

Entropy and state of molecules on gas-liquid and gas-solid interface

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Abstract

It has been shown experimentally that the dependence of the logarithm of the ratio of molar volumes of the phases coexisting at equilibrium on the entropy of the phase transition has more general character than familiar dependence of the logarithm of gas phase pressure on the reciprocal temperature. The presence of common liquid - vapour, crystal - vapour and adsorption lays - vapour coexistence curve for a group of substances has been established. The result has been analysed from standpoint of conversion degrees of freedom of the molecules on passing from gas phase to the surface of condensed phase.

NEW RELATION BETWEEN PHASE EQUILIBRIUM PARAMETERS FOR A ONE-COMPONENT SYSTEM

The equilibrium between a gas phase and a condensed (liquid or solid) phase is described by the rigorous thermodynamic relation

$$v'' dp - v' dp = S'' dT - S' dT, \quad (1)$$

where v'' and S'' are the molar volume and entropy of the gas phase, v' and S' are the corresponding values for the condensed phase, p is the pressure, and T is the temperature. Far from the critical temperature, v''/v' and the second term in Eqn. (1) is neglected. After substituting $v'' = RT/p$ and integrating, the familiar temperature variation of the equilibrium pressure p is obtained:

$$\ln p = - \Delta H/RT + A, \quad (2)$$

where $\Delta H = (S'' - S') \cdot T$ is the enthalpy of phase transition, assumed to be independent of T . Each pure substance is characterised by definite values of ΔH and A . The relation

$$\ln (v''/v') = f(\Delta H/RT), \quad (3)$$

having a unitary property as regards the description of the phase equilibria of different groups of pure substances, is examined in the present study. For a narrow temperature range, Eqn. (3) can be formally expressed analytically on the basis of Eqn. (1) using the activity coefficient γ for the condensed phase:

$$v' dp = RT d \ln \gamma c' = - RT d \ln \gamma' v', \quad (4)$$

where $c = 1/v'$ is the concentration of the test substance. On substituting $p = RT/v''$ and Eqn. (1), rearranging, and integrating in the temperature range where the dependence of ΔU and γ on T may be neglected, we obtain

$$\ln (v''/v') = \Delta U/RT + B = \Delta H/RT + B - 1. \quad (5)$$

where $\Delta U = \Delta H - RT$ is the change in internal energy in the phase transition and B is a constant.

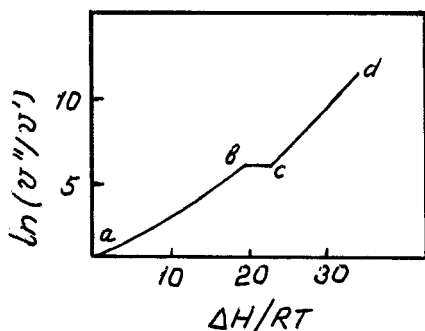


Fig. 1.

Fig. 1 illustrates the general form of the relation between $\ln(v''/v')$ and $\Delta H/RT$ (the phase equilibrium curve) for different states of aggregation of the test substance, for example, water. It passes through the origin of coordinates since at the critical temperature $v'' = v'$ and $\Delta H = 0$. For the liquid state, the ab curve is slightly concave to the $\Delta H/RT$ axis. At the triple point (the bc line), the volume of the condensed phase varies from the volume of the liquid phase at the point b to that of the crystalline phase at the point c . The intermediate values of the volume of the condensed phase v' and of the enthalpy $\Delta H'/\ln(v''/v')$ and $\Delta H/RT$

respectively / along the bc line are determined by the composition of the condensed phase, consisting of a mixture of liquid and crystals. For the crystalline state (cd line), the phase equilibrium curve is nearly linear.

We shall consider the new properties of Eqn. (3) compared with the familiar Eqn. (2). The introduction of the molar volume of the condensed phase v' and use the ratio $\Delta H/RT$ instead of $1/T$ reveal certain general properties of two-phase systems which are independent of the individual characteristics of the substances.

Fig. 2 illustrates the liquid - vapour phase equilibrium curve for a series of pure substances. Line 1 corresponds to the condition where both phases are ideal gases. In this case, the heat of the transition ΔH is equal to the heat of the isothermal compression of the ideal gas $\Delta H = RT \ln(v''/v')$. It describes the limiting case of the coexistence of phases.

