1

Classic Adsorption Theory

1.1 Adsorption Definition

Adsorption is a phenomenon that occurs at the interface between two phases. It might occur at the interface of gas/solid, gas/liquid, liquid/liquid, and liquid/solid, but only the adsorption that occurred at the gas/solid interface is of concern in this book. What is adsorption? It is the phenomenon that the concentration of gas at the interface is higher than that in the bulk phase. How it happens? There are two reasons. The first is due to the electrostatic attraction at the interface and yields so-called chemisorption; the second is due to the attraction of van der Waals force and yields physical adsorption. The former can only adsorb one layer of molecules because the chemical bond is no longer attractive once it is saturated, but each gas molecule can exert van der Waals force; therefore, physical adsorption is not limited to adsorbing just one layer of molecules, and the first layer of molecules adsorbed by chemical adsorption can still yield physical adsorption. The solid is named “adsorbent,” the substance to be adsorbed is named “adsorptive,” and it changes its name to “adsorbate” after being adsorbed. Either electrostatic force or van der Waals force will generate an adsorption potential field near the interface. As internal forces, their strength is limited, so the amount of adsorption is capped. The upper limit of the adsorption capacity is determined by the upper limit of gas phase pressure, which is the saturated vapor pressure, p_0, when the adsorption occurs below the critical temperature because the vapor is liquefied when saturation pressure is reached. How about the situation of the adsorption occurring above the critical temperature when the gas cannot be liquefied? Is there not an upper limit for supercritical adsorption? The answer is **Yes** because there is an upper limit for the internal forces that yield adsorption. However, determining the upper limit is a problem for the adsorption at supercritical temperatures.

According to the Gibbs formalism, adsorption itself is an *excess* quantity. The situation at the gas/solid interface is schematically represented in Figure 1.1 [1]. The molecule’s density near the surface is higher than that in the bulk gas phase due to the adsorption, and a density profile is thus established between the solid surface and the ambient gas phase, but this density profile vanishes over quite a short range. As such, a layer on the solid surface, where adsorbate molecules are concentrated, is referred to the “adsorbed phase,” and a definite thickness (τ) is assumed for it.

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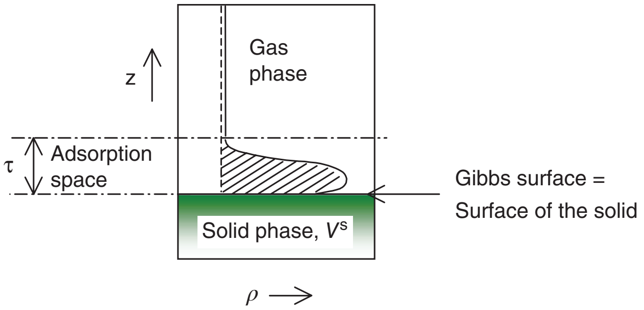

Figure 1.1 Diagrammatic sketch for gas/solid adsorption [1]. The density profile (ρ) shown by a solid line curve indicates it is a function of distance (*z*) normal to the surface in the real system; the broken line shows the case without adsorption; and the chain-dotted line shows the boundary between phases. The shadowed area marks the adsorbed phase and the excess amount of adsorbed substance.

Based on the schematic representation, the adsorbed amount, n, can be determined by either way of the following: First, provided the density profile $\rho(z)$ can be determined or assumed, then

$$n = \int\limits_{\substack{\text{all}\\ \text{adsorption}\\ \text{space}}} (\rho(z) - \rho_g)\, dV \tag{1.1}$$

where ρ is the density of the adsorbed phase at distance z to the solid surface, and ρ_g is the density of the bulk gas phase. The integral indicates that n is a density excess amount of the adsorbed substance, which is usually referred to as "surface excess adsorption" or simply "excess adsorption."

The density profile perhaps may be determined by molecular simulation, it can hardly be measured experimentally. Therefore, the quantity n is often counted another way as is often cited in literature. Suppose the volume of the adsorbed phase in Figure 1.1 is V_a, then the excess adsorption must be:

$$n = n_t - \rho_g V_a = V_a(\rho_a - \rho_g) \tag{1.2}$$

where n_t is the total mass confined in the adsorbed phase, which is usually referred to as the "absolute adsorption." The density of the adsorbed phase ρ_a is implicitly assumed to be uniform in Eq. (1.2), and it is usually esteemed as the density of liquid for vapor adsorption. Since gas cannot be liquefied above the critical temperature, the quantification of the values of ρ_a and V_a is another big problem for the adsorption at the above-critical temperature.

The adsorption of gas on solid can be classified into three regions relative to the critical temperature according to the adsorption behavior:

i) Subcritical region ($T < T_c$)
ii) Near-critical region ($T_c < T < T_c + 10$)
iii) Supercritical region ($T > T_c$)

In the first region, isotherms show the feature of subcritical adsorption, and in the third region, isotherms will show the feature of supercritical adsorption. However, in the second region, the adsorption isotherms must show the feature of adsorption mechanism transition. The transition will occur more or less continuously if isotherms on both sides of the critical temperature belong to the same type; however, a discontinuous transition could happen on isotherms if there is a transformation of isotherm types. For all cases of $T > T_c$ it belongs to "supercritical region." The decisive factor of such classification is only temperature, but irrespective of pressure. This is because a fluid cannot undergo a transition from gaseous to liquid phase at above-critical temperatures regardless of the pressure exerted. This fundamental law of physics determines the different adsorption mechanism for the adsorption at sub- or supercritical temperature.

