to iron in the solar plasmas is discussed.

The classical Debye-Hückel equation indicates separation into two phases for a plasma or electrolyte with a highly unsymmetrical charge pattern such as the solar plasma including highly ionized iron. Pollock and Alder (1) showed that the Debye-Hückel equation gave this result for solar conditions and discussed its implications for the solar neutrino dilemma. They also noted that Debye-Hückel theory was not valid for the iron-rich phase; thus a better theory is needed for reliable prediction of the phase behavior of solar plasma.

While the extension of Debye-Hückel theory to be presented below is approximate, it identifies the major correction needed and shows that the indication of phase separation was false. The present theory is based on classical (rather than quantum) mechanics for the translational motion of the ions (including dissociated electrons); in that domain no phase separation is expected.

In a two-component system the possibility of phase separation is determined by the sign of the second derivative of the Gibbs energy with respect to the fraction of one component. One may use any of several alternate measures of composition on a self-consistent basis; we shall use the fraction of total particles whereby the $z+$ ion and z electrons comprise the $z + 1$ particles assigned to that component. This is equivalent to the volume fraction on an ideal gas basis. Thus we wish to obtain for a mixture with a fixed total of N particles

$$\frac{\partial^2 G}{\partial x^2} = \frac{\partial^2 G^{id}}{\partial x^2} + \frac{\partial^2 G^{ex}}{\partial x^2} \qquad (1)$$

where G^{id} is the Gibbs energy on an ideal gas (or ideal solution) basis and G^{ex} is the excess Gibbs energy. The ideal term is always positive, and if it dominates, no phase separation is possible. But if the second derivative of the excess Gibbs energy becomes sufficiently negative, it may exceed the positive value of the ideal term and separation into two phases may occur.

It proves easier to discuss initially the excess internal energy E^{ex}. One then calculates the excess Helmholz energy by integrating the thermodynamic relationship $[\partial(A/T)/\partial(1/T)]_V = E$ from zero in 1/T to the final value and thereafter one adds the term $VP = -V(\partial A/\partial V)_T$ to obtain G.

The radial distribution or binary correlation functions provide the basis for understanding the present problem. This function $g_{ij}(r_{ij})$ gives the probability of finding ions i and j at distance r_{ij} as a ratio to the purely random probability. Then the excess internal energy of the system is given by the equation

$$E^{ex} = 2\pi V \sum_i \sum_j c_i c_j \int_o^\infty u_{ij} g_{ij} r^2 dr \qquad (2)$$

where c_i, c_j are the concentrations of the particular species and V is the total volume for N particles. Also u_{ij} is the interparticle potential, in this case the coulombic potential $z_i z_j e^2/r_{ij}$. While Debye and Hückel

developed their theory in other terms, it may be restated in this form with the results

$$g_{ij} = 1-(z_i z_j e^2/kT)(e^{-\kappa r}/r) \quad (3)$$

$$\kappa^2 = (4\pi e^2/kT) \sum z_i^2 c_i \quad (4)$$

$$E^{ex} = G^{ex} = kTV\kappa^3/8\pi. \quad (5)$$

This expression for g_{ij} is a linear approximation of a Boltzmann exponential in which the exponent is the last term in equation (3). Thus the simple Debye-Hückel treatment fails if this exponent becomes larger than one for any appreciable range in r.

For the solar plasma it is reasonable to assume that the iron is +24, i.e., retaining only the pair of 1s electrons undissociated, but the exact degree of ionization is not important. We also assume T = 1.7 x 10^7 K (1.5 keV) and P = 10^5 Mbar. Then the radial distribution functions on a Debye-Huckel basis are shown on figure 1. The H^+-e^-, H^+-H^+, and e^--e^- functions depart only slightly from unity and are omitted. The Fe^{+24}-e^- and Fe^{+24}-H^+ functions exceed 2 and drop below zero, respectively, only at small r; hence the error in these cases is moderate. But the Fe^{+24}-Fe^{+24} function becomes large and negative over a major range in r and this leads to a large and spuriously negative value of the integral in equation (2) for this term. A negative value of g_{ij} is, of course, physically impossible, and it arises only

from the linear approximation in equation (3).

