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ISOMORPHISM OF CRITICAL PHENOMENA

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A hypothesis of isomorphism of critical phenomena is proposed, whose essence is that the singularities of physical quantities near the transition points have the same form in various physical objects, provided the thermodynamic variables are properly chosen. The choice consists in selection of an ordering parameter (η) and a conjugate quantity. With the aid of this hypothesis and on the basis of similarity theory, a thermodynamics of critical phenomena is set up for various mixtures and other systems possessing critical-point lines. Singularities of various experimentally observable quantities are calculated and the ranges of applicability of the formulas are estimated. The available experimental material was analyzed. Critical phenomena in dilute solutions are considered in detail. It is shown that in such systems the various types of singularities (strong, of the $\tau^{-\gamma}$ type, and weak, of the $\tau^{-\alpha}$ type) can be smoothed out by admixtures in various temperature ranges ($\tau^{\gamma} \lesssim X$ and $\tau^{\alpha} \lesssim X$, where τ is the reduced temperature deviation from the critical point, α and γ are critical indices, and X is the admixture concentration). The purity and contamination number of a substance in the real experiment is calculated. Some considerations regarding isomorphism of kinetic coefficients are presented.

1. INTRODUCTION

It is known that critical phenomena of different types (second-order phase transitions) reveal similar features. This gives grounds for hoping that the theory of critical phenomena should have a universal character.

Modern phenomenological theory of critical phenomena—similarity theory (see the review [1])—starts from the general fact that the correlation radius of the system grows near the critical point. The model of the substance is not specified too concretely, and therefore this theory is suitable for a description of critical phenomena of various types. The singularities of the thermodynamic quantities near the transition point are described by introducing the so-called "critical exponents" "critical indices"). Similarity theory does not make it possible to find the values of the critical indices, and only establishes universal relations between them. Therefore each type of phase transition should have, generally speaking, its own set of indices.

Unfortunately, similarity theory can be constructed (without additional assumptions) only for a system with an isolated transition point, which is described by two variables (for example, temperature and magnetic field) and consequently, within the framework of the theory, by two independent indices. In real objects, only the critical liquid-gas equilibrium critical point is isolated. All the remaining transitions occur on critical lines or surfaces, depending on the number of independent variables.

We start from the concept of isomorphism of critical phenomena in different real objects. In other words, we assume that when the thermodynamic variables are suitably chosen, the thermodynamic potentials describing the properties of different systems near phase-transition points have the same functional form.

In order to formulate the rule for the choice of the isomorphic variables, we note that a second-order phase transition is connected with violation of the stability with respect to a certain parameter η (the ordering parameter in Landau's terminology[2]) and is characterized by the vanishing of the second derivative of the thermodynamic potential with respect to the ordering parameter:

$$\left(\frac{\partial^2\Psi}{\partial\eta^2}\right)_{T,Y_i} = 0, \qquad (1)$$

where $\Psi = \Psi(T, \eta, Y_i)$ is the thermodynamic potential and Y_i are all the independent variables of the system, with the exception of the temperature and the ordering parameter.

Let us assume that the potential $\Psi(T, \eta, Y_i)$ has, near the transition point, the same functional dependence on T and η for all the systems, the remaining variables Y_i being fixed. This corresponds to the choice of a certain fixed point $Y_i = \{Y_i^{(c)}\}$ on the line (surface) $T_c(Y_i)$. If this point is not singular (cases with singular points should be considered separately), then the critical temperature $T_c(Y_i)$ can be expanded in terms of the variables Y_i.

Let us assume now that the thermodynamic potential as a function of $\tau(Y_i) \equiv [T - T_c(Y_i)]/T_c(Y_i)$ and $\eta(Y_i)$ has the form obtained in similarity theory for a system with an isolated transition point. Thus, the number of independent critical indices remains equal to two as before.

Basing himself on the results of an investigation of decorated lattice models,[4,5] Fisher[3] proposed that the singularities of the thermodynamic quantities remain unchanged when an additional thermodynamic variable ("generalized coordinate") is added, if the value of the "generalized force" conjugate to it is fixed. Fisher's main result is the renormalization of the critical indices on going from an "ideal" system to a "real" one (with increasing number of variables). Fisher's hypothesis in the variant formulated by him is somewhat artificial, but it is easily seen that it is a particular case of the physically natural isomorphism assumption.

Table I. Singularities of thermodynamic quantities near the critical points of binary mixtures

Thermodynamic region	Thermodynamic quantity					
	$c_{X,P}$	$\left(\frac{\partial V}{\partial P}\right)_{T,X}$	$\left(\frac{\partial \mu}{\partial X}\right)_{T,P}$	$c_{V,\mu}$	$\left(\frac{\partial X}{\partial \mu}\right)_{T,V}$	$\left(\frac{\partial P}{\partial V}\right)_{T,\mu} \sim c_{P,\mu}^{-1}$
$z(P) \ll 1$ $z(\mu) \ll 1$	$\tau(P)^{-\alpha}$	$\tau(P)^{-\alpha}$	$\tau(P)^{\gamma}$	$\tau(\mu)^{-\alpha}$	$\tau(\mu)^{-\alpha}$	$\tau(\mu)^{\gamma}$
$z(P) \gg 1$ $z(\mu) \gg 1$	$x(P)^{-\alpha/\beta}$	$x(P)^{-\alpha/\beta}$	$x(P)^{\delta-1}$	$v(\mu)^{-\alpha/\beta}$	$v(\mu)^{-\alpha/\beta}$	$v(\mu)^{\delta-1}$

Note. $\alpha, \beta, \gamma, \delta$ are the indices of specific heat, the coexistence curve, susceptibility, and the critical isotherm [1].

Indeed, the condition for thermodynamic equilibrium is equality of the "generalized forces" (temperature, pressure, chemical potentials, etc.) at all points of the system, whereas the "generalized coordinates" (entropy, density, concentration, etc.) can vary from point to point. Therefore the variables Y_i in condition (1) are always "generalized forces."

