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D.A. GAVRYUSHENKO, K.V. TARADII

Taras Shevchenko National University of Kyiv
(2, Academician Glushkov Prosp., Kyiv 03022, Ukraine)**INFLUENCE OF RADIATION
ON PHYSICAL PROPERTIES OF LIQUIDS**

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Irradiation of condensed media appreciably changes the equilibrium thermodynamic properties of liquid systems; in particular, the thermodynamic equilibrium becomes violated, and the liquid restructuring takes place. The corresponding variations in the physical properties of liquid systems and their consequences have been considered.

Keywords: radiation, phase transition, multicomponent system.

1. Introduction

The creation of new-generation nuclear power installations requires a further development of radiation physics and radiation materials science. First of all, this is associated with physical processes running in such installations and, as a consequence, with the application of qualitatively different constructional materials. A special place among new-generation nuclear reactors is occupied by molten-salt nuclear reactors, with a radioactive melt playing a role of fuel, namely, chemical compounds of a radioactive element (uranium or plutonium) with fluorine dissolved in a melt of inorganic salts [1].

The melts of fluoride salts, when circulating through the active zone of molten-salt nuclear reactors, are irradiated with powerful fluxes of neutrons, electrons, γ -quanta, and decay fragments. Interaction between radiation and atoms in the melt stimulates a considerable number of various processes giving rise to a modification of physical and physico-chemical properties of the melt, as well as to a change in the character of the melt interaction with materials of solid-state constructions of nuclear power installations. As a result of those processes, the parameters of constructional materials and, as a probable consequence, their operation conditions may change.

Moreover, various biological systems also undergo irradiation. The influence of ionizing radiation on live organisms, tissues, cells, and so forth has been studied for many years. However, in those researches, no sufficient attention was paid to the influence of radiation on liquids in biological objects, although this in-

fluence can be substantial. Since a modification of the structural parameters of liquids results in a change of their thermodynamic properties, we have studied the influence of radiation on the thermodynamic properties of liquid systems, the changes in which are driven by a change of the chemical potentials of the liquid and its components under the influence of radiation.

**2. Change of Phase Equilibrium
Parameters if Only One Phase Is Irradiated**

The restoration of a equilibrium structure in liquids is accompanied by a variety of relaxation processes, among which the structural relaxation dominates [2, 3]. The thermal properties of the liquid substantially depend on the characters of those relaxation processes. However, a detailed analysis of relaxation processes and the determination of their contribution to the dynamic values of thermodynamic parameters remain to be a very difficult task and require the further study.

The irradiated medium is not at the equilibrium state, because irradiation induces a permanent deviation of the system from it. As the quasiparticle generation rate, which characterizes the radiation action, increases, this deviation grows. Consequently, the equilibrium state, which is realized in the absence of irradiation, changes and forms a number of states, which are called the thermodynamic branch. The thermodynamic branch is stable in a certain vicinity of the equilibrium state. However, if the deviations are too large, nonlinear backward interrelations become essential, and the thermodynamic branch ceases to be stable. In the region of thermodynamic branch

stability, using the hypothesis about the existence of a local equilibrium, one may unambiguously introduce local thermodynamic functions and consider phase transitions in the framework of thermodynamics relations [4].

Taking advantage of this approach, let us consider the radiation influence on the course of possible phase transitions of the first kind, such as boiling and crystallization, in liquids. The temperature T_0 and the pressure p_0 of the corresponding phase transition are determined from the solutions of the equations describing phase equilibrium conditions. In particular, in the case of a single-component liquid, these equations for boiling and crystallization look like [11]

$$\mu_l(T_0, p_0) = \mu_g(T_0, p_0), \quad (1)$$

$$\mu_l(T_0, p_0) = \mu_s(T_0, p_0), \quad (2)$$

where $\mu_l(T_0, p_0)$, $\mu_g(T_0, p_0)$, and $\mu_s(T_0, p_0)$ are the chemical potentials in the liquid, gas, and solid, respectively, at the phase transition point.