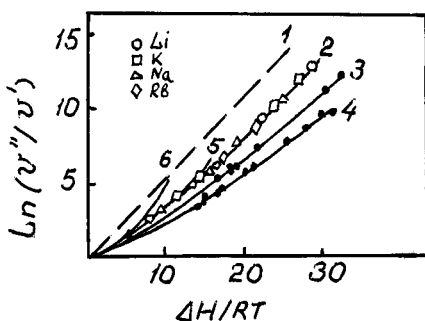


Fig. 2.

In the region above line 1, there are no phase equilibrium lines for real substances. The phase equilibrium curve for helium (curve 6) is close to line 1 between 2.00 and 5.20 K. It is remarkable that, near the λ -transition the phase equilibrium curve touches the limiting line 1. The subsequent curves represent a combination of the liquid - vapour phase equilibrium lines for different pure substances which are close to one another (within $\pm 2\%$). Line 2 combines the curves for alkali metals. For comparison with other substances, Fig. 2 present data for metals at high temperatures, for example, for lithium in the range from 800 to 2000 K.

The phase equilibrium curve for liquid hydrogen (curve 5) approaches closely to line 2. Curve 3 combines the curves for neon, argon, krypton, xenon, methane, nitrogen, oxygen (from below upwards in sequence) at the melting point (the argon group). Curve 4 describes a wider range of substances for different temperatures T (from below upwards): *n*-octane (473 K), *n*-heptane (433 K), sulfur dioxide (323 K), carbon dioxide (216 K), fluorine (368 K), acetylene (192 K), naphthalene (493 K), water (373 K), difluorodichloromethane (203 K), benzene (280 K), ammonia (200 K), fluoro-trichloromethane (213 K); (the water group). It is striking that common group equilibrium lines for these substances are observed not only for the liquid - vapour system

but also for the crystal - vapour system. Fig. 3 presents the phase equilibrium curve for the crystalline state of a group of substances corresponding to curves 3 and 4 in Fig. 2. Symbols designate the values of $\ln(v''/v')$ and $\Delta H/RT$ at the melting point. On curve 1 (in sequence from below upwards): the neon, krypton, xenon, argon, nitrogen, oxygen; on curve 2: carbon dioxide, fluorine, sulfur dioxide, benzene, ammonia, chlorine, water. The enthalpy of sublimation was determined as the sum of the enthalpies of the liquid - vapour (heat of evaporation) and liquid - crystal (heat of fusion) transitions. Similar common phase equilibrium curves are characteristic also of the alkali metals.

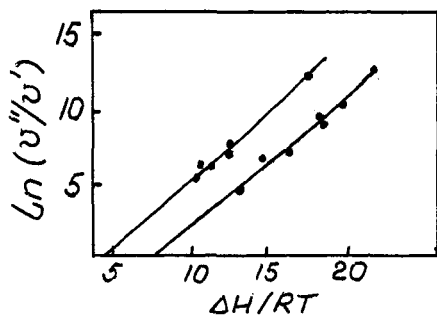


Fig. 3.

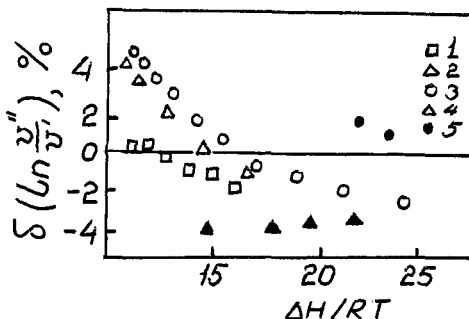


Fig. 4.

We shall consider the physical nature of the unitary property of the phase equilibrium curves noted above. The results have been analysed from the standpoint of the thermodynamic theory of the crystal-vapour equilibrium, developed previously (Ref. 1), in which the dependence of $\ln(v''/v')$ on $\Delta H/RT$ involves the parameter n - the number of translational and rotational degrees of freedom of the molecule converted to vibration on passing from the gas phase to the surface of the solid. The following equation was obtained for the crystal - vapour equilibrium:

$$\ln(v''/v') = \frac{H}{RT} - \frac{(n/2)}{\chi + 1} \ln(\Delta H/RT - 1 + \frac{(n/2)}{\chi + 1}) + \ln(\chi + 1) - \frac{(n/2)}{\chi} - 1, \quad (6)$$

where χ is the multiplier determined when the equation with known values of v' , v'' , ΔH , and n is corrected. For the majority of systems investigated, $\chi = 2$.

