*Journal of Inclusion Phenomena* **1**, 251–262. 0167–7861/84/0013–0251$01.80

# The Description of *P*, *T*, *X*-Phase Diagrams in Systems with Clathrate Formation where the Guest-Guest Interaction is taken into Account. Hydroquinone–Noble Gas Systems

V. R. BELOSLUDOV, YU. A. DYADIN*, G. N. CHEKHOVA
*Institute of Inorganic Chemistry, Academy of Sciences of the U.S.S.R., Siberian Branch, Novosibirsk 630090, U.S.S.R.*

and

S. I. FADEEV
*Institute of Mathematics, Academy of Sciences of the U.S.S.R., Siberian Branch, Novosibirsk, 630090, U.S.S.R.*

(Received: 8 March 1983; revised: 9 December 1983)

**Abstract.** We discuss phase equilibria in the binary guest-host system with clathrate formation where the guest-guest interaction is taken into account. The equations for phase equilibria in this system are derived for the general case, where the initial host α-modification can include guest molecules, and where the host molecules can form several metastable clathrate frameworks whose energies do not differ greatly from one another and from the stable form.

We have applied these equations to the binary noble gas–hydroquinone systems for which the equations simplify considerably. This allowed us to calculate *P*, *T*, *X*-phase diagrams for these systems and to compare them with the diagrams obtained experimentally.

The model employed describes experimental results not only qualitatively (e.g., the increase of the melting temperature of the hydroquinone α-modification with increasing content of the guest) but also quantitatively. It has been shown that consideration of guest-guest interaction even in the hydroquinone systems, in which this interaction is relatively small, improves the description of the phase diagrams.

**Key words:** Clathrate, calculation of the Phase Diagram of binary systems, the role of the guest-guest interaction, thermodynamics, hydroquinone–noble gas systems.

## 1. Introduction

In previous papers [1,2] we have discussed the thermodynamics of the clathrate formation model, and interactions of the guest-guest for the monovariant equilibrium were taken into account:

$$\Gamma_{\text{gas}} + nQ^{\alpha}_{\text{solid}} \rightleftarrows \Gamma nQ^{\beta}_{\text{solid}}$$

where Γ is the guest component; $Q^{\alpha}$, $Q^{\beta}$ (or simply α and β) are stable and metastable modifications, respectively, of the host component in the absence of the guest component. It was shown in these papers that the dispersion and dipole interactions of the guest molecules

---

* Author for correspondence.

can influence considerably the equilibrium degree of filling of the cavities of the clathrate $\beta$-modification of the host, i.e., the stoichiometry of a compound[★].

In the same papers, conditions were formulated which are necessary and sufficient for the degree of filling to change in a stepwise fashion in one and the same framework. In this communication the equations for phase equilibria in the binary guest-host system are derived, the results of reference [1] being used. Here we discuss the general case, when the initial host $\alpha$-modification can include guest molecules (e.g., $\alpha$-hydroquinone [5,6]), the host molecules can form several metastable clathrate frameworks of similar energies, which are stabilized by the guest molecules of the same type under corresponding thermodynamic conditions (the latter is characteristic, e.g., of the water systems [7]). The $P$, $T$-phase diagram fragment of the binary guest ($\Gamma$)-host ($Q$) system, shown in Figure 1, is in accordance with the above statement. It is evident that the appearance of new phases in the system concerned will cause the appearance of new nonvariant points and corresponding lines of monovariant equilibria. As has already been mentioned, we limit ourselves to the consideration of the equilibria only for a certain part of the diagram. This approach can be easily extended to the equilibria in the neighbourhood of the nonvariant points with a different set of phases.

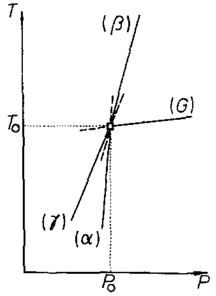

Fig. 1. Schematic picture of the mutual arrangement of the monovariant equilibria curves near the nonvariant point, where $\alpha, \beta, \gamma$, and $G$ phases coexist ($T = T_0, P = P_0$) in the guest-host system, if the mole fraction of guest $X$ in the phases changes in the order $x_\alpha < x_\beta < x_\gamma < x_G$. The phase symbol in brackets indicates the monovariant equilibrium without this phase, i.e., ($\alpha$) is equivalent to $\gamma \rightleftharpoons \beta + G$.

For comparison with experiment, we have chosen hydroquinone–noble gas systems, for which it is possible to make assumptions that simplify computation but from our point of view, retain the characteristic properties of the model.

## 2. Phase Equilibria

### 2.1. MODEL

In the i-phase ($i = \alpha$[★★], $\beta$, $\gamma$) the expressions for the host component chemical potential $\mu_Q^i$ and the guest component chemical potential $\mu_\Gamma^i$ can be represented as

$$\mu_Q^i = \mu_Q^{0i} + \nu_i[kT \cdot \ln(1 - y_i) - \tfrac{1}{2} \cdot y_i^2 U_i] \qquad (1)$$

$$\mu_\Gamma^i = y_i \overline{U}_i + kT \cdot \ln[y_i(1 + S_i)/2h_i(1 - y_i)] \qquad (2)$$

---

[★] It is shown in paper [3] that the introduction of the guest-guest nondirectional interaction changes the expression for the chemical potential of the guest molecules and the sorbtion isotherms derived in [4] but the influence of this interaction on the clathrate composition is not considered.