Let new quasiparticles of the same kind (excited molecules, point defects, and so forth) be generated under the influence of a radiation source, which is stationary in time and uniform in space. The dependence of the chemical potential of non-excited molecules, $\mu_l(T, p, x_l)$, on their concentration x_l looks like [11]

$$\mu_l(T, p, x_l) = \mu_{l0}(T, p) + kT \ln[\gamma_l(T, p, x_l) x_l], \quad (3)$$

where $\mu_{l0}(T, p)$ is the chemical potential of “pure” liquid, i.e. in the absence of irradiation, and $\gamma_l(T, p, x_l)$ is the activity coefficient for the system of non-excited molecules. Note that formula (3) was written in the case where only one kind of quasiparticles with the concentration x_{ex} is generated under the action of radiation. However, it can be generalized to more complicated cases.

In view of the obvious equality $x_l + x_{ex} = 1$, let us rewrite formula (3) in the form

$$\begin{aligned} \mu_l(T, p, x_{ex}) &= \mu_{l0}(T, p) + \\ &+ kT \ln \gamma_l(T, p, x_l) + kT \ln(1 - x_{ex}). \end{aligned} \quad (4)$$

In order to make further calculations simpler, let us consider an ideal binary solution “non-excited particles–excited particles”, i.e. let us put $\gamma_l(T, p, x_l) \equiv 1$. This is eligible if the solution components are similar enough to each other by shapes

and sizes of their molecules, as well as the interaction parameters [11]. In our case, the shapes and the sizes of excited and non-excited molecules are not different, but their interactions can be. Therefore, in what follows, we consider the case of low concentrations of excited molecules, $x_{ex} \ll 1$. Then expression (4) takes the form

$$\mu_l(T, p, x_{ex}) = \mu_{l0}(T, p) - kT x_{ex}. \quad (5)$$

The analysis of formula (5) testifies that the presence of excited molecules with a small concentration x_{ex} always shifts the curve corresponding to the temperature dependence of the chemical potential (the Gibbs thermodynamic potential) of the liquid downward by the magnitude of $kT_0 x_{ex}$. This quantity describes the corresponding reduction of the chemical potential. The same reduction of the chemical potential at small values of $kT_0 x_{ex}$ can also be obtained, if the temperature is elevated by δT . Really, in this case,

$$\left(\frac{\partial \mu}{\partial T}\right)_{p, x_{ex}} \delta T = kT_0 x_{ex} \quad (6)$$

or

$$\delta T = \frac{kT_0}{s(T_0, p_0)} x_{ex}, \quad (7)$$

where s is the entropy calculated per molecule. Hence, it is possible to introduce the effective temperature of a phase transition [5]

$$T_{ref} = T_0 + \frac{kT_0}{s(T_0, p_0)} x_{ex}. \quad (8)$$

One can see that the effective temperature of a phase transition always exceeds the temperature of a phase transition for the non-irradiated medium.

If the system is under isobaric conditions, the appearance of excited molecules results in the pressure variation δp determined by the following expression:

$$\delta p = -\frac{kT x_{ex}}{v_l}, \quad (9)$$

where v_l is the volume calculated per molecule. Hence, in this case, it is possible to introduce the effective pressure of the phase transition

$$p_{ref} = p_0 - \frac{kT x_{ex}}{v_l}. \quad (10)$$

In a similar way, one can come to a conclusion that p_{ref} is always lower than the pressure at the phase transition in the non-irradiated system.

The results obtained for the variation of chemical potentials under the influence of radiation make it possible to analyze this influence on phenomena of the physico-chemical origin, for which the character of evolution is described by relationships between the corresponding chemical potentials. These are phase transitions, solubility, chemical reactions, and the spatial distribution of a substance near the solid surface, the properties of which also change under the action of radiation.