Fig. 4 illustrates the deviations of the experimental values (symbols) from the crystal - vapour phase equilibrium curve (zero line) calculated by Eqn. (6): (1) argon; (2) krypton; (3) xenon; ($n = 3$); (4) carbon dioxide; (5) water ($n = 6$). The experimental value of v'' , v' , and ΔH at different T were found from tables (for water and carbon dioxide) or were calculated (argon, krypton, xenon) by an equation of type (2) with the recommended values of ΔH and A for a definite temperature range. Fig. 4 shows that the maximum deviation of the theoretical values from the experimental ones for $\Delta H/RT$ between 10 and 25 is $\pm 5\%$. The accuracy of the experimental data of different workers does not exceed $\pm 2\%$ according to estimates.

EQUILIBRIUM BETWEEN THE ADSORPTION LAYER AND THE GAS PHASE

Application of this method to adsorption systems makes it possible to follow qualitatively the state of the molecules at the interface. Systems with typical solid adsorbents were examined: graphitised thermal black (GTB), zeolites, activated charcoals, and silica gels.

The principal difficulty consists in determining the molar volume of the adsorbed substance. It is calculated by the equation

$$v' = W/a, \quad (7)$$

where W is the volume of the adsorption space and a is the degree of adsorption. For zeolites, it can be assumed that W is equal to the volume of the large cavities calculated from X-ray diffraction data. The volume of the micropores in porous adsorbents can be determined approximately by Dubinin-Radushkevich equation in the theory of the volume saturation of micropores (TVSM). It is more difficult to determine the adsorption space for non-porous adsorbents with an open surface. To a first approximation, we assume that the volume of the first adsorption layer is equal to the volume of the liquid substance being adsorbed:

$$W = v_1 a_m, \quad (8)$$

where a_m is the mass of the adsorbed substance in the monolayer and v_1 is the molar volume of the liquid substance being adsorbed. The molar volume of the adsorbed substance can be found by substituting the expressions for W in Eqn. (7).

We shall consider initially adsorbents with a homogeneous porosity (zeolite) and a homogeneous surface (graphitised thermal black). The molar volume of the adsorbate in the NaA zeolite was determined by Eqn. (7) using $W = 0.3 \text{ cm}^3 \text{ g}^{-1}$ and that on graphitised thermal black within the monolayer was calculated by Eqn. (8) (a_m was determined from the molecular area ω according to literature data). Figure 5 illustrates the equilibrium curves for carbon dioxide adsorbed on the NaA zeolite (I) at 300 K and on graphite (II) at 193 K (Reference of original experimental works used here may be found in Ref. 1). The dashed curves were calculated by Eqn. (6) for different values of n (indicated against the curves) and $\chi = 2.7$. This value of χ was obtained when Eqn. (6) was adjusted for consistency with data for crystalline carbon dioxide with $n = 5$ (line cd in Fig. 5). The continuous lines are the phase equilibrium curves for carbon dioxide; ab - liquid - vapour; cd - crystal - vapour. The dependence of the differential heat of adsorption q on the degree of saturation of the cavities in the zeolite (I) and of the surface of graphite (II) is indicated in the upper figure ($q = \Delta H$).

It is striking that, over the entire region investigated (from 1 to 9 molecules per cavity of NaA zeolite), the equilibrium curve for adsorbed carbon dioxide is located near the line with $n = 4$. For the linear carbon dioxide molecule, having five degrees of freedom in the gas phase, the retention of one degree of translational or rotational freedom corresponds to this value of n when the molecule enters a cavity of the NaA zeolite. Fig. 5 also presents the equilibrium curve for carbon dioxide adsorbed on the surface of graphitised thermal black. The curve begins with values of n close to unity and, as the degree of adsorption increases, n increases. At the maximum in the heat of adsorption (the upper part of Fig. 5), it reaches the same line with $n = 4$ as for the carbon dioxide/NaA system. It is striking that a significant difference between the heats of adsorption of carbon dioxide on graphitised thermal black and the NaA zeolite (shown in upper part of Fig. 5) and between the temperatures does not affect the value n in the region of complete saturation of the volume of the monolayer on graphitised thermal black and of the zeolite cavities.