Progress in basic science is driven by practical requirements. The appearance of gas bombs in the First World War greatly promoted the research and progress of the subcritical adsorption, but less attention was paid to the adsorption above the critical temperature because the adsorption amount is generally very low. However, this kind of adsorption attracted the attention of researchers when the energy crisis occurred in the 1970s. However, the key problem, i.e., the adsorption mechanism, is still unknown, and its application research in practice is restricted. To explain the relation and difference between the adsorption phenomena above and below the critical temperature, the core knowledge of adsorption theory below the critical temperature must be quoted first, which is the basis of the study on supercritical adsorption, and it also helps to understand the characteristics and problems of the latter.

1.2 Type of Adsorption Isotherms

The adsorbed amount of gas on a given adsorbent is a function of temperature and gas phase pressure. Adsorption isotherm is the functional relation between the adsorbed amount and the gas phase pressure at a constant temperature. The gas phase density is certainly fixed when temperature and pressure are unchanged; therefore, the adsorption isotherm can be also expressed as a function of the adsorbed amount against the gas phase density. Adsorption isotherms are usually acquired experimentally. Isotherms were first divided into five types, as shown in Figure 1.2. If the surface of nonporous adsorbent is completely uniform or close to completely uniform, the isotherm shows the stepwise type, and the stepwise isotherm can also be counted as the sixth type, which is not here concerned because of its limited application. The Type-IV and Type-V isotherms have a hysteresis loop, the lower branch of which is the measured value when the system gradually increases pressure (adsorption line), while the upper branch is the measured value when the system gradually decreases pressure (desorption line).

Type-I is the monolayer adsorption isotherm, and also known as Langmuir-type adsorption isotherm. Adsorption on microporous adsorbents often exhibits a Type-I isotherm because saturation is reached when microporous space is filled. On an open surface or a porous adsorbent with a larger pore size, the adsorption isotherm usually shows a Type-II or Type-III feature, and the adsorption amount increases with the

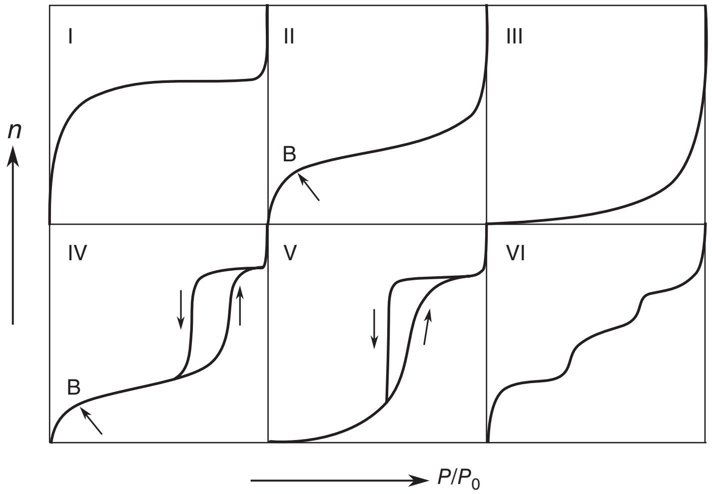

Figure 1.2 Isotherm types of vapor adsorption [2] / with permission of Elsevier.

increase of adsorption pressure. When the adsorption pressure approaches the saturation pressure of the adsorptive ($P/P_0 \rightarrow 1$), infinite multilayer adsorption can occur. When the molecular interaction force between the adsorptive and the adsorbent is greater than that among the adsorptive molecules, the adsorption isotherm appears as Type-II; if the interaction among the adsorptive molecules is greater than the interaction between adsorptive and adsorbent, it appears as Type-III. The Type-IV and Type-V isotherms correspond to the Type-II and Type-III isotherms, respectively, but the adsorption occurs on mesoporous adsorbents and the mesoporous space is gradually filled to achieve saturated adsorption at relative pressure $P/P_0 \rightarrow 1$. According to the International Association for Theoretical and Applied Chemistry [3], when the pore size is smaller than 2 nm it belongs to micropore; if the pore size is between 2 nm and 50 nm it belongs to mesopore; if the pore size is larger than 50 nm it belongs to macropore.

Quite a few adsorption theories were put forward to explain the mechanism of adsorption, based on which mathematical expressions describing different types of adsorption isotherms were established. Essential adsorption theories are introduced as that follows.

1.3 Henry Law

This is the adsorption theory at low surface coverage. For physical adsorption, the state of the adsorbed molecule does not change; the adsorbed molecule does not form a bond with the adsorbent, nor does it dissociate, therefore, it can be considered that the molecules adsorbed on the surface of a uniform solid are independent of each other, and have no interaction with each other when the surface concentration is very low. Under such conditions, there is a linear relationship between the adsorption amount and the gas phase pressure:

$$n = KP \tag{1.3}$$

where n is the adsorbed amount; P is the gas phase pressure; and K is the adsorption equilibrium constant. This relationship is called Henry law, and the adsorption equilibrium constant is called the Henry constant. The dependence of the Henry constant on temperature follows van't Hoff equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H_0}{RT^2} \tag{1.4}$$

where ΔH_0 is the enthalpy difference between the adsorbed state of the adsorptive and the gaseous state. Ignoring the difference in heat capacity between different phases, Eq. (1.4) is integrated to give:

$$K = K_0 \mathrm{e}^{-\Delta H_0/T} \tag{1.5}$$

According to Eq. (1.5), if ln K is plotted against $1/T$, a linear relationship can be obtained over a wide temperature range, and thus ΔH_0 can be evaluated from the slope of the straight line.