[★★] From the point of view of the study of heterogenous equilibria the $\alpha$-modification of the host with the guest molecules included should be considered as a solid solution of the guest in the $\alpha$-modification, but not as a new clathrate compound, being formed in the system.

where

$$U_i = U_i^\delta + S_i^2 U_i^D; \qquad \overline{U}_i = U_i^\delta + S_i U_i^D \tag{3}$$

where $\mu_Q^{0i}$ is the chemical potential of the host $i$-framework; $v_i$ is the number of cavities of type $i$ per molecule of $Q$. $\frac{1}{2}U_i^\delta$, $\frac{1}{2}U_i^D$ are the energies of the dispersion and dipole interactions of the guest molecules between each other respectively, provided that all the dipoles are orientated along some axis (common for all the guest molecules in the $i$-phase) in one of the two directions; an expression for $h$ is found in [4] and has the form:

$$h_i = 2\pi a_i^3 g_i \phi_\Gamma^i(T) \exp[-W_i(0)/kT] \tag{4}$$

where $a_i$ is the dimension of the cavity in the $i$-phase, expressions for $g_i$ and $\phi_\Gamma^i(T) \equiv \phi_\Gamma^i$ are given in [4]★; $W_i(0) \equiv W_i$ is the potential energy of the guest molecule in the host cell (the guest-host interaction); $T$ is the absolute temperature; $k$ is the Boltzmann constant; $S_i$ is the order parameter in the $i$-phase determined by the equation:

$$S_i^{-1} \ln[(1 + S_i)] = -2y_i U_i^D/kT[(1 + S_i)/(1 - S_i)] \tag{5★★}$$

The equations, determining $P_0$, $T_0$ and the compositions of the equilibrium phases in the nonvariant point (Figure 1), are derived from the conditions of equality of the chemical potentials of the system components in all the phases:

$$\mu_Q^\alpha = \mu_Q^\beta = \mu_Q^\gamma = \mu_Q^G, \qquad \mu_\Gamma^\alpha = \mu_\Gamma^\beta = \mu_\Gamma^\gamma = \mu_\Gamma^G. \tag{6}$$

We shall assume that the gas phase is governed by the ideal gas laws, then the expressions for the chemical potentials of the mixture components will be as follows (see, e.g., [8]):

$$\mu_Q^G = kT \cdot \ln[P_Q/kT\phi_Q^G], \qquad \mu_\Gamma^G = kT \cdot \ln[P_\Gamma/kT\phi_\Gamma^G] \tag{7}$$

where $P_Q$, $P_\Gamma$ are partial pressures of the host component and the guest component, which are related to $x_G$ (the mole fraction of the guest in the gas phase) in the following way:

$$P_Q = (1 - x_G)P, \qquad P_\Gamma = x_G P, \tag{8}$$

where $P$ is the total pressure in the system.

### 2.2. NONVARIANT EQUILIBRIUM

The substitution of the corresponding expressions for the chemical potentials of the system components (1), (2), (7), (8) in (6) and the subsequent transformations lead to the set of the transcendental equations with respect to $y_\alpha$, $y_\beta$, $y_\gamma$, $x_G$, $P$, $T$;

$$\Delta\mu^{\alpha\beta} = kT \ln[(1 - y_\beta)^{v_\beta}(1 - y_\alpha)^{-v_\alpha}] + \tfrac{1}{2}(v_\alpha y_\alpha^2 U_\alpha - v_\beta y_\beta^2 U_\beta) \tag{9}$$

$$\Delta\mu^{\beta\gamma} = kT \ln[(1 - y_\gamma)^{v_\gamma}(1 - y_\beta)^{-v_\beta}] + \tfrac{1}{2}(v_\beta y_\beta^2 U_\beta - v_\gamma y_\gamma^2 U_\gamma), \tag{10}$$

$$(1 - x_G)P = A_\gamma(1 - y_\gamma)^{v_\gamma} \cdot \exp(-v_\gamma y_\gamma^2 U_\gamma/2kT), \tag{11}$$

---

★ Here and below index $i$ indicates for which phase $g$ and $\phi$ are determined.

★★ Equations (1)–(5) were obtained by statistical physics methods using the discrete Ising model with admixtures in the approximation of the mean-field type with guest molecules arranged in the centres of the cavities (for calculation of guest-guest interaction only). For the calculation of interaction energy of the guest-host we use only Van der Waals' technique [4].

$$B_\alpha \frac{y_\alpha(1 + S_\alpha)}{(1 - y_\alpha)} \cdot \exp(y_\alpha \overline{U}_\alpha/kT) = B_\beta \frac{y_\beta(1 + S_\beta)}{(1 - y_\beta)} \cdot \exp(y_\beta \overline{U}_\beta/kT), \tag{12}$$

$$B_\beta \frac{y_\beta(1 + S_\beta)}{(1 - y_\beta)} \cdot \exp(y_\beta \overline{U}_\beta/kT) = B_\gamma \frac{y_\gamma(1 + S_\gamma)}{(1 - y_\gamma)} \exp(y_\gamma \overline{U}_\gamma/kT), \tag{13}$$

$$x_G P = B_\gamma \frac{y_\gamma(1 + S_\gamma)}{2(1 - y_\gamma)} \cdot \exp(y_\gamma \overline{U}_\gamma/kT), \tag{14}$$

where

$$\Delta\mu^{ij} = \mu_Q^{0i} - \mu_Q^{0j}, \qquad A_i = kT\phi_Q^G \exp(\mu_Q^{0i}/kT), \qquad B_i = kT \cdot \phi_\Gamma^G h_i^{-1}. \tag{15}$$

The solution of the six-equation set (9)–(14) together with (5) gives values of $P_0$, $T_0$, $y_\alpha$, $y_\beta$, $y_\gamma$, and $x_G$, defining the nonvariant equilibrium of the binary guest-host system concerned.