When a new degree of freedom X_{i+1} appears in the system, the condition (1) takes the form

$$\left(\frac{\partial^2 \Psi^*}{\partial \eta^2}\right)_{T, Y_i, Y_{i+1}} = 0, \tag{2}$$

where Y_{i+1} is the quantity thermodynamically conjugate to X_{i+1}, and $\Psi^* = \Psi^*(T, \eta, Y_i, Y_{i+1})$.

In the present paper, starting from the concept of isomorphism, we consider phase transitions of different types in real objects. We consider in detail critical phenomena in mixtures, since binary liquid mixtures are particularly promising for experimental investigations. A special investigation is made of the case of dilute solutions and of the associated problem of the influence of impurities on the properties of substances near second-order phase-transition points. In addition, we discuss the possibility of isomorphism of kinetic coefficients near critical points.

2. CRITICAL PHENOMENA IN MIXTURES

In binary solutions (critical equilibrium points of liquid-liquid, liquid-gas, gas-gas mixtures and laminating solid solutions), the stability determinant takes the form[2,6]

$$\begin{aligned}\Delta &\equiv \left(\frac{\partial^2 F}{\partial X^2}\right)_{T,V}\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,X} - \left(\frac{\partial^2 F}{\partial V\,\partial X}\right)_T^2 \\ &\equiv \left(\frac{\partial P}{\partial V}\right)_{T,X}\left(\frac{\partial \mu}{\partial X}\right)_{T,P} \equiv \left(\frac{\partial \mu}{\partial X}\right)_{T,V}\left(\frac{\partial P}{\partial V}\right)_{T,\mu}.\end{aligned} \tag{3}$$

Here X is the molecular concentration of one of the mixture components, $F = F(T, V, X)$ is the free energy of the mixture,[1] and $\mu = (\partial F/\partial X)_{T,V} = (\partial \Phi/\partial X)_{T,P}$ is the chemical potential of the mixture.[6] Now, depending on which quantity we choose for the mixture as the ordering parameter ($\eta = x(P) \equiv X - X_c(P)$ or $\eta = v(\mu) \equiv [V - V_c(\mu)]/V_c(\mu)$), we can write in accordance with (1) two equivalent conditions for the critical point of the mixture:

$$\left(\frac{\partial \mu}{\partial X}\right)_{T,P} = \left(\frac{\partial^2 \Phi}{\partial X^2}\right)_{T,P} = 0 \tag{4}$$

or

$$\left(\frac{\partial P}{\partial V}\right)_{T,\mu} = \left(\frac{\partial^2 F^*}{\partial V^2}\right)_{T,\mu} = 0, \tag{5}$$

where

$$F^*(T, V, \mu) = F(T, V, X) - \mu X(T, V, \mu),$$
$$\Phi(T, X, P) = F(T, V, X) + PV(T, X, P).$$

Near the critical point we assume for the free energy F(T, V) of the pure substance the form resulting from similarity theory:[1]

$$F(T, V) = \tau^{2-\alpha} f(v/\tau^{\beta}) + F_0(T, V), \tag{6}$$

where $F_0(T, V)$ is a regular function, α and β are the critical indices of the specific heat and of the coexistence curve, $\tau = (T - T_c)/T_c$, $v = (V - V_c)/V_c$, and f(z) is a certain function with known asymptotic forms.

In accordance with the initial isomorphism assumption we obtain for the binary mixture

$$\Phi(T, X, P) = \tau(P)^{2-\alpha} \varphi\left\{\frac{x(P)}{\tau(P)^{\beta}}\right\} + \Phi_0(T, X, P), \tag{7}$$

$$F^*(T, V, \mu) = \tau(\mu)^{2-\alpha} f^*\left\{\frac{v(\mu)}{\tau(\mu)^{\beta}}\right\} + F_0^*(T\ V, \mu), \tag{8}$$

where

$$\tau(P) \equiv \frac{T - T_c(P)}{T_c(P)}, \quad \tau(\mu) \equiv \frac{T - T_c(\mu)}{T_c(\mu)}.$$

Differentiating expressions (7) and (8), we obtain all the singularities of the thermodynamic quantities near the critical points of the binary mixture (Table I).

Expressions (7) and (8) are equivalent for the description of the thermodynamic properties of mixtures near the critical points, and the choice between them can be made exclusively from considerations of convenience. The real experimental conditions, however, impose limitations on the choice of the thermodynamic variables. Thus, whereas the quantities $(\partial \mu/\partial X)_{T,P}$ and $C_{X,P}$ as functions of $\tau(P)$ are easily measurable quantities for liquid-liquid systems (the experiment is usually carried out in the presence of saturated vapor and the pressure remains practically unchanged), it is quite difficult to ensure constancy of P for liquid-gas systems. It is even more difficult to ensure constancy of μ in the system (this would call for varying the concentration during the course of the measurement), making it practically impossible to observe the singularities of the thermodynamic quantities as functions of $\tau(\mu)$ (the last three columns of Table I), since at a fixed value of the concentration X the chemical potential ceases to be an independent variable and becones a function of T and V.

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[1] Here and throughout all the extensive quantities are referred to one mole of substance.

Table II. Singularities of thermodynamic quantities near the critical points of binary mixtures in terms of the variables T, V, and X