1.4 Langmuir Equation of Monolayer Adsorption

This theory describes the adsorption of a single molecular layer, proposed by Langmuir in 1916 and was originally used to describe chemisorption. Langmuir believed that the interaction force between the adsorbed molecules and the solid surface decreased rapidly with the increase of the distance between them so that the adsorption was limited to a single molecular layer. This applies to chemisorption as well as physical adsorption at low-pressure and high-temperature conditions.

To derive the isotherm equation of monolayer adsorption, Langmuir proposed the following hypotheses:

1. The adsorption is monolayer. Adsorption occurs on the adsorption sites of adsorbent surface. An adsorption site can only absorb one molecule, and the number of adsorption sites is definite. Adsorption reaches saturation when all adsorption sites are full.
2. The energy of the adsorbent surface is uniform. The adsorbed molecules are adsorbed equally at all sites on the surface, and there is no difference in energy.
3. There is no interaction among the adsorbed molecules, and the adsorption and desorption of each adsorbed molecule are independent and not affected by other molecules around it.
4. Adsorption is a dynamic equilibrium. When the adsorption equilibrium is reached at a certain temperature and pressure, the adsorption rate is equal to the desorption rate.

The Langmuir adsorption isotherm equation can be derived by kinetic method. The adsorption rate of adsorptive is related to the degree of blankness of the adsorbent surface. Suppose μ is the number of adsorptive molecules colliding on a unit area of solid surface in unit time, a is the fraction of collision molecules being adsorbed, θ represents the fraction coverage of adsorbent surface, and v_a is the adsorption rate, then we have

$$v_a = a\mu(1 - \theta) \tag{1.6}$$

According to the kinetic theory of molecules, $\mu = P/(2\pi mkT)^{1/2}$, where P is the gas pressure, m is the mass of a gas molecule, k is the Boltzmann constant, and T is the absolute temperature. The desorption rate of the adsorbed molecules on the surface depends on the extent of surface coverage and energy of the molecule. If the exothermic heat of adsorption is q, only those molecules with energies above q can fly away from the surface and return to the gas phase. According to Boltzmann's law, the number of molecules that can fly off the surface is proportional to $\mathrm{e}^{-q/kT}$, so the desorption rate v_d is:

$$v_d = v_0 \theta e^{-q/kT} \tag{1.7}$$

where v_0 is the proportional coefficient. The adsorption and desorption rates are equal at adsorption equilibrium, $v_a = v_d$, which leads to:

$$\theta = \frac{bP}{1 + bP} \tag{1.8}$$

where

$$b = \frac{\alpha \mathrm{e}^{q/kT}}{v_0 (2\pi mkT)^{1/2}} \tag{1.9}$$

If n represents the equilibrium adsorption capacity at a given temperature and pressure, and n_m represents the saturated adsorption capacity of the monolayer, then $n/n_m = \theta$, and is substituted into Eq. (1.8), then it leads to:

$$n = \frac{n_m bP}{1 + bP} \tag{1.10}$$

This is the well-known Langmuir monolayer adsorption isotherm equation, which can well describe the Type-I isotherms, and b is a constant for a given adsorption system at a constant temperature and is called the adsorption equilibrium constant. At high pressures, when $P \to \infty$ (only possible at supercritical temperature), $bP >> 1$, and then $n = n_m$, $\theta = 1$. It means the adsorption capacity tends to saturate at high pressure and no longer changes with pressure. When the pressure is very low and the adsorption amount is quite small, Eq. (1.10) reduces to Henry law:

$$\lim_{P \to 0} n = n_m bP = KP \tag{1.11}$$

In order to obtain the saturation adsorption capacity n_m from the adsorption isotherm, Eq. (1.10) is usually changed to a linear form:

$$\frac{P}{n} = \frac{1}{n_m b} + \frac{P}{n_m} \tag{1.12}$$

When the experimental data of P/n is plotted against P, and a straight line is obtained, then the measured experimental data are in line with the Langmuir model. The saturation adsorption capacity n_m and the adsorption equilibrium constant b can be obtained from the slope and intercept of the straight line. The specific surface area A of the solid can also be obtained from the saturated adsorption capacity n_m:

$$A = n_m a_m L \tag{1.13}$$

where n_m is the saturated adsorption amount per gram of adsorbent, a_m is the cross-sectional area of each adsorbed molecule under monolayer adsorption, which can be estimated from the liquid density of adsorbate in practical application, and L is the Avogadro constant.

1.5 BET Equation of Multilayer Adsorption

The Langmuir isotherm equation successfully explained Type-I adsorption isotherm, but it could not explain the rest types of adsorption isotherms. Brunauer, Emmett, and Teller (BET) extended Langmuir's theory of monolayer adsorption to multilayer adsorption in 1938, which became known as the BET theory. The BET theory believes that the van der Waals force causes physical adsorption; therefore, in addition to the adsorption between adsorbed molecules and solid surface, adsorption can also occur when adsorptive molecules collide on the previously adsorbed molecules, so the adsorption can be multimolecular layers.