### 2.3. MONOVARIANT EQUILIBRIA

(a) By using equality of the chemical potentials of the system components in the phases of monovariant equilibrium $\gamma \rightleftarrows \beta + G$, we obtain the set of equations (10), (11), (13), (14) with respect to $y_\beta$, $y_\gamma$, $x_G$ and $T$ describes curve ($\alpha$) taking into consideration Equation (5).

(b) Curve ($\beta$), i.e., the equilibrium $\gamma \rightleftarrows \alpha + G$ is defined by Equations (5), (11), (14) and Equations (9), (12) (in the last two equations index $\beta$ must be substituted by $\gamma$).

(c) Curve ($\gamma$), i.e., the equilibrium $\beta \rightleftarrows \alpha + G$ is defined by Equations (5), (9), (12) and Equations (11), (14) (in the last two equations index $\gamma$ must be substituted by $\beta$).

(d) Curve ($G$) describing equilibria $\beta \rightleftarrows \alpha + \gamma$ is defined by the set of Equations (5), (9), (10), (12) and (13).

### 2.4. DIVARIANT EQUILIBRIA

The conditions for the coexistence of the $\alpha$- and $\beta$-phases are described by Equations (5), (9), (12); of the $\beta$- and $\gamma$-phases, by (5), (10), (13); of the $\gamma$- and $G$-phases, by (5), (11), (14); of the $\alpha$- and $\gamma$-phases, by (5), (9), (12) (in the last two equations index $\beta$ must be substituted by $\gamma$, $\beta \to \gamma$); of the $\beta$- and $G$-phases by (5), (11), (14) ($\gamma \to \beta$); and of the $\alpha$- and $G$-phases, by Equation (5) and Equations (11) and (14) ($\gamma \to \alpha$).

### 2.5. $P, X$- AND $T, X$-PHASE DIAGRAMS OF THE GUEST-HOST SYSTEM

The solution of the equations given above, allows us to draw the isobaric and isothermal sections of the state diagram of the binary system and it is convenient to pass from variable $y_i$, to variable $x_i$ (where $x_i$ is a mole fraction of the guest in $i$-phase):

$$x_i = \nu_i y_i/(1 + \nu_i y_i) \tag{16}$$

## 3. Calculation of the $P$, $T$, $X$-Phase Diagrams in the Binary Systems Hydroquinone–Noble Gas

Generally, finding the solution to Equations (5), (9)–(14) is a difficult task. We shall find the solution for the hydroquinone–noble gas system because it is one of the simplest for which the $\alpha$ and $\beta$-structures [9,10] and some thermodynamic data are known. Let us consider equilibria in which the liquid $L$-phase (a dilute solution of the guest in hydroquinone melt), the gaseous $G$-phase, and the $\alpha$- and $\beta$-phases of hydroquinone, containing the dissolved guest component can coexist.

Equations describing phase equilibria with the chosen set of phases are obtained from (5), (9)–(14) by the substitution of the expression for $\mu_Q^\gamma$ by that for the chemical potential $\mu_Q^L$ of the liquid hydroquinone $L$-phase and by the substitution of the expression for $\mu_\Gamma^\gamma$ by that for the chemical potential $\mu_\Gamma^L$ of the guest in the melt. Since the solubility of a noble gas in hydroquinone is low, it is possible to use expressions of the dilute solution chemical potentials for $\mu_Q^L$, $\mu_\Gamma^L$ (see [8]). In our case, the guest molecules are not dipoles, i.e., $U_i^D \equiv 0$.

### 3.1. BASIC ASSUMPTIONS

Equations (9)–(14) simplify considerably if the properties of the noble gas–hydroquinone system components are used for which the following assumptions are valid with acceptable accuracy.

(1) The partial vapour pressure of the host component can be neglected ($2.13 \times 10^{-2}$ atm at 173 °C).

(2) The solubility of the guest in the melt is negligibly small.

(3) The guest-host interactions in the cavities of the $\alpha$- and $\beta$-phases do not differ from each other considerably. This assumption is based on the structural data [9,10]★. Since the cavities in the $\alpha$- and $\beta$-frameworks are practically the same, the guest-host interaction in both frameworks in the first coordination sphere is also the same. The interaction of the guest molecules with more remote hydroquinone molecules is essentially weaker, and the interaction for $\alpha$- and $\beta$-framework does not differ significantly because their densities differ only slightly (1.35 and 1.26 g/cm$^3$, respectively).

(4) The guest-guest interaction in the $\alpha$- and $\beta$-frameworks is small, and it can be neglected. This assumption is doubtful. Indeed, the estimation of the maximum energy (with $y = 1$) of the Xe–Xe interaction in the $\beta$-phase, according to the Lennard–Jones formula [11], gives a value of $U_\beta^\delta \simeq 2400$ J mol$^{-1}$★★. The major contribution to this value (about) 90% is made by the interaction of the guests, situated in the cavities, having hexagons on their boundaries and forming 'columns' along the $c$-axis. Since the guests along the $c$-axis in the $\alpha$-modification are situated in the 'columns' of the same kind and at the same distance (~ 5.5 Å) [9], but the 'columns' are situated noticeably farther from each other (22.1 instead of 9.6 Å in the $\beta$-framework), the guest-guest interaction is approximately 10% smaller. In reference [2] it is shown that the dispersion guest-guest interaction of such order for hydroquinone clathrates at the temperatures concerned will lead to the noticeable (10%) change of the degree of filling the cavities. For the lighter guest molecules this correction is correspondingly smaller.

