

## Chapter 15 Interfacial Phenomena

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### Framework of the Chapter

This chapter provides a comprehensive and multi-level discussion from macroscopic to microscopic for the interfacial phenomena, concerning both equilibria and rates, both general principles and characteristic properties, and all the three methods used, experimental, semi-empirical and theoretical. The meanings of the two intensive properties, the interfacial tension  $\sigma$  and the unit interfacial excess  $\Gamma_i$ , and one extensive property, the interfacial area  $A_s$ , are first introduced. They are measurable and peculiar to interfaces. The Gibbs method for defining the interfacial excess is also discussed (15.2). The text then follows by three parts:

#### **I. Thermodynamics of Interfaces**

(1) **Fundamental Equations and Equilibrium Conditions.** The distinguishing feature of these equations is the  $\sigma dA_s$  term or  $A_s d\sigma$  term appeared. The interfacial chemical potential is then introduced. The relations among various thermodynamic functions and the interfacial tension, interfacial area and interfacial excess are derived (15.3).

(2) **Three Important Equations Concerning Interfaces.** They are the Laplace equation that describes the pressure difference between the two sides of a curved interface (15.4), the Kelvin equation that describes the chemical potential and the vapor pressure of a liquid having a curved surface (15.5), the Gibbs isotherm that relates the interfacial tension and the interfacial excess (15.6). We derive these equations and discuss their meanings. Various important interfacial phenomena such as vapor pressures of curved interfaces, metastable equilibria, positive and negative adsorptions are interpreted.

(3) **Wetting and Spreading.** Some general knowledge on the thermodynamic principles of wetting and spreading is presented (15.7).

## II. Equilibrium Characteristics of Interfaces

They are mainly  $\sigma_A T T_i$  or  $T \sigma T_i x_i$  (similar to  $p V T x$  or  $T p x y$ ) relations.

(1) **Vapor-Liquid Interface and Liquid-Liquid Interface** (15.8). The corresponding experimental, semi-empirical and theoretical methods are briefly introduced.

(2) **Surfactants and Insoluble Monolayer Surface Films** (15.9). A general knowledge on those surfactants and films is provided.

(3) **Gas-Solid Interface and Liquid-Solid Interface** (15.10,15.11). This section is the focal point of the part II. The concepts and meanings of the physical adsorption and the chemical adsorption as well as the capillary condensation phenomenon on solid surfaces are introduced. The applications of various semi-empirical models especially the Langmuir model and the BET multi-layer adsorption model are elucidated. A little knowledge on the corresponding experimental method and the theoretical method is provided.

## III. Rate processes on the Interfaces

(1) **Dynamic Interfacial Tension** (15.12). We briefly introduce the interfacial transport phenomena where the interfacial tension changes with time.

(2) **Chemical Reactions in Surface films** (15.13). We briefly introduce the characteristics of chemical reactions in mono-molecular films

(3) **Heterogeneous Catalysis and Kinetics** (15.14,15.15). Theories on the microscopic level are briefly introduced, various possible reaction mechanisms are discussed, and the corresponding reaction rate equations on the macroscopic level are derived. Differences among the diffusion control, the adsorption control and the reaction control are discussed.

# 15.1 Introduction

**Interface** In between two contacting phases in a heterogeneous system, an interface exists. It has five types: gas-liquid, liquid-liquid, liquid-solid, gas-solid and solid-solid. Among them, the interface of gas-liquid or gas-solid is generally called a **surface**.

**Interfacial Layer** When discussing a phase equilibrium such as gas-liquid equilibrium, usually, we consider that the system is composed of a gas phase and a liquid phase, from the former to the latter, some intensive properties such as densities and compositions undergo a sudden change, but the extensive properties are the sum total of the corresponding properties of the two phases. In fact, in between the two phases, there is an interfacial layer located; its thickness is in the order of nanometer, corresponding to several molecules. Along the normal direction, the above mentioned intensive properties change continuously from those of the gas phase to

those of the liquid phase, on the other hand, the extensive properties are the sum total of the corresponding properties of the gas phase, liquid phase and interfacial layer. When the interfacial area is not large, the interfacial layer can always be neglected just as we discussed phase equilibria before. However, in many cases, the effect of the interfacial layer must be carefully considered.

**Interfacial Phase** In physical chemistry, the interfacial layer itself is always treated as a single phase called the interfacial phase, correspondingly, a terminology **bulk phase** is designed specifically for the ordinary gas, liquid and solid phases. By definition, a phase should be a homogeneous part where anyone of all the physical and chemical properties is completely the same everywhere. Therefore, when we treat an interfacial layer as an interfacial phase, we are virtually adopting a model. For a  $K$ -component system, when we describe the state of a bulk phase, gas, liquid or solid, we have  $T$ ,  $p$ ,  $V$  and  $n_i$  or  $x_i$  ( $b_i$ ,  $c_i$ ),  $i=1\sim K$  as the fundamental, directly measurable state functions. For an interfacial phase, we still have  $T$ ,  $p$ ,  $V$ , analogy to  $n_i$  or  $x_i$ , we adopt the interfacial excess amount of substance  $n_i^{(\sigma)}$ , briefly called the interfacial excess hereafter, or the unit interfacial excess  $\Gamma_i (=n_i^{(\sigma)}/A_s)$ ,  $i=1\sim K$ , the superscript  $(\sigma)$  denotes the interfacial phase,  $A_s$  is the interfacial area. Further, for the state functions of an interfacial phase, we have to add the interfacial tension  $\sigma$ , which is a kind of generalized force,  $A_s$  is the corresponding generalized displacement.

**Interfacial Phenomena** All the physical and chemical phenomena concerning interfaces are called the interfacial phenomena. Macroscopically, they can be distinguished as two categories, equilibria and rates. Microscopically, the structure of the interfacial layer is the main concern.