At very low concentration of iron the factors c_{Fe} in equation (4) and c_{Fe}^2 in equation (2) are so small that little error is contributed by the Fe-Fe terms to the reciprocal length κ or the total excess energy in equation (5). But the second derivative with respect to the fraction iron essentially removes the c_{Fe}^2 factor and that term assumes full importance in comparison with the other terms in equation (2). A greatly improved approximation is obtained by a simple substitution of zero for the false negative value of g. Thus if g_{ij} is zero at r'_{ij}, the corrected excess internal energy becomes

$$E^{ex} = - \frac{kTV\kappa^3}{8\pi} - 2\pi V \sum_i \sum_j c_i c_j \int_0^{r'} g_{ij} u_{ij} \, r^2 dr \qquad (6)$$

where the integral covers only that region where $g_{ij} < 0$.

In view of the approximate nature of this basic procedure, approximations were made in the expression for r' and in the conversion from E^{ex} to G^{ex}, but it was verified that these approximations would not significantly affect the final results. Also it was found that the small region of negative g for the Fe-H term had only a small effect, hardly detectable on figure 2 which displays the results for the case of H-Fe plasma under solar conditions. For figure 2 the Gibbs energy includes the terms for mixing electrons with positive ions.

While the curve D-H on figure 2 for the simple Debye-Hückel equation shows a negative curvature from small x up to about 0.4 or 0.5, the "corrected" curve shows a substantial positive curvature across the entire composition range. This was verified by calculation of the second derivative; the negative contribution from the corrected excess Gibbs energy is never as much as one half of the positive contribution from the ideal term. The "ideal" curve is also shown on figure 2.

The linearized Poisson-Boltzmann equation which yields g_{ij} in equation (3) becomes a poorer approximation as the fraction iron increases; hence the "corrected" curve in figure 2 is only a rough estimate in the region of substantial fraction iron. In order to obtain an independent estimate for this region, a different method was used for the case of pure iron. Following in a sense the method of Bjerrum (2), the space was partitioned into an outer region for a Debye-Hückel treatment and inner spheres of radius R around each iron nucleus containing only electrons. A Boltzmann distribution of electrons was assumed, except for the 1s pair, but the coulombic potential for +24e was truncated at about half the thermal de Broglie wavelength. The Debye-Hückel equation for a distance of closest approach of 2R was employed and the excess energy was taken as the total for the electrons within the spheres and for those outside as well for the iron ions. The radius was chosen as small as possible subject to the condition that the

coulombic energy of two spheres at contact not appreciably exceed thermal energy. Reasonable values are R = 0.25 Å and a net charge of 20 protonic units. After integration with respect to 1/T (with appropriate variation of R) and addition of PV, the resulting Gibbs energy is shown by the open circle at x = 1 on figure 2. Since this point is well above the "corrected" curve, one estimates that the true curve toward the right side of figure 2 is above the "corrected" curve and the conclusion of positive curvature (and no phase separation) is reinforced.

This last calculation for pure iron plasma was repeated with the use of a truncated coulomb potential (3) instead of a hard-core in the Debye-Hückel treatment. The result is substantially the same.

While no mathematical proof is offered for the general absence of phase separation in classical unsymmetrical electrolytes, calculations for various examples are convincing to the writer. If one decreases the temperature from the solar case considered above, the degree of ionization of the iron will decrease. Also, for a given degree of ionization, the region of negative g implied by the Debye-Hückel distribution increases. Thus, although the Debye-Hückel equation for fixed z would yield an increasingly negative value of $\partial^2 G^{ex}/\partial x^2$, the "corrected" value for an appropriately decreased z remains smaller than the positive contribution from the ideal term. Eventually, further decrease in temperature at high density, leads to a boundary

beyond which all electron motion is in the quantum domain and the present methods cease to apply.

Explorarory calculations for highly unsymmetrical charge mixtures in electrolyte solutions also indicate no phase separation; this conclusion is in agreement with experiment. As in the case of the plasma containing highly charged ions, there is an association of counter ions with a highly charged ion in solution but this does not lead to phase separation as a function of solute fraction. There are examples in one component electrolytes at low effective temperature where there is a separation into concentrated and dilute phases. This phenomenon has been discussed by Friedman (4). In two-phase equilibrium the dilute phase comprises largely ion pairs while the concentrated phase is either fused-salt-like or metallic, e.g., metal-ammonia systems. While this last type of phase separation might occur in an unsymmetrical mixed electrolyte, it would arise in a very different range of temperature and concentration than that of the hypothetical Debye-Hückel separation discussed above and found not to occur.