### 3.2. NONVARIANT EQUILIBRIUM

From the first three assumptions it follows that $g_\alpha \simeq g_\beta \equiv g$, $W_\alpha \simeq W_\beta \equiv W$, from which it follows that $h_\alpha \simeq h_\beta$, and from Equation (12) it follows that $y_\alpha \simeq y_\beta \equiv y$. We shall assume, just

---

★ The data, used by us [9,10] agree with the data obtained more recently by [20,21] with reasonable accuracy.

★★ The value $U^\delta$ is the energy of the dispersion interaction between the chosen molecule and all other molecules corresponding in this case to 1 g mol. This value is twice as much as the energy of the interaction of the molecules with each other.

as in reference [14], that $\phi_\Gamma^G$ is close to $\phi_\Gamma^\beta$ and $\phi_\Gamma^\alpha$. Then the system of Equations (9)–(15) will take the form:

$$y_0 = 1 - \exp[\Delta\mu_0^{\alpha\beta}/(v_\beta - v_\alpha)kT], \tag{17}$$

$$\Delta\mu_0^{L\alpha}/v_\alpha = \Delta\mu_0^{\alpha\beta}/(v_\beta - v_\alpha), \tag{18}$$

$$P_0 = \frac{kT_0}{2\pi a^3 g}\,\frac{y_0}{1 - y_0}\,\exp(W/kT) \tag{19}$$

(For the designation of the novariant point index '0' is introduced for $P$, $T$, y, $\Delta\mu^{ij}$.) For the solution of Equations (17)–(19) in regard to $P_0$, $T_0$, $y_0$, it is necessary to know $\Delta\mu_0^{\alpha\beta}$, $\Delta\mu_0^{L\alpha}$, $g$, $a$, $W$. The last three values were chosen and calculated in the same way as in reference [4]. The value $\Delta\mu_0^{\alpha\beta}$, in (17) was expressed by the expansion according to $T_0 - T_1$, $P_0 - P_1$

$$\Delta\mu_0^{\alpha\beta} = \Delta\mu^{\alpha\beta}(T_1, P_1) - \Delta H^{\alpha\beta}(T_0 - T_1)/T_1 + \Delta V^{\alpha\beta}(P_0 - P_1) \tag{20}$$

where $T_1$, $P_1$ are the temperature and pressure at which the degree of filling was measured experimentally [12,13]. Using the value of $y$ and formula (27), we shall determine $\Delta\mu^{\alpha\beta}(T_1, P_1) = -352\ \text{J mol}^{-1}$. The choice of values for $\Delta H^{\alpha\beta}$ and $\Delta V^{\alpha\beta}$ is described below (Section 3.3). Near the melting point ($T_m = 445.46$ K, $P_m = 0{,}021$ atm*)$\Delta\mu^{L\alpha}$ can be expressed by the expansion according to $T - T_m$ and $P - P_m$, limiting this expansion to the linear terms:

$$\Delta\mu^{L\alpha'} = -\Delta H_m^{L\alpha}(T - T_m)/T_m + \Delta V_m^{L\alpha}(P - P_m) \tag{21}$$

where $\Delta H_m^{L\alpha}$ is the heat of melting of $\alpha - Q$, equal to 27130 J mol$^{-1}$ [12]; $\Delta V_m^{L\alpha}$ is the volume change during the transition from the $\alpha$-phase to the $L$-phase, equal to 15 cm$^3$/mol (calculated using the $\alpha$-hydroquinone melt density at $447 \pm 1$ K, $\rho = 1.1$ g/cm$^3$). Equation (21) together with (18) gives the expression for $T_0$($v_\alpha = \frac{1}{18}$ [9], $v_\beta = \frac{1}{3}$ [10]):

$$T_0 = T_m\{1 + [v_\alpha\Delta\mu_0^{\alpha\beta}/(v_\beta - v_\alpha) + \Delta V_0^{L\alpha}(P_0 - P_m)]/\Delta H_m^{L\alpha}\} \tag{22}$$

It follows from this equation, in particular, that in the systems under discussion $T_m < T_0$. By the substitution of the expression for $y_0$ (17) and for $T_0$ (22), in Equation (19) we obtain a nonlinear equation with respect to $P_0$. Since the third term in Equation (22) is small in comparison with the first one for pressures $P_0$, satisfying the inequality

$$P_0 - P_m \ll \Delta H^{L\alpha}/\Delta V_m^{L\alpha} = 1.8 \times 10^4\ atm, \tag{23}$$

we take its expression (as the first approximation) according to formula (22) with $P_0 = P_m$ and $P_0$ is calculated according to formulae (17)–(19). Below, we use the iterative method for the calculation of $P_0$.

The calculated and experimental (in brackets) values of $P_0$, $T_0$, $y_0$ and the parameters $\varepsilon$ and $\sigma$ [4] used by us and defining the intermolecular guest-host interaction are given in Table I.

### 3.3. MONOVARIANT EQUILIBRIA

The equations describing monovariant equilibria are derived by analogy with the equations defining the nonvariant point (17)–(19), assumptions 1–4 of Section 3.1 being taken a

---

* Throughout this paper 1 atm = 0.101325 MPa.