**Interfacial Equilibria** Interfacial equilibria study relations between  $\sigma$ ,  $\Gamma_i$  of the interfacial phase and  $T$ ,  $p$ ,  $x_i$  ( $b_i, c_i$ ) of the bulk phase. They have two sides, general principles and characteristic properties. The former are provided by **thermodynamics of interfaces** which gives the fundamental equations for interfacial phases, the criterion of equilibrium when concerning interfaces, and those general relations among various interfacial properties. The latter are mainly relations among  $\sigma$ ,  $A_s$ ,  $T$  and  $\Gamma_i$  (analogy to

$pVTx$  relation of the bulk phase), or among  $T$ ,  $\sigma$ ,  $\Gamma_i$  and  $x_i$  (analogy to  $Tp_{xy}$  relation of the vapor-liquid equilibrium). These characteristic properties have three resources: experimental measurements, semi-empirical methods such as the interfacial equations of state and the adsorption isotherms, theoretical methods based on statistical mechanics and quantum mechanics.

**Interfacial Rates** Interfacial rates study changes of  $\sigma$  and  $\Gamma_i$  with time when the interfacial phase deviates from equilibrium. The changes could be initiated by transport phenomena, or by chemical reactions in the interface. They have also two sides, general principles and characteristic properties. The former includes the **interfacial kinetics** and the **adsorption kinetics**. For the latter, we can list interfacial viscosities, diffusion coefficients, reaction rate coefficients, activation energies, etc.

**Structures of Interfacial Layers** For studying structures, experimental methods are mainly used. The low-energy electron diffraction (LEED, 11.9.4), the X-ray photo electron diffraction (XPD, 11.6.2), the Auger spectroscopy (11.6.3), the scanning tunneling microscopy (STM, 9.6.3), the atomic-force microscopy (AFM, 16.9.4(4)), the field-emission microscopy (FEM, where a large potential is applied between a filament sample and a fluorescent screen, the stripped out electrons cause a pattern on the screen), can give information of the structure, shape and state of molecules in the interfacial layer. On the theoretical side, quantum mechanics and statistical mechanics are respectively used to study the surface chemical bonding and the distribution of molecules in the interfacial layer.

**Applications of Interfacial Phenomena** Applications concern the following fields:

- (1) **Adsorption**, a separation method in laboratory and industry.
- (2) **Heterogeneous catalysis**, using solid catalysts in gas or liquid phase to accelerate the reaction.
- (3) **Surface films**, such as bi-layers, vesicles, LB films.
- (4) **Creation of new phases**, concerning meta-stable equilibria such as superheating, super-cooling and super-saturation, creation of crystal nuclei, crystal growth.

- (5) **Foams and Emulsions.**
- (6) **Friction and Lubrication.**
- (7) **Detergency**, using detergents.
- (8) **Ore Dressing**, such as floatation.

## 15.2 Interfacial Tension and Interfacial Excess

### 1. Interfacial Tension

**Tensions in the Interfacial Layer** The state of molecules in the interfacial layer is different from that in the bulk. In the latter case, the interaction forces a molecule bore from the surrounding molecules are symmetrical in statistical average, they compensate each other. For the interfacial layer, because it is located in between the two different bulk phases, the forces bore from the molecules of the two sides are different, therefore, they are unsymmetrical with a surplus force remained. As a result, molecules in the interfacial layer have a tendency to leave one bulk phase and approach the other. Macroscopically, it shows that the interface will shrink to adopt a shape with a smallest area. Water droplets, mercury droplets and gas bubbles are therefore taking a nearly spherical shape. As early as 1805, Young T, a pioneer of this field, pointed out that an interface could be regarded as a tightly stretched elastic thin film, in which contracting tensions exist resulting in the decrease of the film area. The tensions occur everywhere in the interfaces, but can be shown clearly at the periphery.

**Practical Examples** Figure 15-1(a) shows a soap liquid film in a metal ring, each of the front side and the back side has a gas-liquid interface. A cotton thread loop is placed on the film. In the interfaces inside and outside the thread loop, there are contracting tensions acting on the loop in

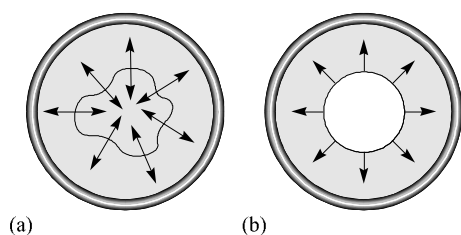


Figure 15-1 Tensions in the interface

the opposite direction along the tangent of the interfaces perpendicular to the periphery as shown in the figure. The tensions are in equilibrium; therefore, the thread loop

maintains its original random shape. Imagine that if we draw a curve to replace the thread loop serving as the common periphery of the interfaces of the two sides, the above mentioned contracted tensions acting on the two sides of the periphery in equilibrium still exist. Now we break the liquid film inside the thread loop, as shown in Figure 15-1(b), the contracted tensions inside the loop disappear, those outside the loop will tow the loop resulting in a circular shape. For another example, Figure 15-2 shows a layer of liquid film in a

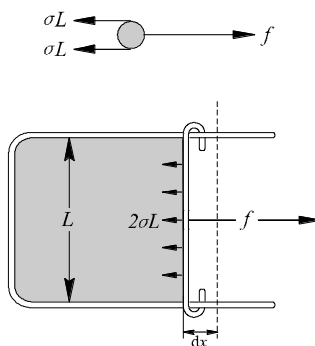


Figure 15-2 Interfacial tension and interfacial work

platinum frame, each of the front side and the opposite side of the film has a gas-liquid interface. If the force  $f$  applied on the movable platinum wire in the direction as shown in the figure does not exist, the liquid film will shrink. Only in the case of applying an external force can the liquid film stably stay in the frame indicating that there are contracting tensions tangent to the interface perpendicular to the periphery existing in the interface on the left side of the movable platinum wire.

**Interfacial Tension** It is usually called the **surface tension** for gas-liquid or gas-solid surfaces. Interfacial tension with a symbol of  $\sigma$  or  $\gamma$  is defined as **the contracted tension per unit length in the interface**. It has a unit of  $\text{N}\cdot\text{m}^{-1}$  or  $\text{J}\cdot\text{m}^{-2}$  (previously,  $\text{dyn}\cdot\text{cm}^{-1}$  was used,  $1\text{dyn}\cdot\text{cm}^{-1}=10^{-3}\text{N}\cdot\text{m}^{-1}$ ). The contracted tension acts on the periphery (imaginary or real) along the tangent direction and perpendicular to the periphery. The total tension is directly proportional to the length of the periphery.