3. Modification of Phase Transition Parameters Under the Action of Radiation

Let us consider the variation of phase transition parameters under the influence of radiation. As was noted above, the condition of phase equilibrium at the phase transition is the equality of the chemical potentials of the substances in both phases. In the case of irradiation at a constant pressure, this condition should be rewritten in the form

$$\begin{aligned} &\mu_{10}(T_{\text{ref}}) + kT_{\text{ref}} \ln [\gamma_1(T_{\text{ref}}, (x_{\text{ex}})_1) \times \\ &\times (1 - (x_{\text{ex}})_1)] = \mu_{20}(T_{\text{ref}}) + \\ &+ kT_{\text{ref}} \ln [\gamma_2(T_{\text{ref}}, (x_{\text{ex}})_2)(1 - (x_{\text{ex}})_2)], \end{aligned} \quad (11)$$

where T_{ref} is a new phase transition temperature (in the general case, $T_{\text{ref}} \neq T_0$), and subscripts 1 and 2 denote different phases. In the case $e_{\text{ex}} \ll 1$, the solution can be regarded as ideal (i.e. we may put $\gamma \equiv 1$). In addition, the quantity $k\delta T = k(T_{\text{ref}} - T_0)$ has the same order of smallness as $kT_0 x_{\text{ex}}$. Then, the following expression is obtained for the temperature shift [6]:

$$\delta T = \frac{kT_0^2}{q(T_0, p_0)} [(x_{\text{ex}})_2 - (x_{\text{ex}})_1], \quad (12)$$

where $q(T_0, p_0)$ is the specific latent heat of phase transition.

Let us consider the case of “liquid–vapor” phase equilibrium. Superscript 2 will denote the liquid phase, and subscript 1 the vapor one. The concentration of quasiparticles (excited molecules) depends on the rates of their generation and decay, i.e. on their lifetime. The generation rate of excited molecules is

proportional to the medium density and the molecular excitation cross-section. In the case of “liquid–vapor” phase equilibrium, the vapor density is larger, but the lifetime of vapor molecules in the excited state can be much longer than the lifetime of the excited state of molecules in the liquid, e.g., if it is governed by collisions of molecules. Therefore, in the case of a single-component substance, if the lifetime of vapor molecules in the excited state does not exceed that of molecules in the liquid, the relation $(x_{\text{ex}})_l > (x_{\text{ex}})_g$ holds true, i.e. the boiling temperature increases. Otherwise, the relation $(x_{\text{ex}})_l < (x_{\text{ex}})_g$ may be obeyed, and the boiling temperature will decrease.

In the case of multicomponent liquids, the excitation cross-sections of particles belonging to different components can be different. Therefore, if the particles with the larger excitation cross-section are mainly evaporated, the condition $(x_{\text{ex}})_l < (x_{\text{ex}})_g$ can be satisfied, and the boiling temperature decreases. Note that the exotic case $T = T_0$ may exist, which takes place provided that the evident condition $(x_{\text{ex}})_l = (x_{\text{ex}})_g$ is satisfied.

Let us consider the case of “liquid–solid” phase equilibrium. Now, subscript 2 will denote the solid, and subscript 1 the liquid. The densities of the liquid and solid phases of the medium and the molecular excitation cross-sections in them are almost identical, but the lifetime of molecular excited state in the solid phase, as a rule, is much shorter than that in the liquid. This circumstance is associated with the fact that the excitation energy of any molecule in the crystal can be quickly redistributed among the other molecules. Therefore, as a rule, we have $(x_{\text{ex}})_s < (x_{\text{ex}})_l$, and the melting temperature decreases. However, in the special case where $(x_{\text{ex}})_s > (x_{\text{ex}})_l$, the melting temperature increases. It should be noted that the case $T_{\text{ref}} = T_0$ is also possible, which is realized provided the condition $(x_{\text{ex}})_s = (x_{\text{ex}})_l$ holds.

Finally, let us consider the case of “gas–solid” phase equilibrium. Now, subscript 2 will denote the solid, and subscript 1 the gas. The molecular excitation cross-sections in the gaseous and solid phases are almost identical. The density of the solid phase considerably exceeds the density of the gaseous phase, but the lifetime of a molecular excited state in the solid phase is usually considerably shorter than the lifetime of a molecular excited state in the gas. There-