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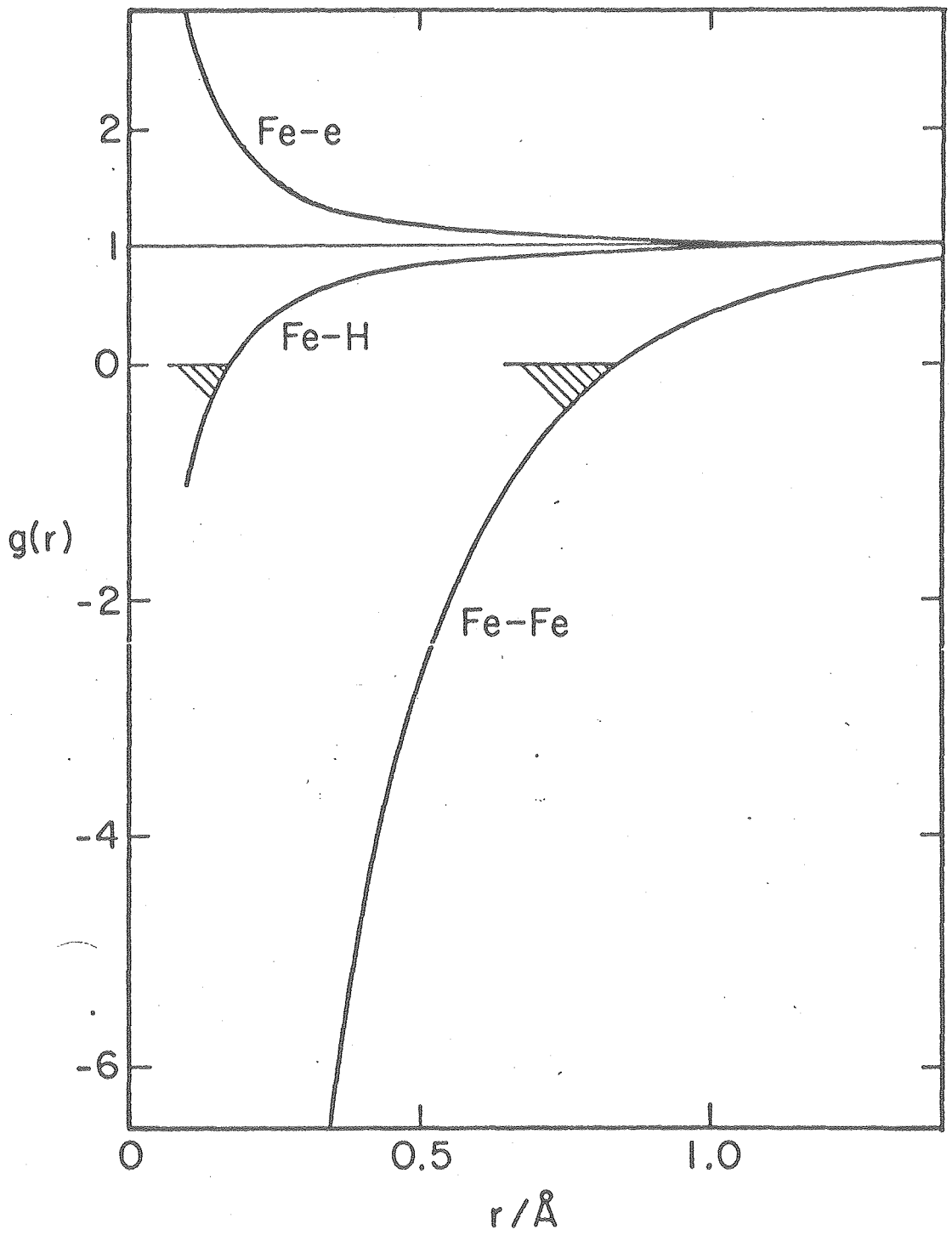
FIGURE CAPTIONS

Figure 1. Radial distribution functions in solar plasma according to classical Debye-Hückel theory. The negative regions are physically impossible and are removed in the corrected calculation.