**Interfacial Work** In the example of Figure 15-2 above, if the length of the movable platinum wire is  $l$ , the total length of the periphery is  $2l$  because there are two interfaces in the front and at the back of the liquid film, respectively. By definition, the total tension is  $2\sigma l$ . Under the equilibrium condition, if the external force  $f=2\sigma l$  makes the movable platinum wire moving a distance  $dx$ , the area of the liquid film increases  $dA_s$ , accordingly,  $dA_s = 2l dx$ . This is a reversible process, the system gains a

reversible work  $\delta W'_R = f dx$ . Because the volume of the liquid film does not change, it is a non-volumetric work usually using a symbol  $W'$ . Substitution of  $f = 2\sigma l$  and  $dA_s = 2l dx$  yields

$$\delta W'_R = \sigma dA_s \quad (15-1)$$

$$\sigma = \delta W'_R / dA_s \quad (15-2)$$

where  $W'_R$  is called a **reversible interfacial work**. The above equations indicate that the interfacial tension equals the reversible interfacial work gained with the increase of a unit interfacial area.

**Numerical Examples** Surface tensions of pure liquids are usually obtained experimentally where the pure liquid contacts with the air saturated with the vapor of the liquid. Table 15-1 presents surface tensions of some pure liquids at different temperatures. The data indicate that the surface

Table 15-1 Surface tensions of several pure liquids,  $\sigma/\text{N}\cdot\text{m}^{-1}$

$t/^\circ\text{C}$	$\text{H}_2\text{O}^{1,2}$	$\text{C}_6\text{H}_5\text{CH}_3$ 3	$\text{C}_6\text{H}_6$ <sup>3</sup>	$\text{CH}_3\text{COOH}$ <sup>4</sup>	$\text{CCl}_4$ <sup>3,5</sup>	$\text{C}_2\text{H}_5\text{OH}$ <sup>4</sup>
0.01	0.07564	—	—	—	0.02949*	—
10	0.07423	0.02972	0.03021	—	0.02827	0.02322
20	0.07275	0.02852	0.02888	0.02759	0.02704	0.02239
30	0.07120	0.02733	0.02756	0.02660	0.02582	0.2155
40	0.06960	0.02615	0.02625	0.02560	0.02459	0.02072
50	0.06794	0.02495	0.02496	0.02461	0.02337	0.01989
60	0.06624	0.02377	0.02367	0.02362	0.02215	0.01906
70	0.06447	0.02258	0.02240	0.02262	0.02092	0.01823

Data: 1. Vargaftik N B, Volkov B N, Voljak L D. J Phys Chem Ref Data, 1983, 12(3):81. 2. Richards T W, Carver E K. J Am Chem Soc, 1921, 43:827. 3. Jasper J J. J Phys Chem Ref Data, 1972, 1(4):841. 4. Vogel A I. J Chem Soc. 1948, 16:1809. 5. Guggenheim F A. J Chem Soc. 1945, 13:253. \*:  $0^\circ\text{C}$

Table 15-2 Interfacial tensions at  $20^\circ\text{C}$

First phase	Second phase	$\sigma/\text{N}\cdot\text{m}^{-1}$	First phase	Second phase	$\sigma/\text{N}\cdot\text{m}^{-1}$
water	n-butanol	0.0018 <sup>1,2</sup>	mercury	water	0.4158(26.7 $^\circ\text{C}$ ) <sup>3</sup>
	Ethyl acetate	0.0068 <sup>1</sup>		ethanol	0.389 <sup>1</sup>
	Benzaldehyde	0.0155 <sup>1</sup>		n-heptane	0.378(25 $^\circ\text{C}$ ) <sup>1</sup>
	benzene	0.0350 <sup>1</sup>		benzene	0.3567(21.1 $^\circ\text{C}$ ) <sup>3</sup>
	n-Heptane	0.0502 <sup>1</sup>			

Data: 1. Girifalco L A, Good R J. J Phys Chem, 1957, 61(4):904-909. 2. Donahue D Joseph, Bartell F E. J Phys Chem, 1952, 56(4):480-484. 3. Butler E B. J Phys Chem, 1963, 67(7):1419-1425.

tension decreases with temperature and will approach zero at the critical point. Table 15-2 presents some data of the liquid-liquid interfacial tensions.

**Spreading Pressure** For the gas-liquid interface of liquid solutions, a spreading pressure  $\pi$  is usually introduced which is defined by

$$\pi \stackrel{\text{def}}{=} \sigma^* - \sigma \quad (15-3)$$

where  $\sigma^*$  and  $\sigma$  are respectively the interfacial tensions of the pure solvent

and the solution contacting with air saturated with the corresponding vapors. Usually  $\sigma^* > \sigma$ ,  $\pi > 0$ . Figure 15-3 is a schematic picture. Imagine using a movable bar to separate the solution and the pure solvent, the forces per unit length bore on the bar from the liquids of the two sides are  $\sigma$  and  $\sigma^*$ , respectively. The net force per unit length is  $\pi$ , which causes the interface of the solution to spread further. This is why it is called the spreading pressure.