Table I. Comparison of the calculated and experimental (in brackets) data [4,12,13,16] in the nonvariant point and at 298 K

| Guest | $\varepsilon$, (K) | $\sigma$, (Å) | Calculation (experiment) | | | | |
|---|---|---|---|---|---|---|---|
| | | | $T_0$, K | $P_0$, atm | $y_0$ | $P_{298}$, atm | $y_{298}$ |
| He | 10.2 | 2.56 | – | – | – | – | – |
| Ne | 36.2 | 2.74 | – | – | – | – | – |
| Ar | 119.5 | 3.408 | 448.0 | 51.0 | 0.304 | 4.57<br>(3.4) | 0.398<br>(0.34) |
| Kr | 166.7 | 3.679 | 447.1<br>(446.3) | 15.2<br>(13.8) | 0.292<br>(0.28) | 0.59<br>(0.4) | 0.396 |
| Xe | 255.3 | 4.069 | 446.8<br>(446.5) | 5.57<br>(5.8) | 0.289<br>(0.30) | 0.08<br>(0.06) | 0.398 |
| $N_2$ | 95.05 | 3.698 | 448.9 | 85.2 | 0.316 | 6.7<br>(5.8) | 0.401 |
| $O_2$ | 117.5 | 3.580 | 447.9 | 47.1 | 0.303 | 3.3 | 0.399 |
| $CH_4$ | 142.7 | 3.810 | 447.3 | 25.0 | 0.296 | 1.02 | 0.398 |
| HCl | 360 | 3.305 | 446.7 | 1.6 | 0.287 | 0.026<br>(0.01) | 0.397 |

into account:

(a) The equilibrium $\alpha \rightleftarrows L + G$ is described by the equations

$$y_\alpha = 1 - \exp[\Delta\mu^{L\alpha}(T, P)/v_\alpha kT], \tag{24}$$

$$P = \frac{kT}{2\pi a^3 g} \frac{y_\alpha}{1 - y_\alpha} \exp[W/kT] \tag{25}$$

(b) The equilibrium $\beta \rightleftarrows L + G$ is described by Equations (24) and (25), where index $\alpha$ must be substituted by index $\beta$.

(c) The equilibrium $\beta \rightleftarrows \alpha + L$ is described by Equation (24) and the following equations $y_\alpha = y_\beta \equiv y$ and

$$(v_\beta - v_\alpha)\Delta\mu^{L\alpha}(T, P) = v_\alpha \Delta\mu^{\alpha\beta}(T, P). \tag{26}$$

(d) The equilibrium $\beta \rightleftarrows \alpha + G$ is described by Equation (25) and $y_\alpha = y_\beta \equiv y$ and

$$y = 1 - \exp[\Delta\mu^{\alpha\beta}(T, P)/(v_\beta - v_\alpha)kT]. \tag{27}$$

To draw the monovariant curves near the nonvariant point we shall express $\Delta\mu^{L\alpha}$ by the first-order expansion in series $\Delta T = T - T_0$ and $\Delta P = P - P_0$.

$$\Delta\mu^{L\alpha}(T, P) = \Delta\mu_0^{L\alpha} - \Delta H^{L\alpha}\Delta T/T_0 + \Delta V_0^{L\alpha}\Delta P. \tag{28}$$

The analogous expansions is correct for $\Delta\mu^{L\beta}$ and $\Delta\mu^{\alpha\beta}$. From the conditions of the nonvariant equilibrium it follows that:

$$\Delta\mu_0^{L\alpha}/v_\alpha = \Delta\mu_0^{L\beta}/v_\beta = \Delta\mu_0^{\alpha\beta}/(v_\beta - v_\alpha) \tag{29}$$

which allows us to determine $\Delta\mu_0^{L\alpha}$ and $\Delta\mu_0^{L\beta}$. In the region concerned we shall neglect the dependence of $\Delta H^{L\alpha}$,$\Delta H^{L\beta}$, $\Delta H^{\alpha\beta}$ and $\Delta V^{L\alpha}$, $\Delta V^{L\beta}$, $\Delta V^{\alpha\beta}$ on $T$ and $P$. Then $\Delta V_0^{L\alpha} = \Delta V_m^{L\alpha} = 15$ cm$^3$/mol; $\Delta V^{\alpha\beta} = \Delta V_0^{\alpha\beta} = -5$ cm$^3$/mol; $\Delta V_0^{L\beta} = \Delta V_0^{L\alpha} + \Delta V_0^{\alpha\beta} =$

$= 10\ \mathrm{cm}^3/\mathrm{mol}$. The value of $\Delta H^{\alpha\beta}$, has been determined as being small: in [14] a value of $-544\ \mathrm{J\ mol}^{-1}$ is given, in [15] values of $-700$–$750$ and $-1088\ \mathrm{J\ mol}^{-1}$ are given, and in [16] values of $-670$, and $-214\ \mathrm{J\ mol}^{-1}$ at 25°C are given. If we assume that $\Delta H^{\alpha\beta}$ is of the order mentioned and that it does not depend on temperature, the calculation of the equilibrium $\beta \rightleftarrows \alpha + G$ at high temperatures gives values different from values obtained experimentally [12]. We have made the reverse calculation using the data on the phase diagram for this equilibrium [12, 13]. The value of $\Delta\mu^{\alpha\beta}(T_1, P_1)$ calculated at a temperature of the order of 446 K for the systems $Q$-Kr, $Q$-Xe [12] according to (27) is equal to $-352 \pm 17\ \mathrm{J\ mol}^{-1}$★, which agrees with the value obtained by direct measurements at 298 K [17]. That is why in calculations in the whole temperature interval we have assumed that $\Delta H^{\alpha\beta} \simeq 0$, then $\Delta H^{L\alpha} \simeq \Delta H^{L\beta}$.

Substituting (28) and the analogous expansions for $\Delta\mu^{L\beta}$ and $\Delta\mu^{\alpha\beta}$ into the equations defining monovariant equilibria, it is possible to calculate numerically the $P$, $T$-phase diagram of the binary system. In Figure 2 the calculated phase diagrams and experimental data are given for comparison.