Thermodynamic region	Thermodynamic quantity					
	$c_{X,P}$	$\left(\frac{\partial V}{\partial P}\right)_{T,X}$	$\left(\frac{\partial \mu}{\partial X}\right)_{T,P}$	$\left(\frac{\partial P}{\partial V}\right)_{T,\mu} \sim c_{P,\mu}^{-1}$	$\left(\frac{\partial X}{\partial \mu}\right)_{T,V} \sim \left(\frac{\partial P}{\partial X}\right)_{T,V}^{-1}$	$c_{V,X}$
$\tau(X) \gg v(X)$	$\tau(X)^{-\alpha/(1-\alpha)}$	$\tau(X)^{-\alpha/(1-\alpha)}$	$\tau(X)^{\gamma/(1-\alpha)}$	$\tau(X)^{\gamma/(1-\alpha)}$	$\tau(X)^{-\alpha/(1-\alpha)}$	$\tau(X)^{\alpha/(1-\alpha)}+\mathrm{const}$
$\tau(V) \gg x(V)$	$\tau(V)^{-\alpha/(1-\alpha)}$	$\tau(V)^{-\alpha/(1-\alpha)}$	$\tau(V)^{\gamma/(1-\alpha)}$	$\tau(V)^{\gamma/(1-\alpha)}$	$\tau(V)^{-\alpha/(1-\alpha)}$	$\tau(V)^{\alpha/(1-\alpha)}+\mathrm{const}$
$\tau(X) \ll v(X)$	$v(X)^{-\alpha/(1-\alpha)}$	$v(X)^{-\alpha/(1-\alpha)}$	$v(X)^{\gamma/(1-\alpha)}$	$v(X)^{\gamma/(1-\alpha)}$	$v(X)^{-\alpha/(1-\alpha)}$	$v(X)^{\alpha/(1-\alpha)}+\mathrm{const}$
$\tau(V) \ll x(V)$	$x(V)^{-\alpha/(1-\alpha)}$	$x(V)^{-\alpha/(1-\alpha)}$	$x(V)^{\gamma/(1-\alpha)}$	$x(V)^{\gamma/(1-\alpha)}$	$x(V)^{-\alpha/(1-\alpha)}$	$x(V)^{\alpha/(1-\alpha)}+\mathrm{const}$

Note. The quantity $(\partial P/\partial V)_{T,\mu}$ determines the intensity of light scattering by density and concentration fluctuations near the critical point of the mixture.

A method that makes it possible to find the dependence of the chemical potential on the volume and on the temperature was proposed by Fisher.[3] We confine ourselves therefore to a brief listing of the results obtained by such a method.

From the definition $X = -(\partial F^*/\partial\mu)_{T,V}$, using expression (8), we obtain ($F^* = F^*\{T, V, \mu, \tau(T, \mu), v(V, \mu)\}$)

$$X = -\left(\frac{\partial F^*}{\partial \tau}\right)_{v,V,\mu,T}\left(-\frac{1}{T_c}\frac{dT_c}{d\mu}\right) - \left(\frac{\partial F^*}{\partial v}\right)_{\tau,T,\mu,V}\left(-\frac{1}{V_c}\frac{dV_c}{d\mu}\right) - \left(\frac{\partial F_0^*}{\partial \mu}\right)_{v,V,\tau,T}. \tag{9}$$

Expanding $(\partial F_0^*/\partial\mu)_{v,V,\tau,T}$ in a series about the critical point $\mu = \mu_c$, $T = T_c[\mu_c] = T_c(x)$, $V = V_c(\mu_c) = V_c(X)$, putting $X = X_c$ and representing $T_c(\mu)$ in the form

$$T_c(\mu) = T_c(X) + \frac{dT_c}{d\mu}\Delta\mu, \tag{10}$$

we obtain from (9) and (10) the equation[2]

$$\frac{A}{T_c}\,M\frac{T_c}{l\mu}\left[\tau(X) - \frac{1}{T_c}\frac{dT_c}{d\mu}\Delta\mu\right]^{1-\alpha} + a\tau(X) - bv(X) - c\Delta\mu = 0, \tag{11}$$

where

$$a = \frac{B}{T_c}\frac{dT_c}{d\mu} - \left(\frac{\partial P}{\partial T}\right)_{V,\mu}\frac{1}{V_c}\frac{dV_c}{d\mu} - a', \qquad a' = T_c\frac{\partial^2 F_0^*}{\partial\mu\,\partial T},$$

$$b = V_c\frac{\partial^2 F_0^*}{\partial\mu\,\partial V}, \quad c = \frac{1}{T_c}\frac{dT_c}{d\mu}\left[\frac{B}{T_c}\frac{dT_c}{d\mu} - \left(\frac{\partial P}{\partial T}\right)_{V,\mu}\frac{1}{V_c}\frac{dV_c}{d\mu} - \frac{dX}{dT_c}\right].$$

The solution of Eq. (11) for $\tau(X) \gg v(X)$ (on the isochore) in the temperature region

$$\tau(X) \ll \xi^{-1}\tau(X)^{1-\alpha} \equiv \left[\frac{T_c}{A(dT_c/d\mu)(dT_c/dX)}\left(1 - \frac{a'}{T_c}\frac{dT_c}{dX}\right)\right]^{-1}\tau(X)^{1-\alpha} \tag{12}$$

is of the form $\Delta\mu = T_c(dT_c/d\mu)^{-1}\{\tau(X) - [\xi\tau(X)^{1/(1-\alpha)}\}$, and then

$$\tau(\mu) = [\xi\tau(X)]^{1/(1-\alpha)}. \tag{13}$$

In the region $\tau(X) \gg \xi^{-1}\tau(X)^{1-\alpha}$, we obviously obtain

$$\tau(\mu) = \left(1 - \frac{a'}{T_c}\frac{dT_c}{dX}\right)\tau(X). \tag{14}$$

We can find analogously the solutions of (11) in the case $v(X) \gg \tau(X)$ (on the isotherm)

$$\tau(\mu) = \left\{\frac{bT_c}{A}\left(\frac{dT_c}{d\mu}\right)^{-1}v(X)\right\}^{1/(1-\alpha)}, \tag{15}$$

$$v(\mu) = v(X) - \frac{T_c}{V_c}\frac{dV_c}{d\mu}\left(\frac{dT_c}{d\mu}\right)^{-1}\tau(X). \tag{16}$$

Since we have $z(\mu) \equiv v(\mu)/\tau(\mu)^\beta \ll 1$ even on the isotherm (in the T-V-X space), formula (16) is needed here only for the differentiation of (B) with respect to $\tau(X)$ (for example, to determine $C_{V,X}$).

Substituting (13)–(16) in the expression for the free energy

$$F(T, V, X) = F^*(T, V, \mu) + X\mu(T, V, X),$$

we easily obtain the singularities of any thermodynamic quantity in terms of the variables T, V, and X (see Table II).