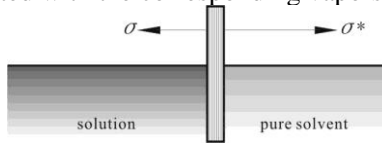


Figure 15-3 Spreading pressure

## 2. Unit Interfacial Excess

**Modeling** Consider a real system composed of two bulk phases  $\alpha$  and  $\beta$ , and an interfacial layer shown in Figure 15-4(a). For the amount  $n_i^{(\text{layer})}$  of the component  $i$  in the interfacial layer, we can write

$$n_i^{(\text{layer})} = n_i - n_{i,\text{real}}^{(\alpha)} - n_{i,\text{real}}^{(\beta)} \quad (15-4)$$

where  $n_i$  is the total amount of component  $i$  in the system,  $n_{i,\text{real}}^{(\alpha)} = V_{\text{real}}^{(\alpha)} c_i^{(\alpha)}$ ,  $n_{i,\text{real}}^{(\beta)} = V_{\text{real}}^{(\beta)} c_i^{(\beta)}$ , here  $V_{\text{real}}^{(\alpha)}$ ,  $V_{\text{real}}^{(\beta)}$  and  $c_i^{(\alpha)}$ ,  $c_i^{(\beta)}$  are volumes and concentrations of the component  $i$  of the  $\alpha$  phase and the  $\beta$  phase, respectively, the total volume of the system is the sum of  $V_{\text{real}}^{(\alpha)}$ ,  $V_{\text{real}}^{(\beta)}$  and the volume of the interfacial layer  $V^{(\text{layer})}$ . However, since the thickness of the interfacial layer is only in the order of nanometer, on the other hand, the change of intensive

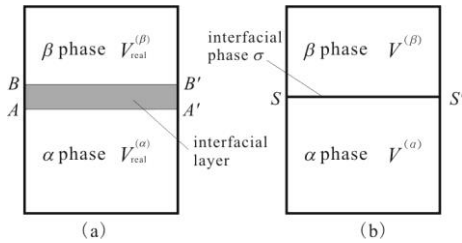


Figure 15-4 Real system and Gibbs interface model, interfacial phase is planar.

properties from the  $\alpha$  phase to the  $\beta$  phase is continuous, therefore, the boundaries  $AA'$  and  $BB'$  are difficult to determine accurately resulting in the arbitrariness of  $n_i^{(\text{layer})}$  estimated by Eq. (15-4). This difficulty is usually solved by modeling.

**Gibbs Interfacial-Phase Model** The model was proposed by Gibbs J W in 1878. The essentials include the following four points:

(1) The interfacial layer is abstracted as a geometric planar interfacial phase called a **Gibbs interface** with zero thickness and zero volume. The symbol adopted is also  $\sigma$  (the same as the symbol of interfacial tension, but



used in different occasions).  $SS'$  in Figure 15-4(b) is a Gibbs interface  $\sigma$ .

(2) Intensive properties of the  $\alpha$  phase and the  $\beta$  phase are completely the same as those of the  $\alpha$  phase and the  $\beta$  phase in a real system. Concentrations of the component  $i$  are still  $c_i^{(\alpha)}$  and  $c_i^{(\beta)}$ . Volumes of the two phases are  $V^{(\alpha)}$  and  $V^{(\beta)}$ , while  $V^{(\alpha)} \neq V_{\text{real}}^{(\alpha)}$ ,  $V^{(\beta)} \neq V_{\text{real}}^{(\beta)}$ , the total volume of the system is the sum of the two phases,  $V = V^{(\alpha)} + V^{(\beta)}$ .

(3) **Interfacial Excess and Unit Interfacial Excess** The amount of the component  $i$  in the interfacial phase  $n_i^{(\sigma)}$  is called the interfacial excess, it is the difference between the total amount  $n_i$  and the amount of two bulk phases  $n_i^{(\alpha)} + n_i^{(\beta)}$  for the component  $i$ .  $n_i^{(\sigma)}$  is then defined and expressed by

$$\begin{aligned} n_i^{(\sigma)} &\stackrel{\text{def}}{=} n_i - n_i^{(\alpha)} - n_i^{(\beta)} \\ &= n_i - V^{(\alpha)} c_i^{(\alpha)} - V^{(\beta)} c_i^{(\beta)} = n_i - V c_i^{(\alpha)} + V^{(\beta)} (c_i^{(\alpha)} - c_i^{(\beta)}) \end{aligned} \quad (15-5)$$

The unit interfacial excess  $\Gamma_i$  with a unit of  $\text{mol} \cdot \text{m}^{-2}$  is defined by

$$\Gamma_i \stackrel{\text{def}}{=} n_i^{(\sigma)} / A_s \quad (15-6)$$

**Physical Picture of Interfacial Excess** Figure 15-5 depicts two bulk phases  $\alpha$  and  $\beta$ , and an interfacial layer  $BB'A'A$  for a real system,  $SS'$  is the Gibbs interface which artificially divides the  $\alpha$  phase from the  $\beta$  phase. The solid lines in Figure 15-5 (a) and (b) depict real concentrations of the solvent 1 and the solute 2 at different height, respectively. They change gradually from the  $\alpha$  phase to the  $\beta$  phase. The solute 2 exhibits notable enrichment in the interfacial layer in this example. Concentrations of the solvent 1 and the solute 2 for the Gibbs model are shown simultaneously as the corresponding dotted lines in Figure 15-5(a) and (b), respectively. As shown in the figure, the dotted lines coincide with the solid lines in most part but exhibit step-like sudden change at  $SS'$ .

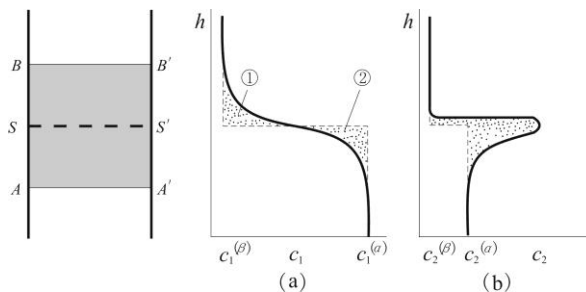


Figure 15-5 Concentrations of solvent and solute at different height in real system and in Gibbs model

Since the ordinate represents the height, the volume is proportional to the height when the area is kept unchanged, therefore,  $n_i$ , the total amount of component  $i$  is proportional to the area in between the solid line and the ordinate in Figure 15-5 (a) and (b), on the other hand, the amount of the component  $i$  in two bulk phases,  $n_i^{(\alpha)} + n_i^{(\beta)}$ , is proportional to the area in between the dotted line and the ordinate. According to Eq.(15-5), the interfacial excess  $n_i^{(\sigma)}$  should be proportional to the difference between the former and the latter, which is the shadowed area. For the solvent 1, see Figure (a), it is the algebraic sum of ①(positive) and ②(negative). For the solute 2, see Figure (b), the shadowed part is all positive in this example. We can then conclude that the interfacial excess  $n_i^{(\sigma)}$  is the residual part of the component  $i$  when the real concentration distribution in the interfacial layer is replaced by concentrations of the bulk phase  $\alpha$  and the bulk phase  $\beta$  in the Gibbs model, respectively, it is the amount of the component  $i$  after deducting the contribution of the bulk phases. Divide  $n_i^{(\sigma)}$  by  $A_s$ , we obtain  $\Gamma_i$ .