The BET theory accepts the Langmuir theory's assumption that adsorption is localized and that the energy on the solid surface is uniform. Besides, further assumptions are made:

1. The adsorption heat of the first layer Q_1 is similar to q in the Langmuir theory, which is a constant related to the solid surface. The adsorption heat of the second and subsequent layers is equal to the liquefaction heat of the vapor.
2. The hypothesis in the Langmuir theory that adsorption is dynamically balanced is applicable to the adsorption of each layer, and the adsorption of the second layer does not need to wait until the first layer is full, and the adsorption can be carried at the same time on each layer. So, the adsorption pattern is shown in Figure 1.3.

Based on the above assumptions, the BET equation can be derived. Let θ be the percentage coverage of solid surface, then

$$\sum_{i=0}^{\infty} \theta_i = 1 \tag{1.14}$$

Let n_m be the saturated adsorption capacity of the first layer, then the adsorption amount, n, is:

$$n = n_m \sum_{i=0}^{\infty} i\theta_i \tag{1.15}$$

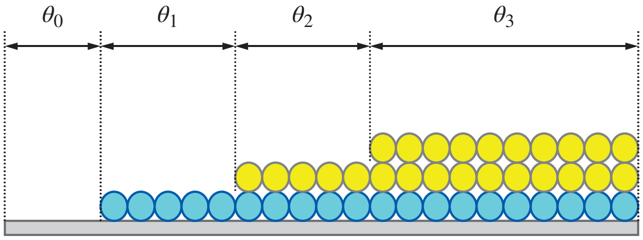

Figure 1.3 The adsorption mechanism assumed by BET theory.

Because the adsorption rate of gas molecules on the zero layer to form the first layer is equal to the desorption rate of the first layer molecules to form the zero layer,

$$\begin{aligned}\alpha_1 P\theta_0 &= \alpha_1'\theta_1 \exp\left(\frac{-E_1}{RT}\right)\\ \alpha_2 P\theta_1 &= \alpha_2'\theta_2 \exp\left(\frac{-E_2}{RT}\right)\\ &\vdots\\ \alpha_{\mathrm{i}} P\theta_{\mathrm{i}-1} &= \alpha_{\mathrm{i}}'\theta_{\mathrm{i}} \exp\left(\frac{-E_{\mathrm{i}}}{\mathrm{RT}}\right)\end{aligned}$$

Based on the assumption introduced by BET, the adsorption heat from the second layer is equal to the condensation heat of the gas:

$$E_2 = E_3 = \cdots = E_{\mathrm{i}} = E_{\mathrm{l}}$$

Let

$$\frac{\alpha_2'}{\alpha_2} = \frac{\alpha_3'}{\alpha_3} = \cdots = \frac{\alpha_{\mathrm{i}}'}{\alpha_{\mathrm{i}}} = \mathrm{g}$$

It leads to

$$n = n_m \frac{C\sum_{i=1}^{\infty} i x^i}{1 + C\sum_{i=1}^{\infty} x^i} \tag{1.16}$$

where

$$\mathrm{C} = \frac{\alpha_1 g}{\alpha_1'} \exp\left(\frac{E_1 - E_{\mathrm{l}}}{RT}\right) \tag{1.17}$$

$$x = \frac{P}{g} \exp\left(\frac{E_{\mathrm{l}}}{RT}\right) \tag{1.18}$$

Because

$$\frac{P_0}{g} \exp\left(\frac{E_{\mathrm{l}}}{RT}\right) = 1$$

Therefore

$$x = \frac{P}{P_0}$$

The linear BET equation is thus obtained:

$$\frac{P}{n(P_0 - P)} = \frac{1}{n_\mathrm{m} C} + \frac{C-1}{n_\mathrm{m} C} \cdot \frac{P}{P_0} \tag{1.19}$$

If we plot $\frac{P}{n(P_0 - P)}$ against $\frac{P}{P_0}$, then n_m can be evaluated, and if the size of the adsorbed molecule is known, the specific surface area of the adsorbent can be evaluated.

1.5.1 Interpretation of BET Equation for Type-II and Type-III Isotherms

The adsorption of gas molecules on open solid surfaces at subcritical temperature usually shows isotherms of Type-II or Type-III, and Type-II isotherms are more common. Type-II and Type-III isotherms differ in shape with a difference in the value of C. The isotherm gradually transforms from Type-II to Type-III following the decrease of C value. When C $\gg$1, i.e., $E_1 \gg E_L$, the attraction force of the solid surface on the adsorbed molecules is greater than that in-between the adsorbed molecules, i.e., adsorption of the first layer is much stronger than subsequent layers, and the second layer begins after the first layer is close to saturation, so the isotherm has a relatively obvious inflection point (point B) in the lower P/P_0 region. After that, with the increase of P/P_0, multimolecular layer adsorption began to occur, and with the increase of adsorbed layers, the adsorption amount gradually increased until the adsorption pressure reached saturation, and liquefaction occurred. At this time, the adsorption amount rose vertically at constant pressure, which is the Type-II isotherm as shown in Figure 1.4. When the value of C is small, i.e., $E_L \gg E_l$, the interaction between the solid surface and the adsorbed molecules is weaker, while the interaction between the adsorbed molecules is stronger, then Type-III isotherm appears. Differently from Type-II isotherms, the adsorption of a multimolecular layer often begins before the monolayer adsorption is completed because of the stronger interaction between the adsorbed molecules.