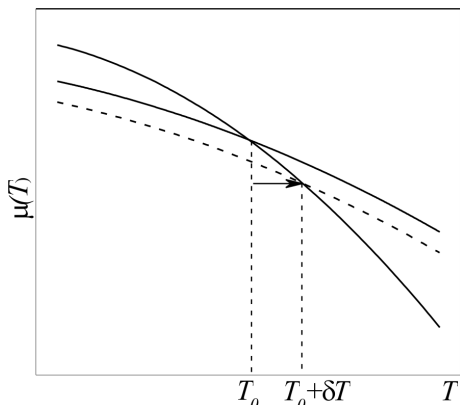


Fig. 1. Shift of phase transition temperature at a constant pressure

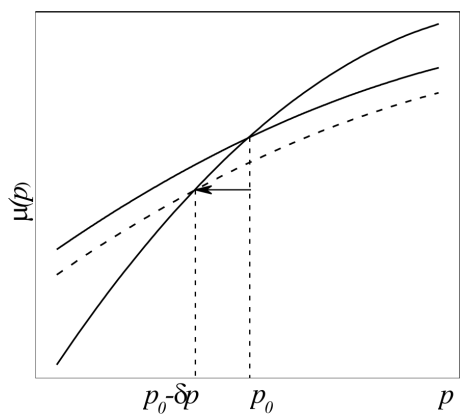


Fig. 2. Shift of phase transition pressure at a constant temperature

fore, different relations between the numbers of excited molecules in those two phases are possible for a single-component medium, depending on the specific values of generation and decay rates of excited molecules in the gaseous and solid phases. In particular, if $(x_{ex})_s > (x_{ex})_g$, the sublimation temperature increases; otherwise, it decreases.

In the case of multicomponent liquids, when the excitation cross-sections of particles belonging to different components are different, the relations between the concentrations of excited molecules in the gaseous and solid phases for different components can also be different. This fact makes it possible to separate the medium components by means of the medium sublimation under irradiation.

The condition of phase equilibrium during the phase transition under the influence of radiation and

at a constant temperature can be written in the form

$$\begin{aligned} &\mu_{10}(p_{ref}) + kT_0 \ln[\gamma_1(p_{ref}, (x_{ex})_1) \times \\ &\times (1 - (x_{ex})_1)] = \mu_{20}(p_{ref}) + \\ &+ kT_0 \ln[\gamma_2(p_{ref}, (x_{ex})_2)(1 - (x_{ex})_2)], \end{aligned} \quad (13)$$

where p_{ref} is a new effective pressure at the phase transition (in the general case, $p_{ref} \neq p_0$), and subscripts 1 and 2 denote different phases. Performing the procedure described above in the case $e_{ex} \ll 1$, we obtain the following expression for the pressure shift:

$$\delta p = -\frac{kT_0}{v_2 - v_1} [(x_{ex})_2 - (x_{ex})_1], \quad (14)$$

where v_1 and v_2 are volumes per particle in phases 1 and 2, respectively.

Figure 2 illustrates the corresponding pressure shift for a phase transition of the first kind, provided that the temperature is constant. If subscript 2 denotes the solid, and subscript 1 the liquid (the case of “liquid–solid” phase equilibrium), the melting pressure can decrease, increase, or remain invariant depending on the sign of the difference $[(x_{ex})_s - (x_{ex})_l]$, i.e. on the medium densities, molecular excitation cross-sections, and molecular lifetimes in different phases.

In the case of the “liquid–vapor” phase equilibrium, subscript 2 denotes the liquid phase, and subscript 1 the vapor one. Then, if $(x_{ex})_l < (x_{ex})_g$, the boiling pressure decreases; otherwise, it increases. The case $p_{ref} = p_0$ is realized under the condition $(x_{ex})_l = (x_{ex})_g$. Finally, let us consider the case of the “gas–solid” phase equilibrium. Let subscript 2 denote the solid, and subscript 1 the gas in this case. Then, $(x_{ex})_s < (x_{ex})_g$, the sublimation pressure decreases; otherwise, it increases.

In the case of a multicomponent medium, the signs and the magnitudes of pressure change can be different for different components. This circumstance makes it possible to separate the multicomponent medium into its components.