It is interesting that  $n_i^{(\sigma)}$  could be either positive or negative. For instance, if  $SS'$  is moved upward,  $n_1^{(\sigma)}$  will be negative, but the real  $n_i^{(\text{layer})}$  is always positive.

**(4) Gibbs Unit Interfacial Excess** Because  $V^{(\alpha)}$  and  $V^{(\beta)}$  vary with the position of  $SS'$ ,  $n_i^{(\sigma)}$  and  $\Gamma_i$  are therefore with arbitrariness. Gibbs proposed that the solvent 1 is adopted as a reference to define a relative (to solvent 1) unit interfacial excess for the solute  $i$ , called the Gibbs unit interfacial excess with a symbol  $\Gamma_i^{(1)}$ . The following are two different versions of the definition:

**Definition (version 1)** Apply Eq.(15-5) respectively to the solvent 1 and the solute 2, after eliminating  $V^{(\beta)}$ , we obtain

$$n_i^{(\sigma)} - n_1^{(\sigma)} \frac{c_i^{(\alpha)} - c_i^{(\beta)}}{c_1^{(\alpha)} - c_1^{(\beta)}} = (n_i - Vc_i^{(\alpha)}) - (n_1 - Vc_1^{(\alpha)}) \frac{c_i^{(\alpha)} - c_i^{(\beta)}}{c_1^{(\alpha)} - c_1^{(\beta)}}$$

We can see that in the right side of the equation, those  $SS'$ -position dependent variables  $V^{(\alpha)}$  and  $V^{(\beta)}$  do not appear, to obtain a  $SS'$ -position independent Gibbs unit interfacial excess,  $\Gamma_i^{(1)}$  is therefore defined by the left side of the equation as follows:

$$\Gamma_i^{(1)} \stackrel{\text{def}}{=} \Gamma_i - \Gamma_1 \frac{c_i^{(\alpha)} - c_i^{(\beta)}}{c_1^{(\alpha)} - c_1^{(\beta)}} \quad (15-7)$$

The fraction component of the second term in the right side is a conversion factor which transforms  $\Gamma_1$  of the reference 1 to a value commensurate with the component  $i$ .  $\Gamma_i^{(1)}$  is therefore the difference of  $\Gamma_i$  and this conversion value, which is independent of the position of  $SS'$ . When  $i=1$ ,  $\Gamma_1^{(1)} = 0$ , it is natural that 1 related to 1,  $\Gamma_1^{(1)}$  is of course zero.

**Definition** (version 2) Because Eq.(15-7) can be used for any position of  $SS'$ , as a specific case, we can imagine moving  $SS'$  just to the middle of the concentration distribution line of the solvent 1 in Figure 15-5(a), making a favorable situation that the absolute area of ① just equals that of ② then they cancel each other, in this case,  $\Gamma_1^{(1)} = \Gamma_1 = 0$ . From Eq.(15-7), we have correspondingly  $\Gamma_i^{(1)} = \Gamma_i$ . This special case can then be used as the other more intuitive version for the definition of  $\Gamma_i^{(1)}$ ,

$$\Gamma_i^{(1)} \stackrel{\text{def}}{=} \Gamma_i \quad (\Gamma_1 = 0) \quad (15-8)$$

It is the interfacial excess  $\Gamma_i$  when  $\Gamma_1$  of the solvent equals zero.

It is worth emphasizing that we should pay attention to the difference between  $\Gamma_i^{(1)}$  in Gibbs model and the ordinary  $\Gamma_i$ .

**Guggenheim Interface Model** Another model was proposed by Guggenheim E A in 1940. The interfacial phase he supposed has thickness and volume. According to the specified principles, the unit interfacial excess obtained is also independent of the thickness of the interfacial phase. The final expression of the equation is very similar to that of the Gibbs model.

**Adsorption** The phenomena of matters enriched or repelled (anti-enriched) in the interfacial layer are called the adsorption.

**Unit Interfacial Adsorption** The unit interfacial excess  $\Gamma_i$  can also be called the unit interfacial adsorption, accordingly,  $\Gamma_i^{(1)}$  is the Gibbs unit interfacial adsorption for solute  $i$ .

When  $\Gamma_i^{(1)} > 0$ , solute  $i$  is enriched in the interfacial layer, it is called the **positive adsorption**.

When  $\Gamma_i^{(1)} < 0$ , solute  $i$  is repelled in the interfacial layer, it is called the **negative adsorption**.

### 3. Specific Surface Area $A_{s0}$

It is defined as the surface area per unit mass of a substance,

$$A_{s0} \stackrel{\text{def}}{=} A_s / m = A_s / (\rho V) \quad (15-9)$$

$A_{s0}$  is a measure of the degree of dispersion. In the equation,  $m$  is mass,  $\rho$  is density. Table 15-3 shows changes of the surface area and the specific surface area when a spherical water drop with a radius  $10^{-2}\text{m}$  is dispersed. We can see that when it is dispersed to tiny droplets with a radius from  $10^{-7}\text{m}$  (100nm) to  $10^{-9}\text{m}$  (1nm), the surface area increases  $10^5$  to  $10^7$  fold. This is one of the reasons why nano materials have very special and

Table 15-3  $A_s$  and  $A_{s0}$  for spherical water drops after dispersed

Radius, $r/\text{m}$	Number of droplets after dispersed	$A_s/\text{m}^2$	$A_{s0}/(\text{m}^2\text{kg}^{-1})$
$10^{-2}$	1	$1.26 \times 10^{-3}$	$3 \times 10^{-1}$
$10^{-3}$	$10^3$	$1.26 \times 10^{-2}$	3
$10^{-4}$	$10^6$	$1.26 \times 10^{-1}$	$3 \times 10$
$10^{-5}$	$10^9$	1.26	$3 \times 10^2$
$10^{-6}$	$10^{12}$	$1.26 \times 10$	$3 \times 10^3$
$10^{-7}$	$10^{15}$	$1.26 \times 10^2$	$3 \times 10^4$
$10^{-8}$	$10^{18}$	$1.26 \times 10^3$	$3 \times 10^5$
$10^{-9}$	$10^{21}$	$1.26 \times 10^4$	$3 \times 10^6$

distinguished properties (the other reason might be the quantum effect).