The results of the transition from T, P, X to T, V, X are obtained in analogy with (13)–(16) with the following change of variables:

$$V_c \to X_c, \quad v(X) \to x(V), \quad v(\mu) \to x(P), \quad \mu \to P.$$

Naturally, the singularities of the thermodynamic quantities as functions of $\tau(V)$ at $X = X_c$ or of $x(V)$ at $T = T_c$ coincide with those obtained as functions of $\tau(X)$ at $V = V_c$ or of $v(X)$ at $T = T_c$ (Table II).

We emphasize that the solutions of Eq. (11) in the form (13) (and consequently all the singularities given in Table II) are obtained only if condition (12) is satisfied.

We note that owing to the smallness of α, there exists a very wide intermediate region of τ, in which these terms remain on the same order. Thus, at $\alpha = 0.1$ the quantity $\tau^{1-\alpha}$ becomes larger than τ by one order of magnitude only when τ changes from 1 to 10^{-10}. Therefore prime importance attaches to the coefficients in (11) and (12). Namely, depending on these coefficients, the renormalization of (13) will be observed or will remain entirely inaccessible to observation.

3. POSSIBILITY OF EXPERIMENTAL OBSERVATION OF THE RENORMALIZATION OF THE CRITICAL INDICES

The solution (13) of Eq. (11) is valid in the region $\tau(X) \ll \xi^{-1/\alpha}$.[3] This means that the singularities of the

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[2] In deriving (11) we assumed that $z(\mu) \equiv \nu(\mu)/\tau(\mu)^\beta \ll 1$, and used the known asymptotic form of the function f(z) [1]. Then $C_{V,\mu} = -T\partial^2 F^*/\partial T^2 = -(1-\alpha)A\tau(\mu)^{-\alpha} - B$. It can be shown that the assumption $z(\mu) \ll 1$ is valid both when $\tau(x) \gg v(X)$ and when $\tau(X) \ll v(X)$ in a sufficiently close vicinity of the critical point.

[3] In the case of a logarithmic singularity of the specific heat, the limit of the corresponding region is

$$\tau \sim \exp\left\{T_c/D\frac{dT_c}{d\mu}\frac{dT_c}{dX}\right\}, \qquad D = D'\left(1 - \frac{a'}{T_c}\frac{dT_c}{dX}\right);$$

D′ is the coefficient in the formula $C_{V,\mu} = -D'\ln\tau(\mu) - B$.

different thermodynamic quantities listed in Table II can be observed experimentally in this region, which is as a rule quite narrow. However, even in the case when $\tau(X) \gg \xi^{-1/\alpha}$ (the region in which the critical indices do not change), the change of the singularities of the thermodynamic quantities can be connected with the coefficient preceding $\tau(X)$ in relation (14). The rate of growth of the corresponding quantity can either increase or decrease, depending on the sign of the derivative dT_c/dX.

Owing to the smallness of α, there exists a sufficiently wide intermediate region that can extend over several orders in τ and in which both mechanisms of distortion of the singularities are active. This means that the experimental results in this region can hardly be interpreted to any definite degree. As the critical point is approached, the index that can be ascribed to the given quantity changes.

Let us consider some concrete systems.

1. In the case of a liquid-liquid phase equilibrium, the critical mixing temperature usually depends little on the pressure, and the region $\tau(V) \ll (\xi^*)^{-1/\alpha}$ is very narrow. Here

$$\xi^* = \frac{T_c}{A^*(dT_c/dP)(dT_c/dV)}\left(1 - \frac{a'^*}{T_c}\frac{dT_c}{dV}\right),$$

A^* is the coefficient in the formula $C_{P,X} = -(1-\alpha) \times A^*\tau(P)^{-\alpha} - B^*$. For the methanol-cyclohexane system, for example (the results of an investigation of the specific heat $C_{P,X}$ of this system are given in [7]), we have $(\xi^*)^{-1} \approx 2 \times 10^{-2}$, and therefore for all reasonable values of α ($\lesssim 0.2$), up to the experimentally unattainable region $\tau \sim 10^{-8} - 10^{-16}$, relation (14) is valid, there is no renormalization of the critical indices, and $C_{V,X}$ increases and follows (lagging) the singularity of $C_{P,X}$. For the same reason, in the region $\tau \gg 10^{-8} - 10^{-16}$, the singular increments of the quantities $(\partial V/\partial P)_{T,X}$ and $(\partial V/\partial T)_{P,X}$ are very small (they contain the quantity dT_c/dP in the coefficients of the singular parts) and they are difficult to observe.

An analogous regularity is observed near the λ transition in helium, where $(\xi^*)^{-1}$ is also a small parameter.[8]

2. A similar situation can arise in the investigation of the critical points of liquid-gas equilibrium in mixtures, where, owing to the weak dependence of T_c on X (for example in solutions of isotopes or in the presence of an extremum on the $T_c(X)$ curve), $C_{V,X}$ will increase practically over the entire experimentally attainable region. If $dT_c/dX = 0$ (extremum) then (see (12)) $C_{V,X} \sim C_{V,\mu} \sim C_{P,X} \sim \tau(X)^{-\alpha}$, and

$$\left(\frac{\partial V}{\partial P}\right)_{T,X} = \frac{C_{P,X}}{C_{V,X}}\left(\frac{\partial V}{\partial P}\right)_{T,S} = \text{const.}$$

Another unique case is the critical point of an azeotropic mixture,[6] where $(\partial P/\partial X)_{T,V} = 0$ and therefore $(\partial P/\partial V)_{T,X} = 0$, as at the critical point of the pure substance. It is important, however, that at this point $dT_c/dX \neq 0$, and in the region defined by the inequality (12) we have

$$\left(\frac{\partial P}{\partial V}\right)_{T,X} \sim \tau(X)^{\gamma/1-\alpha} \text{ and } C_{V,X} \sim \tau(X)^{\alpha/1-\alpha} + \text{const},$$

i.e., the specific heat $C_{V,X}$ remains finite.