Figure 2. The Gibbs energy for iron-hydrogen plasma under solar conditions. The curves are explained in the text.



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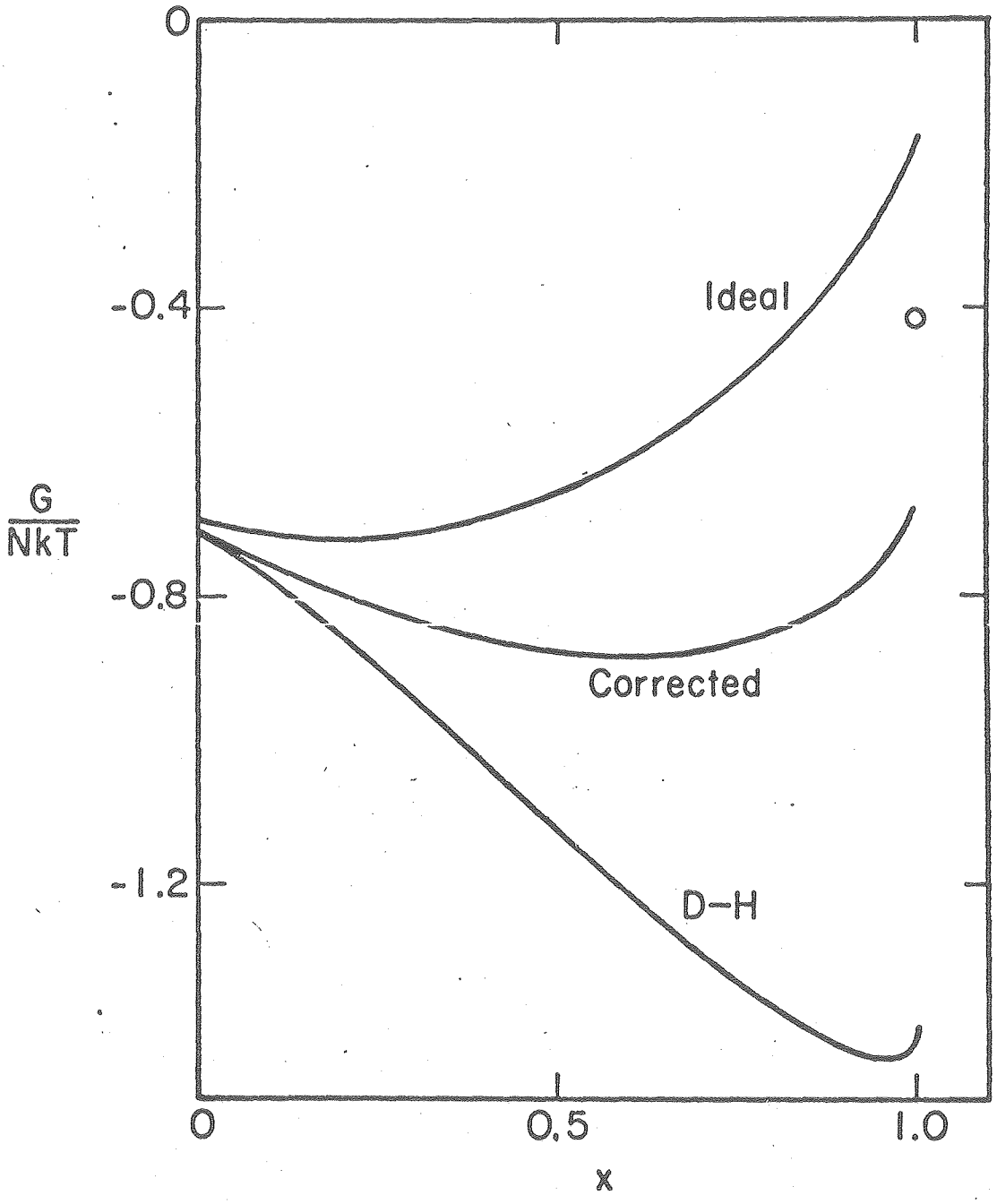

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