**Example** 1kg of water is dispersed to droplets with a radius of  $10^{-8}\text{m}$  at  $25^\circ\text{C}$ . Estimate the minimum work needed.

**Solution:** Density of water  $\rho = 1.00 \times 10^3 \text{kg} \cdot \text{m}^{-3}$ , surface tension  $\sigma = 0.0720 \text{N} \cdot \text{m}^{-1}$ ,

$$W'_R = \sigma \Delta A_s \approx \sigma A_s = \sigma (m/\rho) (4\pi r^3/3)^{-1} (4\pi r^2) = 3m\sigma/(\rho r)$$

$$= [3 \times 1 \times 0.0720 / (1.00 \times 10^3 \times 10^{-8})] \text{J} = 21.6 \times 10^3 \text{J}$$

Note: Since the isobaric specific heat capacity of water is  $4.179 \text{kJ} \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$ , the work is corresponding to a temperature rise of  $5.17 \text{K}$ .

## I. Thermodynamics of Interfaces

### 15.3 Fundamental Equations and Equilibrium Conditions

#### 1. Fundamental Equations for systems with interfacial phases

**Gibbs Function of Interfacial Phase** Besides pressure, we have the interfacial tension in the interfacial phase, for describing the state, we have

to add one more variable, usually adopt the interfacial area  $A_s$ . Take the Gibbs function for example, we can write the fundamental equation,

$$G^{(\sigma)} = G^{(\sigma)}(T^{(\sigma)}, p^{(\sigma)}, A_s, n_1^{(\sigma)}, n_2^{(\sigma)}, \dots, n_K^{(\sigma)}) \quad (15-10)$$

Comparing with the corresponding equations of gas, liquid and solid phases, Eq.(15-10) has one more independent variable  $A_s$ . Correspondingly, in writing its differential form, we have one more partial derivative  $G^{(\sigma)}$  to  $A_s$ ,

$$dG^{(\sigma)} = -S^{(\sigma)}dT^{(\sigma)} + V^{(\sigma)}dp^{(\sigma)} + \left( \frac{\partial G^{(\sigma)}}{\partial A_s} \right)_{T, p, n_j} dA_s + \sum_{i=1}^K \mu_i^{(\sigma)} dn_i^{(\sigma)} \quad (15-11)$$

Since  $dG = dW'_R$  under the condition of isothermal, isobaric and unchanged composition, also due to Eq.(15-1)  $dW'_R = \sigma dA_s$ , we have

$$\sigma = \left( \frac{\partial G^{(\sigma)}}{\partial A_s} \right)_{T, p, n_j} \quad (15-12)$$

The interfacial tension is a specific interfacial Gibbs function.

**Fundamental Equations for Interfacial Phase** From Eqs.(15-11, 15-12), combining relations among  $U$ ,  $H$ ,  $A$ ,  $G$ , we obtain the fundamental equations in differential forms for the interfacial phase as follows:

$$dU^{(\sigma)} = T^{(\sigma)}dS^{(\sigma)} - p^{(\sigma)}dV^{(\sigma)} + \sigma dA_s + \sum_i \mu_i^{(\sigma)} dn_i^{(\sigma)} \quad (15-13)$$

$$dH^{(\sigma)} = T^{(\sigma)}dS^{(\sigma)} + V^{(\sigma)}dp^{(\sigma)} + \sigma dA_s + \sum_i \mu_i^{(\sigma)} dn_i^{(\sigma)} \quad (15-14)$$

$$dA^{(\sigma)} = -S^{(\sigma)}dT^{(\sigma)} - p^{(\sigma)}dV^{(\sigma)} + \sigma dA_s + \sum_i \mu_i^{(\sigma)} dn_i^{(\sigma)} \quad (15-15)$$

$$dG^{(\sigma)} = -S^{(\sigma)}dT^{(\sigma)} + V^{(\sigma)}dp^{(\sigma)} + \sigma dA_s + \sum_i \mu_i^{(\sigma)} dn_i^{(\sigma)} \quad (15-16)$$

$$0 = S^{(\sigma)}dT^{(\sigma)} - V^{(\sigma)}dp^{(\sigma)} + A_s d\sigma + \sum_i n_i^{(\sigma)} d\mu_i^{(\sigma)} \quad (15-17)$$

Eq.(15-17) is the **Gibbs-Duhem equation** for the interfacial phase. It can be briefly derived as follows: Keeping  $T^{(\sigma)}$ ,  $p^{(\sigma)}$ ,  $\sigma$  and  $\mu_i^{(\sigma)}$  unchanged then integrating Eq.(15-16), we have

$$G^{(\sigma)} = \sigma A_s + \sum_i \mu_i^{(\sigma)} n_i^{(\sigma)} \quad (15-18)$$

By differentiating this equation and comparing with Eq. (15-16), we have Eq.(15-17).