For the critical azeotropic ethane-carbon dioxide mixture investigated in [9], the parameter is

$$\xi^{-1} \approx \frac{A}{T_c}\frac{dT_c}{d\mu}\frac{dT_c}{dX} \approx 10^{-1}$$

and when $\alpha \approx 0.1-0.2$ the renormalization region is $\tau \sim 10^{-5} - 10^{-10}$, which does not contradict the measurements of $C_{V,X}$ in this mixture.[10] However, since the intermediate region for this system is close to the measurement region, the critical index that can be obtained by approximating the experimental curve by means of the expression $C_{V,X} = -A\tau^{-\alpha^*} - B$, lies in the interval $\alpha > \alpha^* > -\alpha/(1-\alpha)$ and is not a constant quantity.

3. A limiting case that is the opposite of the preceding one,

$$dT_c/d\mu \sim dT_c/dP = \infty$$

is realized in the so-called hypercritical point,[11] when the upper and lower critical mixing points coalesce with increasing pressure (for example, the system heavy water–picoline[11]).

To obtain the singularities of the thermodynamic quantities at such a point, we rewrite (8) in the equivalent form

$$\Phi(T,X,P) = p(T)^{2-\alpha}\varphi\left\{\frac{x(T)}{p(T)^{\beta}}\right\} + \Phi_0(X,P,T), \tag{17}$$

where $p(T) = [P - P_c(T)]/P_c(T)$. If $dP_c/dT = 0$ (i.e., there is no linear term in the expansion of P_c in terms of T), then

$$\begin{gathered}(\partial\mu/\partial X)_{P,T} \sim p(T)^{\gamma} \sim \tau^{2\gamma},\\ (\partial V/\partial P)_{T,X} \sim p(T)^{-\alpha} \sim \tau^{-2\alpha},\\ C_{P,X} = C_{V,X} = \text{const}, \quad (\partial V/\partial T)_{P,X} = \text{const},\end{gathered} \tag{18}$$

$$\left(\frac{\partial V}{\partial P}\right)_{X,S} = \frac{C_{V,X}}{C_{P,X}}\left(\frac{\partial V}{\partial P}\right)_{T,X} \sim \tau^{-2\alpha},$$

and finally $(\partial P/\partial T)_{X_c,V_c} = (\partial\mu/\partial T)_{X_c,V_c} = 0$, since $(\partial P/\partial T)_{X,V} = dP_c/dT$ and $(\partial\mu/\partial T)_{X,V} = d\mu_c/dT$ at the critical point. The hypercritical point is apparently one of the few objects where it is actually possible to observe singularities of the isothermal and adiabatic compressibilities in mixtures.

4. In order to be able to compare the results of the experimental investigation of the liquids and solids, we make a few remarks concerning the place the latter occupy in the general isomorphic scheme. We immediately call attention to the fact that in phase transitions in solids the resultant ordering is usually weakly connected with the mechanical stability of the lattice. Therefore the regular part of the free energy near the transition point does not depend on the variable that characterizes the ordering parameter, and it is necessary to write in lieu of (7) and (8) (for example, for an incompressible ferromagnet)

$$F(T, m) = \tau^{2-\alpha}f(m/\tau^{\beta}) + F_0(T), \tag{19}$$

where m is the magnetic moment and $\partial F/\partial m = h$ is the magnetic field. After subtracting from the pressure (chemical potential) of the liquids its value at the critical volume (concentration) $P(V_c, T)$ (or $\mu(X_c, T)$), the thermodynamic relation for the liquids also reduces to the form identical with the formulas that follow from (19). For example, for $z \equiv v/\tau^{\beta} \ll 1$ we get

$$C_{P-P(V_c,T)} \sim C_V \sim \tau^{-\alpha}, \tag{20}$$

(Compare with $C_h \sim C_m \sim \tau^{-\alpha}$), where $C_P \sim (\partial V/\partial P)_T \sim \tau^{-\gamma}$.

In the case of a compressible ferromagnet, there are grounds for assuming [12] that in the region defined by the inequality (12), where the renormalization of (13) might be observed, the second-order phase transition is transformed into a first-order transition at a nonzero shear modulus.

We note also that various inhomogeneities, which are always present in solids, make the question of the experimental determination of the renormalizations of the critical indices in these objects quite problematic.

4. DILUTE SOLUTIONS. INFLUENCE OF IMPURITIES ON THE PROPERTIES OF SUBSTANCES NEAR THE CRITICAL POINTS

The isomorphism hypothesis makes it possible to consider the experimentally and theoretically important problem of the influence of impurities on the properties of substances near second-order phase-transition points. The problem of dilute solutions ($X \ll 1$) is a problem of the influence of impurities.

The distinguishing feature of the description of dilute solutions near the critical points, as compared with ordinary dilute solutions, lies in the appearance of the additional small parameter τ.

Let us consider first the transition to the critical point of liquid-gas equilibrium of a pure substance. Although we have already noted above the equivalence of the potentials $\Phi(T, X, P)$ and $F^*(T, V, \mu)$ for binary mixtures, it is more convenient in the description of dilute solutions to use the potential $F^*(T, V, \mu)$, for in this case the ordering parameter $v(\mu)$ goes over in natural fashion into the ordering parameter of the pure liquid.

In view of the fact that in (9) X_c is determined only by the regular part of $F^*(T, V, \mu)$, we have at $X \ll 1$ the obvious equality[2,6]

$$X = X_c = -\left(\frac{\partial F^*}{\partial \mu}\right)_{\tau=0,\, v=0} = \exp\left\{\frac{\mu_c}{RT_c}\right\}. \qquad (21)$$

Experiment[13] shows that $T_c(X)$ and $V_c(X)$ are linear functions of the concentration, and therefore

$$T_c(X) = T_c^{(0)} + \frac{dT_c}{dX}\exp\left\{\frac{\mu_c}{RT_c}\right\}, \qquad (22)$$

$$V_c(X) = V_c^{(0)} + \frac{dV_c}{dX}\exp\left\{\frac{\mu_c}{RT_c}\right\}, \qquad (23)$$

where $T_c^{(0)}$ and $V_c^{(0)}$ are the critical temperature and volume of the pure substance. Then

$$\frac{dT_c}{d\mu} = \frac{1}{T_c}\frac{dT_c}{dX}\exp\left\{\frac{\mu_c}{RT_c}\right\} = \frac{dT_c}{dX}\frac{X}{T_c}, \qquad (24)$$

i.e., in the quantity that determines the region of renormalization of the singularities of different thermodynamic quantities there appears a small parameter X. Inside the "cone"

$$\tau \ll \left\{\frac{AX}{RT_c^2}\left(\frac{dT_c}{dX}\right)^2\right\}^{1/\alpha} \qquad (25)$$

(for $X \ll 1$, $a' \sim X \ln X$ and $1 - (a'/T_c(dT_c/dX \approx 1$ the renormalization of (13) is observed and the solution cannot be regarded as dilute no matter what the value of X.