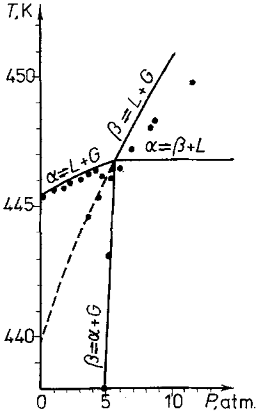

Fig. 2. $P$, $T$-Phase diagrams of the hydroquinone–xenon systems. Calculation: continuous lines – stable equilibria, dotted lines – metastable equilibria. Experimental data [12] are presented by dots.

### 3.4. DIVARIANT EQUILIBRIA

The equations defining divariant equilibria and taking into consideration our assumption, are as follows: the $\alpha$, $L$-phase equilibrium is defined by Equation (24); the $\beta$, $L$-phase equilibrium by Equation (24), in which index $\alpha$ must be substituted by $\beta$, $\alpha \to \beta$; $\alpha$, $G$-phase equilibrium – by Equation (25), $\beta$, $G$-phase equilibrium – by Equation (25), in which $\alpha \to \beta$; the $\alpha$, $\beta$-phase equilibrium by equations $y_\alpha = y_\beta \equiv y$ and (27); and the $L$, $G$-phase equilibrium by the equation $X_G = 1$. These equations allow us to draw $P$, $X$- and $T$, $X$-sections of the $P$, $T$, $X$-diagram phase. $P$, $X$- and $T$, $X$-sections for the system $Q$-Xe are given in Figure 3.

---

★ This value was calculated without taking into account the guest-guest interaction.

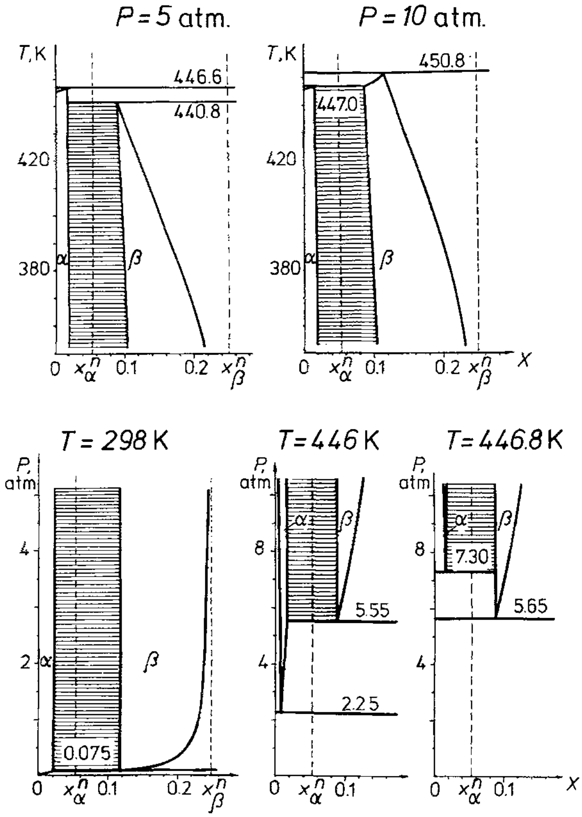

Fig. 3. Isobaric and isothermal sections of the $P$, $T$, $X$-phase diagram of the hydroquinone–xenon system. $X_\alpha^n$, $X_\beta^n$ are mole fractions of a guest component in the hypothetic case, when the cavities in $\alpha$- and $\beta$-hydroquinone frameworks are completely filled.

## 4. Taking into Account the Guest-Guest Interaction

In hydroquinone clathrates (especially at high temperatures), the guest-guest interaction is weaker than in other clathrates, since the cavities are relatively small (molecules with relatively small energy of dispersion interaction can be placed in them), and the volume of the cavities is a small part of the whole crystal volume★. But even in these systems, the guest-guest interaction is rather clearly revealed. In Table II values of $\Delta\mu^{\alpha\beta}$, obtained from the data concerning the clathrate composition for three variants of calculation are given. They are ($\Delta\mu^{\alpha\beta} \equiv \Delta\mu$):

(1) $\alpha$-hydroquinone does not dissolve the guest component and the guest-guest interaction in the $\beta$-phase is extremely small (approximation of Van der Waals and Platteeuw [4]),

$$\Delta\mu_1 = v_\beta RT \ln(1 - y) . \qquad (30)$$

---

★ In clathrate hydrates with cubic structure 1 this interaction for the guests of the same type is more than twice as strong as in hydroquinone.

Table II. Calculation[a] of $\Delta\mu$J mol$^{-1}$ for hydroquinone from the data on the degree of filling the cavities: $\Delta\mu_1$ calculated without regard for the guest component solubility in the $\alpha$-modification and without regard for the guest-guest interaction; $\Delta\mu_2$ calculated with regard for this solubility; $\Delta\mu_3$ calculated with regard for the guest solubility and the guest-guest interaction.

| Guest | $T$, K | $P$, atm | $y$ | $\Delta\mu_1$ | $\Delta\mu_2$ | $\Delta\mu_3$ |
|---|---|---|---|---|---|---|
| Ar | 298.2 | 3.4 | 0.340 | -343 | - | (-334) |
| Kr | 446.3 | 13.8 | 0.280 | -407 | -339 | -329 |
| | 353.2 | 2.3 | 0.280 | -322 | - | (-311) |
| | 328.2 | 1.19 | 0.310 | -337 | - | (-324) |
| | 303.2 | 0.55 | 0.330 | -337 | - | (-321) |
| | 298.2 | 0.40 | 0.340 | -343 | - | (-327) |
| Xe | 446.5 | 5.8 | 0.300 | -441 | -368 | -341 |
| | 353.2 | 0.6 | 0.370 | -452 | -377 | -336 |
| | 328.2 | 0.26 | 0.390 | -450 | -375 | -329 |
| $CH_4$ | 298.3 | 0.83 | 0.391 | -410 | -342 | -320 |
| | 283.6 | 0.47 | 0.399 | -400 | -334 | -311 |
| $CH_3F$ | 323.0 | 0.33 | 0.383 | -432 | -360 | - |
| | 298.2 | 0.12 | 0.416 | -445 | -371 | - |

[a] The correction for $\Delta\mu$ as a result of the pressure change in the interval concerned is negligible and has been ignored.