**Fundamental Equations for Gibbs Interfacial Model** The above equations can be applied to any interfacial model. For the Gibbs model,  $V^{(\sigma)} = 0$ ,  $p^{(\sigma)}dV^{(\sigma)}$  and  $V^{(\sigma)}dp^{(\sigma)}$  terms disappear. Those  $U^{(\sigma)}$ ,  $H^{(\sigma)}$ ,  $A^{(\sigma)}$ , and  $G^{(\sigma)}$  in these equations are named respectively as the **interfacial excess thermodynamic energy**, the **interfacial excess enthalpy**, the **interfacial**

**excess Helmholtz function** and the **interfacial excess Gibbs function**. They are all extensive properties, if generally expressed as  $X^{(\sigma)}$ , similar to Eq.(15-5) of the interfacial excess, they can be defined as

$$X^{(\sigma)} \stackrel{\text{def}}{=} X - X^{(\alpha)} - X^{(\beta)} \quad (15-19)$$

$X$  represents a total thermodynamic property of the system.

**Interfacial Tension** From Eqs.(15-13, 15-14, 15-15, 15-16),

$$\sigma = \left( \frac{\partial U^{(\sigma)}}{\partial A_s} \right)_{S,V,n_j} = \left( \frac{\partial H^{(\sigma)}}{\partial A_s} \right)_{S,p,n_j} = \left( \frac{\partial A^{(\sigma)}}{\partial A_s} \right)_{T,V,n_j} = \left( \frac{\partial G^{(\sigma)}}{\partial A_s} \right)_{T,p,n_j} \quad (15-20)$$

Now we can have a comprehensive understanding toward the interfacial tension. Its definition is the contracted tension per unit length in the interface. It is also related to the reversible interfacial work, the thermodynamic energy, the enthalpy, the Helmholtz function and the Gibbs function per unit interface by Eq.(15-2) and Eq.(15-20), but we have to pay attention to the corresponding subscripts in the partial derivatives.

**Specific Interfacial Enthalpy  $H_A$**  Because  $S = -(\partial G / \partial T)_p$ ,

$H^{(\sigma)} = G^{(\sigma)} + TS^{(\sigma)} = G^{(\sigma)} - T(\partial G^{(\sigma)} / \partial T)_p$ , we can obtain

$$H_A \stackrel{\text{def}}{=} \left( \frac{\partial H^{(\sigma)}}{\partial A_s} \right)_{T,p,n_j} = \sigma - T \left( \frac{\partial \sigma}{\partial T} \right)_p \quad (15-21)$$

### Fundamental Equations for Heterogeneous Systems

For a heterogeneous system composed of two bulk phases  $\alpha$  and  $\beta$ , and an interfacial phase  $\sigma$ , we can write the corresponding fundamental equations in differential form as follows, comparing to ordinary equations for heterogeneous systems, a new term  $\sigma dA_s$  or  $A_s d\sigma$  appears,

$$dU = \sum_{\delta=\alpha,\beta,\sigma} (T^{(\delta)} dS^{(\delta)} - p^{(\delta)} dV^{(\delta)} + \sum_i \mu_i^{(\delta)} dn_i^{(\delta)}) + \sigma dA_s \quad (15-22)$$

$$dH = \sum_{\delta=\alpha,\beta,\sigma} (T^{(\delta)} dS^{(\delta)} + V^{(\delta)} dp^{(\delta)} + \sum_i \mu_i^{(\delta)} dn_i^{(\delta)}) + \sigma dA_s \quad (15-23)$$

$$dA = \sum_{\delta=\alpha,\beta,\sigma} (-S^{(\delta)} dT^{(\delta)} - p^{(\delta)} dV^{(\delta)} + \sum_i \mu_i^{(\delta)} dn_i^{(\delta)}) + \sigma dA_s \quad (15-24)$$

$$dG = \sum_{\delta=\alpha,\beta,\sigma} (-S^{(\delta)} dT^{(\delta)} + V^{(\delta)} dp^{(\delta)} + \sum_i \mu_i^{(\delta)} dn_i^{(\delta)}) + \sigma dA_s \quad (15-25)$$

$$0 = \sum_{\delta=\alpha,\beta,\sigma} (S^{(\delta)} dT^{(\delta)} - V^{(\delta)} dp^{(\delta)} + \sum_i n_i^{(\delta)} d\mu_i^{(\delta)}) + A_s d\sigma \quad (15-26)$$

## 2. Equilibrium Criterion and Equilibrium Conditions when Interfacial Phases Exist

**Equilibrium Criterion** Consider a closed heterogeneous system composed of an interfacial phase  $\sigma$  and two bulk phases  $\alpha$  and  $\beta$ , the system

has reached thermal equilibrium and mechanical equilibrium. Since we have interfacial work  $\sigma dA_s$ ,

$$dW = -\sum_{\delta=\alpha,\beta,\sigma} p^{(\delta)} dV^{(\delta)} + \sigma dA_s \quad (15-27)$$

According to Eq.(1-25) and Eq.(2-18) of the first and the second law,

$$dU = dQ + dW = dQ - \sum_{\delta=\alpha,\beta,\sigma} p^{(\delta)} dV^{(\delta)} + \sigma dA_s \quad (15-28)$$

$$\sum_{\delta=\alpha,\beta,\sigma} T^{(\delta)} dS^{(\delta)} - dQ \geq 0 \quad (15-29)$$

Combining Eqs.(15-22, 15-28, 15-29), we obtain the equilibrium criterion for heterogeneous systems containing interfacial phases,

$$\sum_{\delta=\alpha,\beta,\sigma} \sum_i \mu_i^{(\delta)} dn_i^{(\delta)} \leq 0 \quad (15-30)$$

Comparing with Eq.(3-53)  $\sum_{\alpha=1}^{\pi} \sum_{i=1}^K \mu_i^{(\alpha)} dn_i^{(\alpha)} \leq 0$  for the case without interfacial phase, we can see that they are formally the same.

Using the same procedure in 3.4 of Chapter 3, we can write the following equilibrium conditions,

$$\textbf{Thermal Equilibrium} \quad T^{(\alpha)} = T^{(\beta)} = T^{(\sigma)} = T \quad (15-31)$$

$$\textbf{Mechanical Equilibrium} \quad p^{(\alpha)} = p^{(\beta)} = p^{(\sigma)} = p \quad (15-32)$$

$$\textbf{Phase Equilibrium} \quad \mu_i^{(\alpha)} = \mu_i^{(\beta)} = \mu_i^{(\sigma)} = \mu_i \quad (15-33)$$

$$\textbf{Chemical Equilibrium} \quad \sum_B \nu_B \mu_B = 0 \quad (15-34)$$

We have to point out that Eq.(15-32) can only be used in the case when the interface is planar. For curved interface, refer to the next section.