Let us find, for example, the quantity $(\partial X/\partial \mu)_{T,V}$. Differentiating (8) twice with respect to μ and taking (22) into account, we obtain

$$\left(\frac{\partial X}{\partial \mu}\right)_{T,V} = \frac{1}{T_c}\frac{A}{(RT_c)^2}\left(\frac{dT_c}{dX}\right)^2 X^2 \tau(X)^{-\alpha/(1-\alpha)} + \frac{X}{RT_c}. \qquad (26)$$

In the region $\tau^\alpha \ll X$ we have $(\partial X/\partial \mu)_{T,V} \sim \tau(X)^{-\alpha/(1-\alpha)}$, and in the region $\tau^\alpha \gg X$ we have $(\partial X/\partial \mu)_{T,V} \sim X$, just as in ordinary dilute solutions. The specific heat $C_{V,X}$ is found from the thermodynamic equality

$$C_{V,X} = C_{V,\mu} - T\left(\frac{\partial \mu}{\partial T}\right)^2_{V,X}\left(\frac{\partial X}{\partial \mu}\right)_{T,V}. \qquad (27)$$

In the region $\tau^\alpha \ll X$ we have (taking into account (26), (27), and $(\partial\mu/\partial T)_{V,X} \approx d\mu/dT_c$)

$$C_{V,X} \sim \tau(X)^{\alpha/(1-\alpha)} + 1/X + \text{const}, \qquad (28)$$

i.e., on moving to the critical point of the pure substance along the critical line of the solution, the specific heat $C_{V,X}$ becomes infinite like $1/X$. When $\tau^\alpha \gg X$ we get $C_{V,X} \sim C_{V,\mu} \sim \tau(X)^{-\alpha}$, and finally, taking (22) into account we obtain a specific heat $C_{V,X} \sim X^{-\alpha}$ when $T = T_c^{(0)}$ and $V = V_c^{(0)}$. The singularities of the other quantities, which are listed in Table III, were obtained in similar fashion.

Let us consider now the behavior in dilute solutions of quantities having "strong" singularities.

From (3) it is easily seen that

$$\left(\frac{\partial \mu}{\partial X}\right)_{T,P} = \left(\frac{\partial P}{\partial V}\right)_{T,\mu}\left(\frac{\partial \mu}{\partial X}\right)_{T,V}\left(\frac{\partial P}{\partial V}\right)^{-1}_{T,X}. \qquad (29)$$

Recognizing that when $\tau^\alpha \gg X$

$$\left(\frac{\partial P}{\partial V}\right)_{T,\mu} \sim \tau(X)^\gamma, \quad \left(\frac{\partial P}{\partial V}\right)_{T,X} \sim \left(\frac{\partial X}{\partial \mu}\right)_{T,V} \sim X, \qquad (30)$$

we obtain from (29) in the region $\tau^\gamma \ll X \ll \tau^\alpha$

$$\left(\frac{\partial \mu}{\partial X}\right)_{T,P} \sim \frac{\tau(X)^\gamma}{X^2}, \qquad (31)$$

and only for $\tau^\gamma \gg X$ do we get

$$\left(\frac{\partial V}{\partial P}\right)_{T,X} \sim \left(\frac{\partial V}{\partial P}\right)_{T,\mu} \sim \tau(X)^{-\gamma} \text{ and } \left(\frac{\partial \mu}{\partial X}\right)_{T,P} \sim \frac{1}{X}. \qquad (32)$$

Thus, the properties of dilute solutions near the critical point of the pure substance are determined by the presence of two "cones" $\tau^\alpha \sim X$ and $\tau^\gamma \sim X$ (see Table III). In the region $\tau^\gamma \lesssim X$ there occurs the "killing" of the strong singularity of $(\partial V/\partial P)_{T,X} \sim \tau^\gamma$ and the appearance of a singularity of $(\partial \mu/\partial X)_{T,P}$ (it can be revealed, for example, by the decrease of the diffusion coefficient). In the region $\tau^\alpha \lesssim X$, the singularity of the specific heat $C_{V,X}$ is "killed," singularities of $(\partial X/\partial \mu)_{T,V}$ and $(\partial V/\partial P)_{T,X}$ appear, and renormalization of (13) occurs.

The appearance of two regions $\tau^\alpha \sim X$ and $\tau^\gamma \sim X$ when an impurity is added to a pure substance is a feature characteristic only of critical phenomena in laminating systems. In the case of other second-order phase transitions in mixtures (mixtures of ferromagnets, λ transition in the He^3–He^4 solution, etc.) there exists only the region $\tau^\alpha \sim X$, where renormalization of all the critical indices takes place.