The experimentally measured Type-II isotherm usually presents a fairly long straight-line (segment BC in Figure 1.4). The starting point B of the straight-line segment indicates the completion of monolayer adsorption; therefore, the corresponding

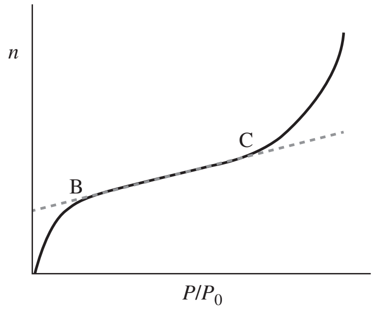

Figure 1.4 Typical Type-II isotherm showing point B.

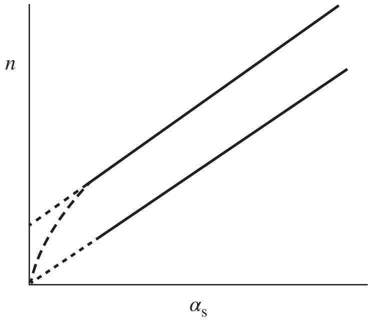

Figure 1.5 The α_s-plot for Type-II isotherms.

adsorption amount at this point, n_b, is equal to its monolayer capacity, and the specific surface area of the adsorbent can be calculated based on Eq. (1.13).

Determination of point B in Type-II isotherms measured experimentally is sometimes not so strict, especially for a group of samples of the same substance. So long as the specific surface area of one sample is accurately determined, α_s-plot can be used to easily determine the specific surface area of the other samples. The normalized adsorption amount is named as α_s and

$$\alpha_s = \frac{n}{n_{0.4}}$$

where $n_{0.4}$ is the adsorption amount corresponding to the relative pressure $P/P_0 = 0.4$. The α_s-plot shown in Figure 1.5 is a plot of the adsorption amount n against α_s to obtain a set of lines, and the slope of these lines b_α is equal respectively to their $n_{0.4}$. If the specific surface area of a sample is known as A_k, and the slope of its α_s-plot is $b_{\alpha,k}$, then the specific surface area of another sample A_{uk} can be calculated as:

$$A_{uk} = \frac{b_{\alpha,uk}}{b_{\alpha,k}} \times A_k \tag{1.20}$$

where the subscript k means "known" and uk means "unknown," and $b_{\alpha,uk}$ is the plot slope of the sample to be evaluated.

1.5.2 Limitations of the BET Equation

1. Assumption of surface homogeneity
   Like the Langmuir equation, the BET model also thinks that adsorption is localized, which contradicts the assumption that the second and above layers are liquid.
2. It is not true that the adsorbed molecules in the same layer are only attracted by the adsorbed molecules on the solid surface or the adsorbed molecules below, and there is no interaction between adjacent molecules on the same layer.

The BET model can well explain the adsorption phenomenon on an open surface, but if the adsorbent is porous, then the adsorption space is limited, and the number of layers adsorbed is limited by pore size.

1.6 Potential Equations of Multilayer Adsorption

For multilayer adsorption, Polanyi proposed another theory from the adsorption potential point of view in 1914. According to the theory, there is an attractive potential field on the surface of the solid, and gas molecules are attracted to the solid surface due to the action of the potential field. The potential field action decreases with the increase of the distance to the solid surface, and the potential field action drops to zero at the main body of the gas phase. Points with equal adsorption potential are connected to form an equipotential surface, as shown in Figure 1.6. Just like the atmosphere surrounding the Earth, molecules closer to the solid surface are more attracted and thus are denser. If the adsorption capacity is expressed by weight w, then,

$$w = \int_0^{\infty} (\rho_x - \rho_{\mathrm{g}})\, dV \tag{1.21}$$

where ρ_{g} is the density of the bulk gas phase, and ρ_x is the density of the adsorbed phase at the x layer of the potential field. According to the adsorption potential theory, physical adsorption is entirely due to van der Waals attraction, and the adsorption process is similar to that of vapor compression. Let consider the simplest case: assume that the gas is ideal and follows the state equation of ideal gas, while the adsorbed phase is a liquid phase with a density of ρ_{L} and incompressible. The work done when the ideal gas is compressed from the equilibrium pressure P to the vapor saturation pressure P_0 at a constant temperature is:

$$\varepsilon_x = RT\ln\frac{P_0}{P} \tag{1.22}$$

Volume of the adsorbed phase, V_{a}, is:

$$V_{\mathrm{a}} = \frac{w}{\rho_{\mathrm{l}}} \tag{1.23}$$

Dubinin is the pioneer in applying the adsorption potential theory to the adsorption on microporous adsorbents and obtained significant results, which gave us a further understanding of the adsorption process of gas in micropores. Most adsorbents used in modern technology, such as activated carbon, synthetic and natural zeolite, silica gel, and its inorganic gel, are microporous adsorbents. Although these adsorbents sometimes also contain larger pores (meso- or macropores), it is the micropores that determine the adsorbability of the adsorbent. The basic starting point of the Dubinin–Polanyi's micropore filling theory is that the adsorption mechanism in