We shall consider in greater detail the curves for the partition of the adsorbed substance when a monolayer is formed on the surface of graphitised thermal black. As in Fig. 5 a family of equilibrium curves obtained by Eqn. (1) for $\chi = 2$ and varying integral values of n is illustrated in Fig. 6. As shown before, the line with $n = 3$ and 6 correspond to the crystalline state of two groups of

substances: the noble gases ($n = 3$) and the "water group" ($n = 6$). The symbols denote the experimental values of $\ln(v''/v')$ and $\Delta H/RT$ recalculated by Eqn. (8) from data for the adsorption isotherm and heat of adsorption of various substances on graphitised thermal black: (a) xenon (162 K); (b) argon (77.8 K); (c) krypton (77.8 K); (d) n-hexane (298 K).

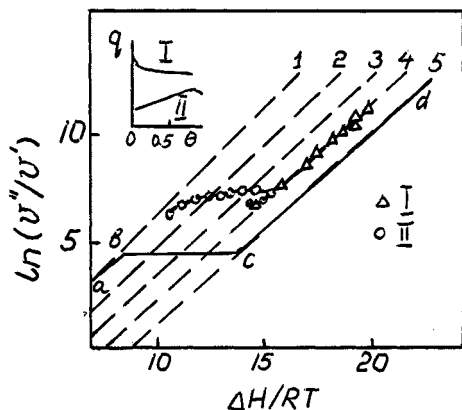


Fig. 5

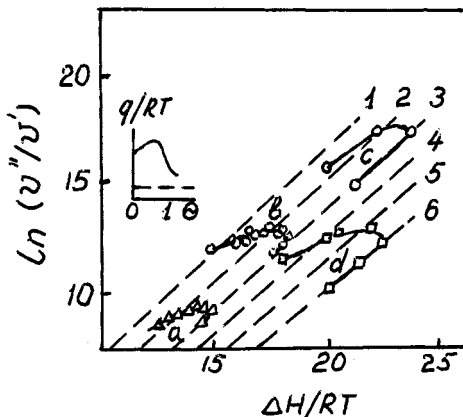


Fig. 6

The dependence of q/RT on the degree of saturation of the monolayer is shown schematically in the upper part of Fig. 6. After the completion of a continuous monolayer, the heat of adsorption diminishes to a value close to the heat of condensation of the normal liquid (dashed line). The equilibrium curves for argon, krypton and xenon in Fig. 6 have a characteristic shape. They begin with values of $\ln(v''/v')$ and $\Delta H/RT$ close to the corresponding values in the Henry region for $n = 1$. With increase in concentration, the equilibrium curves move into the region of high values of n and at the maximum heat of adsorption (upper Figure) reach the line with $n = 3$. The extent of this section is different for each adsorbate and is highest for krypton. The section for argon and xenon is appreciably shorter. The curve for n-hexane adsorbed on graphitised thermal black at 298 K has a similar shape. It begins near the line with $n = 2$ and then shifts towards higher n . In the region of the maximum heat of adsorption, it reaches the line with $n = 6$, corresponding to the crystalline state, and on further increase in the degree of adsorption it coincides with this line.

Thus the examples presented show that in a continuous monolayer the adsorbed molecules on the surface of graphitised thermal black are fully localised. After the formation of the monolayer and transition to the second layer, the equilibrium curve shifts into the region of low values n (not shown in Fig. 6).