On the isotherm ($\tau(X) \ll v(X)$) it is also possible to separate several regions: when $v(X)^\alpha \ll X$ there takes

Table III. Singularities of thermodynamic quantities in dilute solutions near the critical point of the pure substance

Thermodynamic region	Thermodynamic quantity							
	$c_{V,X}$	$\left(\frac{\partial V}{\partial P}\right)_{T,X} \sim c_{P,X}$	$\left(\frac{\partial V}{\partial P}\right)_{T,\mu} \sim c_{P,\mu}$	$\left(\frac{\partial X}{\partial \mu}\right)_{V,T}$	$\left(\frac{\partial X}{\partial \mu}\right)_{P,T}$	$\left(\frac{\partial \mu}{\partial T}\right)_{V,X}$	$\left(\frac{\partial V}{\partial X}\right)_{P,T}$	$\left(\frac{\partial P}{\partial X}\right)_{V,T}$
$\tau(X)^\alpha \ll X$	$\tau^{\alpha/(1-\alpha)} + X^{-1}$	$\tau^{-\alpha/(1-\alpha)}$	$\tau^{-\gamma/(1-\alpha)}$	$X^2\tau^{-\alpha/(1-\alpha)}$	$X^2\tau^{-\gamma/(1-\alpha)}$	X^{-1}	const	$\tau^{\alpha/(1-\alpha)}$
$\tau(X)^\gamma \ll X \ll \tau(X)^\alpha$	$\tau^{-\alpha}$	X^{-1}	$\tau^{-\gamma}$	X	$X^2\tau^{-\gamma}$	$\ln X$	X^{-1}	const
$\tau(X)^\gamma \gg X$	$\tau^{-\alpha}$ $X^{-\alpha}\,(T = T_c^{(0)},$ $V = V_c^{(0)})$	$\tau^{-\gamma}$ $X^{-1}\,(T = T_c^{(0)},$ $V = V_c^{(0)})$	$\tau^{-\gamma}$	X	X	$\ln X$	X^{-1}	const

Table IV. Singularities of thermodynamic quantities in the presence of equilibrium impurities near the Curie point of a pure ferromagnet

Thermodynamic region	Thermodynamic quantities				
	$c_{X,\,h=0}$	$\left(\frac{\partial h}{\partial m}\right)_{T,\mu} = \left(\frac{\partial h}{\partial m}\right)_{T,X}$	$c_{\mu,\,h=0}$	$\left(\frac{\partial \mu}{\partial T}\right)_X$	$\left(\frac{\partial \mu}{\partial X}\right)_T$
$\tau^\alpha \ll X$	$\tau^{\alpha/(1-\alpha)} + X^{-1}$	$\tau^{\gamma/(1-\alpha)}$	$\tau^{-\alpha/(1-\alpha)}$	X^{-1}	$\tau^{\alpha/(1-\alpha)}$
$\tau^\alpha \gg X$	$\left\{\begin{matrix}\tau^{-\alpha}\\ X^{-\alpha}\,(T = T_k^0)\end{matrix}\right.$	τ^γ	$\tau^{-\alpha}$	$\ln X$	X^{-1}

place renormalization of (15), and when $v(X)^{(1-\beta)/\beta} \gg X$ the ratio becomes larger than unity and the thermodynamic quantities cease to depend on $\tau(\mu)$, with $v(\mu) \sim v(X)$, and finally in the region $v(X)^{\delta-1} \gg X$ we have

$$\left(\frac{\partial P}{\partial V}\right)_{T,X} \approx \left(\frac{\partial P}{\partial V}\right)_{T,\mu} \sim v(X)^{\delta-1}.$$

It is meaningful, in our opinion, to pose the question differently and to speak of an impurity influencing the singularities and of an impurity without any influence. Indeed, solving the inequality (25) with respect to X, we obtain for the region in which the influence of the impurities is significant

$$X > \frac{RT_c^2}{A\,(dT_c/dX)^2}\tau^\alpha \equiv \xi_X\tau^\alpha. \qquad (33)$$

Since the singularities are experimentally observed only in the interval $10^{-1} < \tau < 10^{-8}$, we can put in (33) $\tau^\alpha \sim 1$. Then for all $X > \xi_X$ the substance will be "dirty" and the singularities renormalized. At a concentration $X < 0.1\xi_X$, a substance chosen for the measurements can be regarded as practically pure.

The free energy of a mixture of ferromagnets near the Curie point, in accordance with the isomorphism hypothesis, is of the form

$$F^*(T, m, \mu) = \tau(\mu)^{2-\alpha} f^*\left\{\frac{m}{\tau(\mu)^\beta}\right\} + F_0(T, \mu). \qquad (34)$$

Since, as already noted in Sec. 3, the regular part of the free energy of the ferromagnet does not depend on m (or h), then $(\partial h/\partial X)_{T,\,m=0} \equiv 0$ above the transition point. Therefore for $\tau^\alpha \ll X$ we have

$$\left(\frac{\partial h}{\partial m}\right)_{T,\mu} = \left(\frac{\partial h}{\partial m}\right)_{T,X} \sim \tau(\mu)^\gamma \sim \tau(X)^{\gamma/(1-\alpha)}, \qquad (35)$$

i.e., the susceptibility at X = const has the same singularity as at μ = const, unlike the liquids, where

$$\left(\frac{\partial V}{\partial P}\right)_{T,\mu} \sim \left(\frac{\partial X}{\partial \mu}\right)_{P,T} \sim \tau(X)^{-\gamma/(1-\alpha)},$$

$$\left(\frac{\partial V}{\partial P}\right)_{T,X} \sim \left(\frac{\partial X}{\partial \mu}\right)_{T,V} \sim \tau(X)^{-\alpha/(1-\alpha)}$$

(see Tables III and IV).

It must be emphasized that we are dealing here only with thermodynamic (equilibrium) impurities.

Inasmuch as in solids the principal role is apparently played by "frozen-in" (non-equilibrium) impurities, the renormalizations in such objects can be carried out only for well-founded estimates of the degree of non-equilibrium.

In concluding this section let us estimate the influence of impurities in two concrete systems.

1. He^4–He^3 mixture. In this case we obtain for the renormalization region, in accordance with formula (25),

X	0,1	0,2	0,4
$(X^{-1}\xi_X)$	30	12	3
τ	10^{-12}	10^{-5}	10^{-1}

The foregoing estimates show that the interpretation of the results of the measurement of the specific heat $C_{P,X}$ in the He^4–He^3 mixture[14] is apparently not quite correct. Although at $X \approx 0.1$ the renormalization region has apparently not yet been reached, in accordance

$$\xi_X \approx \frac{RT_c}{A\,(dT_c/dX)^2} \sim 1,$$

with the foregoing statement (see Sec. 3) the intermediate region already covers part of the measurement interval. At $X \approx 0.2$ the entire measured region is intermediate and cannot be interpreted. Finally, at $X \approx 0.4$ the critical index of the specific heat is renormalized in the entire measurement interval. Such a complexity of the interpretation is connected with the fact that and the inequality (33) is very sensitive to weak changes of the parameters. Moreover, solutions with concentrations 0.1–0.4 cannot be regarded as dilute, and therefore a comparison with formulas (25) and (33) can be carried out only accurate to the order of magnitude.