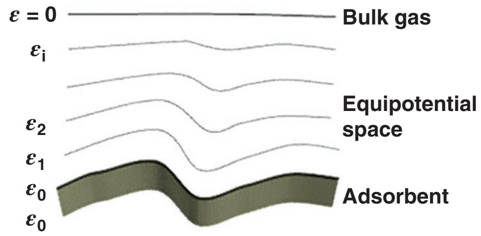

Figure 1.6 Sketch of the adsorption potential field.

micropores is pore filling, rather than the formation of adsorbed films layer by layer on the pore wall. Dubinin and Radushkevich redefined the thermodynamic interpretation of the Polanyi adsorption potential. If constant A represents the differential molar adsorption work and is considered to be equal to the negative value of the Gibbs function of adsorption, $-\Delta G$, then

$$A = -\Delta G = RT\ln\frac{P_0}{P} \tag{1.24}$$

Since Dubinin believed that micropore adsorption was a volumetric filling process, the second parameter, micropore filling degree, θ, was introduced and defined by the following formula:

$$\theta = \frac{w}{w_0} \tag{1.25}$$

where w_0 is the weight to fill the total volume of micropores, and w is the weight to fill part of the volume under the relative pressure P/P_0. One of Dubinin's basic assumptions is that θ is a function of A:

$$\theta = f\left(\frac{A}{E}\right) \tag{1.26}$$

Or

$$\theta = f\left(\frac{A}{E_0\beta}\right) \tag{1.27}$$

where E is the adsorption characteristic energy, E_0 is the adsorption characteristic energy of a reference vapor (usually benzene), and β is the similarity factor ($\beta = 1$ for the reference vapor). Based on the assumption that the aperture follows Gaussian distribution, Dubinin and Radushkevitch derived at the following formula:

$$\theta = \exp\left[-\left(\frac{A}{E_0\beta}\right)^2\right] \tag{1.28}$$

This is the usual form of the D-R equation. Combining (1.28), (1.24), and (1.25) gives:

$$w = w_0 \exp\left[-\left(\frac{RT\ln\frac{P_0}{P}}{E_0\beta}\right)^2\right] \tag{1.29}$$

Or

$$w = w_0 \exp\left[-B\left(\frac{T}{\beta}\log\frac{P_0}{P}\right)^2\right] \tag{1.30}$$

And the relationship between E_0 and β is:

$$E_0 = 0.001915\sqrt{(1/\beta)} \tag{1.31}$$

For plotting convenience, Eq. (1.30) is often converted to:

$$\log w = \log w_0 - D\log^2\left(\frac{P_0}{P}\right) \tag{1.32}$$

where

$$D = B\left(\frac{T}{\beta}\right)^2 \tag{1.33}$$

Plotting log w against $\log^2(P_0/P)$, Eq. (1.32) results in a straight line, whose intercept corresponds to the weight w_0 needed to fill the micropore volume V_0, and whose slope corresponds to D. The adsorption amount w is expressed in liquid weight of the adsorbed material. The micropore volume V_0 can be obtained through liquid density ρ_L. When adsorption is below the critical temperature and near the boiling point, ρ_L can be the standard liquid density of the adsorbed vapor. The D-R diagram of many systems is a good straight line in a wide range of relative pressures. When the pressure approaches saturation pressure, i.e., $\log^2(P_0/P) \to 0$, the straight line will sometimes bend upward, which is caused by multilayer adsorption or capillary condensation in mesopores. Therefore, the micropore volume V_0 should generally be obtained by extrapolation from the lower part of the relative pressure. To increase the applicability of the D-R equation, Dubinin and Astakhov further extended the D-R equation by introducing an additional parameter φ and assuming that θ is a function of A and φ:

$$\theta = f\left(\frac{A}{E}, \varphi\right) \tag{1.34}$$

Parameter φ is called the "heterogeneity factor" and is related to the surface heterogeneity caused by the distribution of pore sizes. They further assume that the pore size distribution is Weibull rather than Gaussian, and that Eq. (1.34) and the Weibull distribution do not change with temperature and thus obtained an analytical form of the adsorption equation. The Weibull distribution function F(A) is normalized in the following form:

$$F(A) = 1 - \exp\left[-\left(\frac{A}{E}\right)^{\varphi}\right] \tag{1.35}$$

It can be seen from Eq. (1.35) and Eq. (1.24) that F(A) = 0, when $A = 0$ (that is, at $P \to P_0$), but when the value of P is very small ($P \to 0$), A will reach a very high value, while F(A) tends to be 1. Therefore, F(A) has the property of volume ratio for the unfilled micropores, i.e., $(1-\theta)$, so

$$F(A) = 1 - \theta = 1 - \exp\left[-\left(\frac{A}{E}\right)^{\varphi}\right] \tag{1.36}$$

After simplification, we have:

$$\theta = \exp\left[-\left(\frac{A}{E}\right)^{\varphi}\right] \tag{1.37}$$

Or

$$\theta = \exp\left[-\left(\frac{A}{E_0\beta}\right)^{\varphi}\right] \tag{1.38}$$

After the same transformation as for the D-R equation, the final result is obtained:

$$\log w = \log\ w_0 - D' \log^{\varphi}\left(\frac{P_0}{P}\right) \tag{1.39}$$

This is known as the D-A equation, which is a more general form of the D-R equation (parameter $\varphi = 2$ in the D-R equation). Experimental data show that $\varphi = 2$ for activated carbon and φ is about 4–6 for zeolite.