(2) $\alpha$-hydroquinone dissolves the guest component, but the guest-guest interaction is not taken into account. In this case (when the condition $y_\alpha = y_\beta \equiv y$ is observed, see above),

$$\Delta\mu_2 = (\nu_\beta - \nu_\alpha)RT\ln(1 - y)\,. \tag{31}$$

(3) A correction for the guest-guest interaction is inserted into $\Delta\mu_2$. For the simplification of the calculation with acceptable accuracy for the systems concerned we can consider

$$U_\alpha \simeq U_\beta \equiv U, \qquad \Delta\mu_3 = (\nu_\beta - \nu_\alpha)[RT\ln(1 - y) - y^2 U/2] \tag{32}$$

(derived from (9), the conditions mentioned above were observed).

From Table II it can be seen that $\Delta\mu$ does not depend definitely on temperature in all the cases in the interval 280–446 K within the range of the experimental error. It testifies to the fact that the absolute value of $\Delta H^{\alpha\beta}$ is not more than 40–60 J mol$^{-1}$. The values of $\Delta\mu_1$ and $\Delta\mu_2$ evidently depend on the nature of the guest: the bigger the guest-guest Van der Waals interaction, the bigger is the absolute value of $\Delta\mu$. This suggests that the guest-guest interaction makes a noticeable contribution to the clathrate stoichiometry and must not be neglected. The value of $\Delta\mu_3$ does not depend on the nature of the guest within experimental accuracy.

It is interesting to note that in all probability in the systems with Ar (298.2 K) and Kr (at 298.2–353.2 K) the metastable equilibrium is realized, with the participation of $\alpha$-hydroquinone, which has not dissolved the guest-component in itself. Values of $\Delta\mu_3$ (in brackets in Table II), calculated for this supposition form all the data available, that are characterized by a mean value of $-326 \pm 10$ J mol$^{-1}$[★]. Some experimental facts suggest that realization of the metastable equilibrium concerned is possible. It would be natural to suppose that in the systems discussed the rate of clathrate formation increases with the increase of Van der Waals interaction of the guests with each other and with the framework. It confirms, e.g., the data in

---

[★] As it is evident from the above it is not necessary for every system to introduce its own value $\Delta\mu$ explaining $\Delta\mu$ changes by the $\beta$-framework distortion as it has been done in work [16]. The assumption of the $\beta$-framework in the systems discussed seems artificial, since the molecules of the guest set discussed have dimensions that do not exceed the dimensions of the hydroquinone $\beta$-framework cavity.

reference [16] where it is noted, that $CH_3F$ reacts with hydroquinone practically immediately after the necessary pressure is achieved, but the $CH_4$/hydroquinone reaction has an induction period of the order of 36–48 h. On the other hand, in a number of papers [4,12,13,17–19] it is noted that clathrate formation in the $Q$-guest systems at temperatures below 100 °C is hampered. To avoid the kinetic difficulties connected with the $\alpha$-hydroquinone destruction, the authors tried various methods: including the use of an inert solvent [4,17–19] and vibromilling [12,13]. But with all these methods for the initiation of a reaction it is necessary to create pressures (concentration), exceeding essentially equilibrium pressures (e.g., even for xenon it must be four times higher [4]). Such supersaturation cannot be created for the $\alpha$-phase since here conditions are created under which it is unstable (the $\beta$-phase is realized). Therefore, to our mind, from the point of view of the attainment of the true equilibrium the only reliable experiments are those which were carried out at high temperatures ($T > 100$ °C) and with 'reactive' heavy guests.

Since the guest-guest interactions in the systems concerned are small, the corrections dealing with these interactions can be taken into consideration according to the theory of perturbation. In the first approximation from Equations (9)–(14) (taking into consideration dispersion interactions and, according to assumption 3, for such estimation it is enough to consider $U_\alpha \simeq U_\beta \equiv U$) for the changes in the nonvariant point $T_0$, $P_0$, $y_0$ it follows that:

$$\Delta y/y_0 = (y_0 - 1)U/2kT_0\,, \tag{33}$$

$$\Delta P/P_0 = y_0 U/2kT_0 \tag{34}$$

and $\Delta T \simeq U_\alpha - U_\beta$ (for Xe, taking into consideration that $U_\alpha \neq U_\beta$, $\Delta T/T_0 \simeq 4.5 \times 10^{-5}$. Corrections for formulae (33) and (34) for the $Q$-Xe system are $\Delta y/y \simeq 0.07$, $\Delta p/p \simeq -0.1$.

Corrections for the mono- and divariant equilibria are calculated in a similar way.