2. In the methanol-cyclohexane system, the critical temperature changes strongly when water is added ($T_C^{-1} dT_C/dX \approx 10$). Therefore according to (33), for impurities with concentration $X \ll 2 \times 10^{-3}$, the substance will behave like a pure one. However, when $X \gg 10^{-2}$, to the contrary, there will always be observed a renormalization, and consequently, the "killing" of the singularity of the specific heat. Real experiments lie precisely in the intermediate region and therefore are difficult to interpret quantitatively. Already at $X \approx 0.5\%$ the region of renormalization extends over $\tau \lesssim 10^{-3}$. Let us call attention, however, to the fact that the inequality (25) contains a numerical parameter $(A/R)^{1/\alpha}$. Since this parameter can be different above and below T_C ($A_+/A_- \approx 1.5$–2), the corresponding estimates above and below T_C can differ by three orders of magnitude.

We thus have an explanation of the fact that at $T < T_C$ the influence of impurities and other "smearing factors" on singularities of different thermodynamic quantities extends much farther away from T_C than when $T > T_C$.

5. ISOMORPHISM OF KINETIC COEFFICIENTS

Starting with the hypothesis of isomorphism of critical phenomena in different systems, we can obtain certain suggestions concerning the singularities of kinetic coefficients near phase-transition points.

The kinetic coefficients (ζ) are defined here as the coefficients of proportionality between the fluxes (j) and the gradients of the corresponding generalized forces (Y_i) causing these fluxes.

Since the critical temperature of the system and the ordering parameters are themselves defined by specifying the generalized forces: $T_C = T_C(Y_i)$, $\eta = \eta(Y_i)$, it follows that the presence of gradients of these forces leads to the occurrence of gradients of $\tau(Y_i)$ and $\eta(Y_i)$, and consequently to additional absorption of energy, connected with the relaxation with respect to these two parameters. The corresponding kinetic coefficients can, generally speaking, be singular functions of $\tau(Y_i)$ and $\eta(Y_i)$.

We represent all the kinetic coefficients in the form of a sum of two quantities

$$\zeta = \zeta_0 + \zeta', \tag{36}$$

where ζ_0 is the regular part of the coefficient ζ, and ζ' is the part connected with the relaxation of the parameters τ or η, and is generally speaking singular.

We shall consider henceforth by way of an example the critical points of liquid-vapor (liquid-liquid) equilibrium of a binary mixture. The role of Y_i is played in such a system by the chemical potential μ and by the temperature T, and the equations for the fluxes are of the form

$$\begin{aligned} \mathbf{j}^{(1)} &= -\tilde{\gamma} \nabla T - T \tilde{\beta} \nabla \mu, \\ \mathbf{j}^{(2)} &= -\tilde{\alpha} \nabla \mu - \tilde{\beta} \nabla T, \end{aligned} \tag{37}$$

$j^{(1)}$ is the entropy flux in the system and $j^{(2)}$ is the diffusion flux of one of the components.

Since the decay of the density fluctuations is described by acoustic equations and is not accompanied by energy dissipation, the heat flux is connected only with relaxation of the parameter $\tau(\mu)$:

$$\mathbf{j}'^{(1)} = -T_c \tilde{\gamma}' \nabla \tau(\mu) = -T_c \tilde{\gamma}' \left\{ \nabla \tau(\mu_c) - \frac{1}{T_c} \frac{dT_c}{d\mu} \nabla \mu \right\}. \tag{38}$$

Comparing this expression with the first equation of (37), we obtain

$$\tilde{\beta}' = -\frac{1}{T_c} \frac{dT_c}{d\mu} \tilde{\gamma}'. \tag{39}$$

Analogously, from the expression for the flux $j^{(2)}$ we have

$$\mathbf{j}'^{(2)} = -T_c \tilde{\beta}' \nabla \tau(\mu) = -T_c \tilde{\beta}' \left\{ \nabla \tau(\mu_c) - \frac{1}{T_c} \frac{dT_c}{d\mu} \nabla \mu \right\}. \tag{40}$$

Comparing (40) with the second equation of the system (37) we get

$$\tilde{\alpha}' = -\frac{dT_c}{d\mu} \tilde{\beta}' = \frac{1}{T_c} \left(\frac{dT_c}{d\mu} \right)^2 \tilde{\gamma}'. \tag{41}$$

Relations (41) show that the additions to the kinetic coefficients $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ coincide, accurate to factors that do not depend on τ.

In the spirit of the isomorphism hypothesis, we can assume further that the singularity of the coefficient $\tilde{\gamma}$ in the binary mixture coincides with the singularity of the coefficient of thermal conductivity in the pure liquid (see [15]) ($\tilde{\gamma}$ is the heat-conduction coefficient at a fixed value of the chemical potential).

This means that

$$\tilde{\gamma}' \sim \left(\frac{\partial P}{\partial V} \right)_{T,\mu}^{-1/2}. \tag{42}$$

As already noted above, at a near-zero concentration (X) of one of the components, the derivative $dT_C/d\mu \sim X$. Therefore the additions to the coefficients $\tilde{\alpha}$ and $\tilde{\beta}$ are proportional respectively to X^2 and X.

Finally we thus obtain

$$\tilde{\gamma}' \sim \tau^{-\nu/2}, \quad \tilde{\beta}' \sim -X\tau^{-\nu/2}, \quad \tilde{\alpha}' \sim X^2\tau^{-\nu/2}. \tag{43}$$

It is interesting to note that a more detailed calculation of the kinetic coefficients in binary mixtures[16] confirms the formulas (41)–(43).

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