Kaganer proposed a deformation of the D-R equation in 1959, which can be used for the determination of the specific surface area of adsorbent. He used the concept of surface coverage to replace the concept of micropore filling in the D-R equation and replaced (w/w_0) with (n/n_m) to obtain the following:

$$\log\left(\frac{n}{n_\mathrm{m}}\right) = -D \log^2\left(\frac{P_0}{P}\right) \tag{1.40}$$

where n is the adsorption amount at relative pressure (P/P_0), n_m is the saturated adsorption amount of monolayer. Eq. (1.40) is called the DRK equation. The specific surface area of adsorbent can be obtained from n_m. The equation is often used to measure the specific surface area of microporous adsorbents.

D-R, D-A, and DRK equations have been used effectively to describe the adsorption on microporous solids, especially in describing the adsorption on microporous carbonaceous adsorbents or activated carbons with great success. The disadvantage of D-R, D-A, and DRK equations is that they cannot be reduced to Henry law when the adsorption amount approaches zero, which is, however, necessary for any thermodynamic isotherm equation. Therefore, the D-R, D-A, and DRK equations have no definite physical meaning for the low-pressure range.

All the above isotherm equations can be used to determine the specific surface area, pore volume, or pore size distribution of adsorbents under different conditions, and nitrogen is the most suitable adsorptive in such tests. The volumetric method for adsorption measurement is generally recommended, which has good precision under relatively high pressure and is advantageous for measuring pore size distribution. To remove something physically adsorbed from the surface of the adsorbent before adsorption measurement, it is preferable to expose the surface to a high vacuum under strict conditions (temperature and residual pressure) depending on the gas/solid adsorption system. For conventional surface area measurements, it is not necessary to remove something that is chemically adsorbed. The usual degassing temperature is 150 °C, but for microporous adsorbents such as pumice or activated carbon, the degassing temperature may be as high as 350–400 °C, at which the residual pressure can be reduced to ~10^{-2} Pa after 6–10 hours of degassing. The purity of adsorptive gases is also important for the accuracy of adsorption measurements.

When adsorption isotherm has been measured, an appropriate calculation method should be chosen according to the isotherm type. Microporous and mesoporous materials have many practical applications. The former shows Type-I adsorption isotherm and the corresponding calculation can be done by choosing the Langmuir equation or D-R, D-A, and DRK equations, while the latter mostly shows Type-II adsorption isotherm and the BET equation can be considered.

1.7 Kelvin Equation of Capillary Condensation

Adsorption progresses continuously from multilayer adsorption to capillary condensation when the adsorption occurs on porous solids. In this process, smaller pores are filled first with liquid adsorbate. Capillary condensation occurs because liquids have a lower saturated vapor pressure in smaller pores under the action of surface tension. Information about pore structure and distribution of pore sizes can be obtained through the study.

Saturated vapor pressure on a curved surface is different from that on a flat surface. The saturated vapor pressure on the convex surface is higher than that on the flat surface, and the saturated pressure on the concave surface is lower than that on flat surface. When adsorption occurs on a porous adsorbent, the adsorbate molecules can generally moisten the solid surface, so the liquid condensed in the hole usually has a concave meniscus.

The Kelvin formula in the capillary is:

$$\Delta P = \frac{2\sigma}{r_\mathrm{m}} \tag{1.41}$$

where σ is the surface tension of the liquid in the hole, and r_m is the average radius of curvature. If you want to describe a curved surface, two radii of curvature shown in Figure 1.7 are generally needed, and the average radius of the curvature is as follows:

$$\frac{2}{r_\mathrm{m}} = \frac{1}{r_1} + \frac{1}{r_2}$$

For spherical surfaces

$$r_1 = r_2 = r_\mathrm{m}$$

For cylindrical surfaces

$$r_2 = \infty,\ r_\mathrm{m} = 2r$$

If a single-component system is at gas (β) liquid (α) two-phase equilibrium, the chemical potential of the gas and liquid phases is equal:

$$\mu^\alpha = \mu^\beta$$

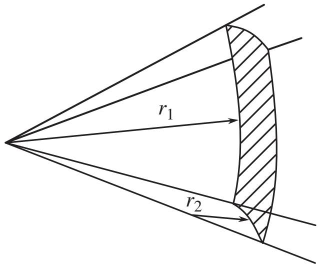

Figure 1.7 The radii of curvature.

If a small fluctuation is given to cause the system to change from one equilibrium state to another under isothermal conditions, then

$$\begin{aligned} d\mu^{\alpha} &= d\mu^{\beta} \\ d\mu^{\alpha} &= -S^{\alpha}dT + V^{\alpha}dP^{\alpha} \\ d\mu^{\beta} &= -S^{\beta}dT + V^{\beta}dP^{\beta} \\ V^{\alpha}dP^{\alpha} &= V^{\beta}dP^{\beta} \end{aligned} \tag{1.42}$$

where V is phase volume. According to formula (1.41),

$$dP^{\beta} - dP^{\alpha} = d\frac{2\sigma}{r_{\mathrm{m}}}$$

By substituting Eq. (1.42) into the above equation, we obtain:

$$d\left(\frac{2\sigma}{r_{\mathrm{m}}}\right) = \frac{V^{\alpha} - V^{\beta}}{V^{\beta}} dP^{\alpha} \tag{1.43}$$