In Figure 4 the calculated curves $y(T)$ are given for the monovariant equilibrium $\beta \rightleftharpoons \alpha + G$ for the three cases described at the beginning of this Section. In the same figure, known experimental data are given. The experimental data for Xe, $CH_4$, and Kr (at $T = 446.3$ K) are well described by curve 3, i.e., with regard to the guest-guest interaction. The data for $CH_3F$ seem reasonable, too. The experimental data for Ar and Kr at temperatures below

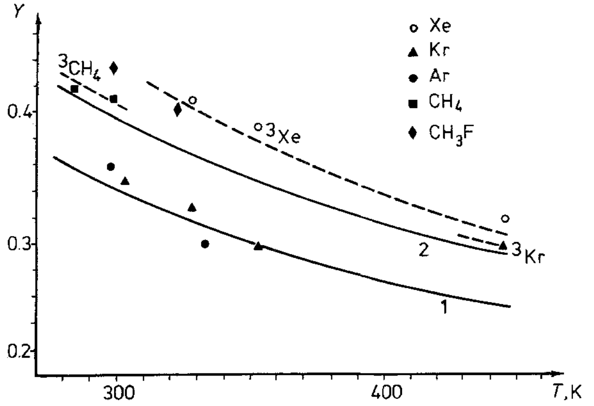

Fig. 4. Calculated curves for the monovariant equilibrium $\beta \rightleftharpoons \alpha + G$: curve 1 – calculation according to [4], equation (30), curve 2 – according to equation (31), curves 3 – according to (32) with introduction of corrections for the guest-guest interaction. Experimental data [12] are presented by dots.

100 °C are satisfactorily described by curve 1, one of the explanations of this is given earlier in this work. The set of equations has no solution for He and Ne. It points to the fact that there is no pressure under which the $\beta$-phase becomes more stable than the $\alpha$-phase. The last conclusion is correct only with in the accuracy of the assumptions made.

The authors would not like to consider the results obtained by them as absolutely irreproachable, since a number of assumptions, made to simplify the solution of the set of equations and the inaccuracy of some of the initial data undoubtedly make the final results less accurate. However, even in the ideal approximation (without regard for the guest-guest interaction) taking into account the guest solubility in the $\alpha$-phase gives not only the qualitatively correct $P$, $T$, $X$-phase diagram representation (e.g. a noticeable increase of the melting point of the hydroquinone $\alpha$-modification in the presence of the guest) but also quite a satisfactory quantitative description. Taking into account the guest-guest interaction makes this description better.

## Acknowledgement

The authors gratefully acknowledge the work of N.V. Udachina in translating this article into English.

## References

1. V. R. Belosludov, Yu. A. Dyadin, O. A. Drachiova, and G. N. Chekhova: *Izv. Sib. Otd. Akad. Nauk S.S.S.R., Ser. Khim. Nauk* **9**, 60–67 (1979); *C. A.* 91, 163770u (1979).
2. V. R. Belosludov, Yu. A. Dyadin, and S. I. Fadeev: *Izv. Sib. Otd. Akad. Nauk. S.S.S.R., Ser. Khim. Nauk* **7**, 57–63 (1981); *C. A.* 95, 103481y (1981).
3. M. Sitarski: *Rocz. Chem.* **49**, 159 (1975).
4. J. H. Van der Waals and J. C. Platteeuw: *Adv. Chem. Phys.* **2**, 1–57 (1959).
5. H. M. Powell: *J. Chem. Soc.* 298–301 (1950).
6. J. E. Mock, J. E. Myers, and E. A. Trabant: *Ind. Eng. Chem.* **53**, 1007–1010 (1961).
7. Yu. A. Dyadin and I. S. Terekhova: *Izv. Sib. Otd. Akad. Nauk S.S.S.R., Ser. Khim. Nauk* **9**, 88–96 (1980) *C. A.* 93, 174601g (1980).
8. L. D. Landau and E. M. Lifshits: *Statisticheskaya Fizika*, p. 113. Nauka, (1964).
9. V. I. Alekseev, V. I. Andrianov; T. M. Polyanskaja, G. N. Chekhova, Yu. A. Dyadin, and V. V. Bakakin: *Abstracts of Reports In 2nd All-Union Conference On Organic Crystalchemistry*, Zvenigorod 103 (1978).
10. H. M. Powell: *J. Chem. Soc.* 61–65 (1948).
11. C. Kittel: *Introduction to Solid State Physics*, 4th Edn. (Russian Translation) p. 117. Nauka (1978).
12. Yu. N. Kazankin, A. A. Palladiev and A. M. Trofimov: *Zh. Obshch. Khim.* **42**, 2607–2611 (1972); *C. A.* 78, 76317g (1973).
13. Yu. N. Kazankin, A. A. Palladiev and A. M. Trofimov: *Zh. Obshch. Khim.* **42**, 2611–2615 (1972); *C. A.* 78, 76316q (1973).
14. D. F. Evans and R. E. Richards: *J.Chem. Soc.* 3932–3936 (1952).
15. D. F. Evans and R. E. Richards: *Proc. Roy. Soc., London* **A223** 238–250 (1954).
16. R. L. Deming, T. L. Carlisle, B. J. Lauerman, J. T. Muckerman, A. R. Muirhead, and W. C. Child: *J. Phys. Chem.* **73**, 1762–1766 (1969).
17. J. H. Helle, D. Kok, J. C. Platteeuw, and J. H. Van der Waals: *Rec. Trav. Chim. Pays-Bas* **81**, 1068–1074 (1962).
18. G. N. Chekhova, T. M. Polyanskaja, Yu. A. Dyadin, and V. I. Alekseev: *Zh. Strukt. Khim.* **16**, 1054–1060 (1975); *J. Struct. Chem* **16**, 966–971 (1975); *C. A.* 84, 172412m (1976).
19. M. F. Pushlenkov and V. A. Ignatov: *Zh. Obshch. Khim.* **48**, 1170–1171 (1978); *C. A.* 89, 31671m (1978).
20. S. C. Wallwork and H. M. Powell: *J. Chem. Soc., Perkin Trans.* **2**, 641–646 (1980).
21. S. V. Lindeman, V. E. Shklover, and Yu. T. Struchkov: *Cryst. Struct. Commun* 1173–1179 (1981).