ADSORPTION ON INHOMOGENEOUS ADSORBENTS

"Vulkan" carbon black, AC and CC activated charcoals, finally porous silica gel KSK-2, and non-uniformly porous silica gel with a dehydrated surface (NPS) were assigned to such adsorbents. The adsorption of benzene on these adsorbents has been investigated. The molar volume of the adsorbed benzene v' on activated charcoal by Eqn. (7) for published values of W . For the remaining adsorbents, the value of a_m was determined initially and the volume v' was calculated for $a < a_m$ by Eqn. (8); in the region $a > a_m$ it was assumed that $v' = v^{Equi}$. Fig. 7 and Fig. 8 presents the equilibrium curves for benzene adsorbed on these adsorbents. They are located near two equilibrium lines - for the liquid (line ab) and crystalline (line cd) states.

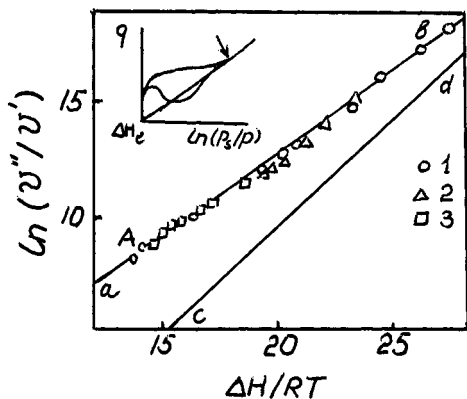


Fig. 7

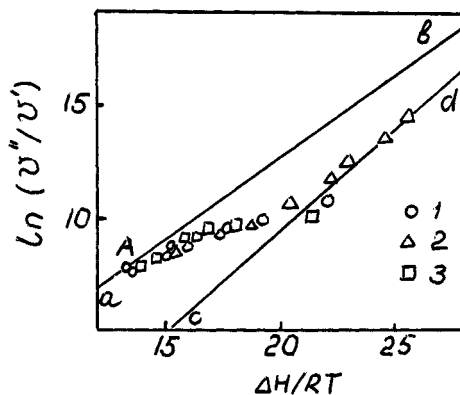


Fig. 8

The equilibrium curves for benzene adsorbed on carbon adsorbents are grouped along the line for the liquid state. On activated charcoals AC (2) and CC (1) in the region close to saturation, there is a maximum on the heat of adsorption curves (upper part of Fig. 7) associated with the evolution of heat on decreasing the area of the adsorption layer - gas interface. The equilibrium curves for benzene adsorbed on the charcoals AC and CC are therefore restricted to the region extending from low coverages to the point of inflection indicated by an arrow. The adsorption on the non-porous carbon black "Vulkan" (3) has no heat of adsorption maximum and all points, ranging from low degrees of adsorption to saturation, are represented in Fig. 7. The equilibrium curves for benzene adsorbed on carbon adsorbents begin on the line for the liquid state at the point A and with increase in $\Delta H/RT$ pass to the region of cooled and supercooled benzene. Formally, it is possible to determine the temperature of supercooled benzene corresponding, for example, to the extreme point for adsorbed benzene (~ 200 K). The disposition of the equilibrium curves for benzene adsorbed on carbon adsorbents along the line for the liquid state is probably responsible for the temperature invariance of the characteristic curve in TVSM.

The benzene adsorbed on silica adsorbents: finely porous silica gel S-337 (2), coarsely porous silica gel KSK-2 (1) and non-uniformly porous silica gel with a dehydrated surface (NPS) (3) is in a different state (Fig. 8). The heat of adsorption on these silica gels also passes through a maximum close to saturation. As for the carbon adsorbents, sections ranging from low coverages to the beginning of the maximum were therefore selected here. It is striking that in the region of low degrees of adsorption (hundredths of a monolayer for KSK-2 and MPS and up to the beginning of the hysteresis loop for the silica gel S-337), the equilibrium curve coincides with the line for crystals. With increase in the degree of adsorption, the equilibrium curve for adsorbed benzene coincides with the line for the liquid and approaches point A on saturation. The region between the liquid and crystalline states is occupied by benzene adsorbed in the first layer on the surface of the silica gels KSK-2 and NPS. Thus the above thermodynamic analysis of the state of the adsorbed substance on the surfaces of solid adsorbents of different chemical nature and with different geometries leads to conclusions which do not conflict with modern ideas about physical adsorption and about the state of molecules on the solid-gas interface.

REFERENCE

1. G.I. Berezin, Russian J. Phys. Chem. **64**, 995-998, 999-1003, 1990.