Because $V^{\alpha} \ll V^{\beta}$, formula (1.43) may be rewritten as:

$$d\left(\frac{2\sigma}{r_{\mathrm{m}}}\right) = -\frac{RT}{V^{\alpha}} \frac{dP^{\beta}}{P^{\beta}} \tag{1.44}$$

Since

$$\int_{r_{\mathrm{m}}}^{\infty} \frac{2\sigma}{r_{\mathrm{m}}} = -\int_{P}^{P_0} \frac{RT}{V^{\alpha}} d\ln P$$

The Kelvin equation is thus obtained:

$$\ln\frac{P}{P_0} = -\frac{2\sigma V_l}{RT} \cdot \frac{1}{r_{\mathrm{m}}} \tag{1.45}$$

1.7.1 Notes on Kelvin Equation

1. The Kelvin equation gives a quantitative relationship between pore size and the relative pressure when pore condensation occurs. For the pore with certain size, the phenomenon of capillary condensation begins only when the relative pressure P/P_0 reaches a specific value corresponding to the pore size, and the larger the hole, the greater the pressure required for condensation. When $r_{\mathrm{m}} \approx \infty$, $P = P_0$, i.e., when condensation occurs on a plane, the pressure is equal to the saturated vapor pressure. Before capillary condensation occurred, multilayer adsorption had already occurred on the pore wall, i.e., capillary condensation occurred on the adsorbate film. During the process of capillary condensation, multilayer adsorption continued. When studying the problem, we often discuss capillary condensation and multilayer adsorption separately, which is only a simplified means to deal with the problem, but it does not mean that the two processes are completely separate.
2. About the Kelvin Radius: As shown in Figure 1.8,

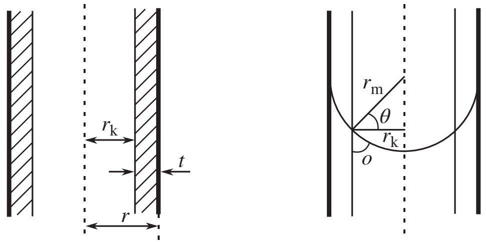

Figure 1.8 Definition of the Kelvin radius.

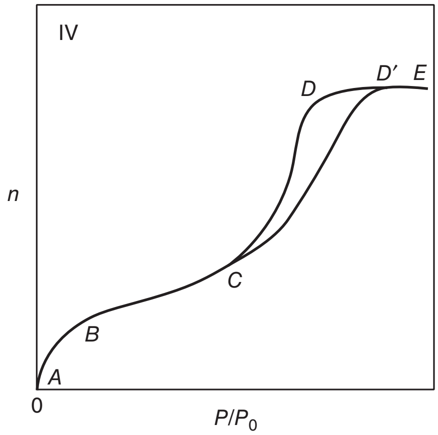

Figure 1.9 The generation process of Type-IV isotherm.

$$\begin{aligned} r &= r_k + t \\ r_m &= \frac{r_k}{\cos\theta} \\ \ln\frac{P}{P_0} &= -\frac{2\sigma V_l \cos\theta}{r_k RT} \end{aligned} \tag{1.46}$$

r_k is called the Kelvin radius, and in practice, $\theta = 0$ is usually taken to simplify the problem, in which case $r_k = r_m$.

The Scope of Application: The Kelvin equation is derived from a thermodynamic formula, which is not applicable to pores with molecular scale aperture (not suitable for micropores). For macropores, due to the large pore size, the pressure of capillary condensation is very close to the saturated vapor pressure, which is difficult to measure in experiments. Therefore, the Kelvin equation is most effective when dealing with condensation in mesopores.

Interpretation of Type-IV and Type-V Isotherms by Kelvin Equation: When the gas is adsorbed on mesoporous adsorbent at subcritical temperatures, a single molecular layer is first formed. Corresponding to the AB segment of Figure 1.9, when adsorption of the single molecular layer is close to saturation (reaching point B), and the adsorption of multiple molecular layers begins to occur. From point A to point C, the BET equation can be used since only the adsorption of multiple molecular layers occurs. The capillary condensation begins when the relative pressure reaches a specific value corresponding to the Kelvin radius, at which capillary condensation occurs. If the pore size distribution of the adsorbent is relatively narrow (the pore size is relatively uniform), the CD segment will be relatively steep, and if the pore size distribution is relatively wide, the adsorption capacity will change slowly with the relative pressure, such as the segment CD′. When all holes are filled, the adsorption reaches saturation, which is the DE segment. For the difference between Type-IV and Type-V isotherms, just refer to Type-II and Type-III isotherms of this chapter. Type-V isotherm will appear when the interaction between the adsorptive and the adsorbent is relatively weaker.

References

1. Zhou, L. (2002). Adsorption isotherms for the supercritical region (Chapter 4). In: *Adsorption: Theory, Modeling and Analysis* (ed. J. Toth), 211–250. New York: Marcel Dekker, Inc.
2. Gregg, S.J. and Sing, K.S.W. (1982). *Adsorption, Surface Area and Porosity*, 2e. London: Academic Press.
3. IUPAC Manual of Symbols and Terminology. (1972). Appendix 2, part1, colloid and surface chemistry. *Pure Appl. Chem*. 31 (4): 578–638.