4. The Influence of Radiation on the Solubility in Binary Solutions

Let us consider the influence of radiation on the solubility processes. When a solid is dissolved in a liquid,

the condition of thermodynamic equilibrium is the same as in the case of a phase transition:

$$\mu_1(T, p) = \mu_2(T, p, x), \quad (15)$$

where $\mu_1(T, p)$ is the chemical potential of molecules of the solid in the crystalline phase, and $\mu_2(T, p, x)$ the chemical potential of molecules of the solid dissolved in the liquid phase to the concentration x [7]. In this case, the solubility is described by the Planck–van Laar equation for the saturated solution [8],

$$\left(\frac{\partial x}{\partial p}\right)_{T, \text{sat}} = -\frac{v_{2, \text{sat}} - v_{2, s}}{kT \left(\frac{\partial \ln[\gamma(T, p, x)]}{\partial x}\right)_{T, p}}, \quad (16)$$

where $v_{2, \text{sat}}$ is the partial volume of a dissolved substance in the liquid, and $V_{2, s}$ the partial volume of a dissolved substance in the solid phase, as well as by the equation

$$\left(\frac{\partial x}{\partial T}\right)_{p, \text{sat}} = \frac{q_2}{kT^2 \left(\frac{\partial \ln[\gamma(T, p, x)]}{\partial x}\right)_{T, p}}, \quad (17)$$

where q_2 is the specific heat of the dissolution of a solid substance in the saturated solution.

As was noted above, if the system is irradiated, there arise excited molecules in the liquid, which can be considered from the thermodynamic viewpoint as the third component in the solution. It is evident that the appearance of another component should affect the solubility processes. This problem was carefully considered in the framework of statistical physics in works by Sysoev and Terletskii [9, 10], where the variation of the third component concentration was related to the corresponding variations in the pressure and temperature. The influence of the third component substantially depends on the concentration of excited molecules in the systems (liquid and solid ones). If the concentration of excited molecules in the solid is much lower than that in the liquid solution, the solubility of the solid in the liquid increases [11] by a value of δx determined from the following equation [12]:

$$kT\delta x_{\text{ex}} = \left[kT + \left(\frac{\partial \ln \gamma_2}{\partial x}\right)_{T, p} \right] \delta x. \quad (18)$$

If only entropic effects are taken into account (this is the case where $\gamma_3(T, p, x) = 1$), expression (18)

becomes substantially simpler:

$$\delta x_{\text{ex}} = \delta x. \quad (19)$$

This effect is easy to be explained from the physical viewpoint. As was indicated above, radiation distorts the near-range order in the liquids and forms specific vacancies. These vacancies become filled with the redundant molecules of the dissolved medium. In the opposite case where only the molecules of the solid are excited, the solubility of the medium decreases by a value of δx , which is also determined by expression (19). This effect can be easily explained from the physical viewpoint if one takes into consideration that radiation distorts the regular structure of the crystal and generates defects in the crystal lattice. Certainly, in order to reduce the value of Gibbs thermodynamic potential, the atoms of dissolved medium have to return back into the crystal.

5. Conclusions

Irradiation excites some fraction of molecules in various phases, giving rise to the reduction of their chemical potentials. The variation of chemical potentials under the influence of radiation inevitably brings about the shifts of the first-order phase transition points. Depending on the medium properties in various phases (density, scattering and excitation cross-sections, excited molecule lifetime, and others) and radiation parameters (the type of bombarding particles, their spectrum, flux density, and fluence), both the shift of the phase transition temperature at a constant pressure and the shift of the phase transition pressure at a constant temperature are possible. The regularities in the influence of radiation on the solubility of solids in liquids are established.

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Д.А. Гаврюшенко, К.В. Тарадій

ВПЛИВ РАДІАЦІЙНОГО ОПРОМІНЕННЯ НА ФІЗИЧНІ ВЛАСТИВОСТІ РІДИН

Резюме

Радіаційне опромінення конденсованого середовища призводить до помітної зміни рівноважних термодинамічних властивостей рідинних систем. Під час радіаційного опромінення в рідинах порушується термодинамічна рівновага, і відбувається перебудова структури рідини. Такі зміни і відповідні їх наслідки розглядаються у даній статті.