### 3. Interfacial Chemical Potential

The peculiarity of the above thermodynamic treatment is that the thermodynamic functions are defined in a traditional way as usual. However, a deficiency is accompanied that the Eq.(15-18)  $G^{(\sigma)} = \sigma A_s + \sum_i \mu_i^{(\sigma)} n_i^{(\sigma)}$  resulted does not observe the assembling equation (3-12)  $X = \sum_{i=1}^K n_i X_i$ . The problem lies in the fact that in terms of Eq.(15-16),  $\mu_i^{(\sigma)} = (\partial G^{(\sigma)} / \partial n_i)_{T,p,A_s,n_{j \neq i}}$ , the chemical potential is no longer a partial molar quantity because the subscript  $A_s$  is an extensive property. To remedy this defect, we define a new function, the interfacial chemical potential  $\mu_i^{(\sigma)'} as:$

$$\mu_i^{(\sigma)'} \stackrel{\text{def}}{=} \mu_i^{(\sigma)} + \sigma A_{si} \quad (15-35)$$

where  $A_{si}$  is the partial molar interfacial area of the component  $i$ ,  $A_s = \sum_i n_i^{(\sigma)} A_{si}$ . Eq.(15-16) turns to be

$$dG^{(\sigma)} = -S^{(\sigma)}dT^{(\sigma)} + V^{(\sigma)}dp^{(\sigma)} + \sum_i \mu_i^{(\sigma)'} dn_i^{(\sigma)} \quad (15-36)$$

Obviously, the interfacial chemical potential  $\mu_i^{(\sigma)'} = (\partial G^{(\sigma)} / \partial n_i)_{T, p_s, n_{j \neq i}}$  is a partial molar quantity, and  $G^{(\sigma)} = \sum_i \mu_i^{(\sigma)'} n_i^{(\sigma)}$  obtained observes the assembling equation. Besides defining a new chemical potential  $\mu_i^{(\sigma)'}$ , defining a new enthalpy,  $H^{(\sigma)'} \stackrel{\text{def}}{=} H^{(\sigma)} - \sigma A_s$ , is also an effective alternative.

## 15.4 Laplace Equation

### Mechanical-Equilibrium Condition When Curved Interfaces Exist

When we treat the planar interface in the preceding section,  $V$  and  $A_s$  are two mutually independent variables. If curved interfaces exist in the system, as the volume changes, the area of the interface will change accordingly,  $V$  and  $A_s$  relate to each other. In the following, we adopt the change of Helmholtz function  $A$  as the equilibrium condition to derive. Suppose an isothermal system composed of  $\alpha$  phase,  $\beta$  phase and a curved interfacial phase  $\sigma$  of the Gibbs model has reached equilibrium. Pressures and volumes of various phases are  $p^{(\alpha)}$ ,  $p^{(\beta)}$ ,  $p^{(\sigma)}$ ,  $V^{(\alpha)}$ ,  $V^{(\beta)}$  and  $V^{(\sigma)}=0$ , respectively. Interfacial tension is  $\sigma$ , interfacial area is  $A_s$ . Figure 15-6 shows an example, where  $\alpha$  phase is a droplet of pure liquid,  $\beta$  phase is a gas. Since the interfacial phase has no thickness, we can consider that  $p^{(\sigma)}$  equals  $p^{(\alpha)}$ . The total volume of the system is kept unchanged, but the volumes of  $\alpha$  phase and  $\beta$  phase undergo infinitesimal changes  $dV^{(\alpha)}$  and  $dV^{(\beta)}$ , correspondingly, the area of the  $\sigma$  phase changes  $dA_s$ . From the differential form of the fundamental equation (15-24), and Eq.(15-30)  $\sum_{\delta=\alpha, \beta, \sigma} \sum_i \mu_i^{(\delta)} dn_i^{(\delta)} = 0$  for equilibrium, we have

$$dA = -p^{(\alpha)} dV^{(\alpha)} - p^{(\beta)} dV^{(\beta)} + \sigma dA_s$$

Since  $dV^{(\beta)} = -dV^{(\alpha)}$ , the above equation turns to

$$dA = -p^{(\alpha)} dV^{(\alpha)} + p^{(\beta)} dV^{(\alpha)} + \sigma dA_s$$

In the case of isothermal, isochoric and only volumetric work is concerned, the equilibrium criterion is simply  $dA=0$ . Let  $dA$  in Eq.(15-36) equals zero,

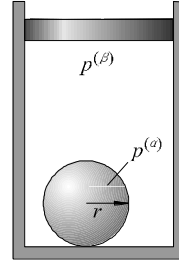


Figure 15-6 System with curved interface



after simple derivation, we obtain

$$p^{(\alpha)} = p^{(\beta)} + \sigma \frac{dA_s}{dV^{(\alpha)}} \quad (15-37)$$

This is the mechanical-equilibrium condition for systems with curved interfaces. It is called the **Laplace equation**. Because only state functions are involved in the final form, the application of the equation is not limited by the isochoric condition used during the derivation.

**Spherical Liquid Droplet (l) in Gas (g)** Suppose the radius of the droplet is  $r$ ,  $V^{(l)} = 4\pi r^3/3$ ,  $dV^{(l)} = 4\pi r^2 dr$ ,  $A_s = 4\pi r^2$ ,  $dA_s = 8\pi r dr$ ,  $dA_s/dV^{(l)} = 2/r$ , substitution into Eq.(15-37) yields

$$p^{(l)} = p^{(g)} + 2\sigma/r \quad (15-38)$$

For the non-spherical liquid droplet with two principal radii of curvature  $r_1$  and  $r_2$ , derivation yields

$$p^{(l)} = p^{(g)} + \sigma(1/r_1 + 1/r_2) \quad (15-39)$$

From the above two equations we can see that the pressure inside the liquid droplet is greater than that of the gas phase, the smaller the droplet, the larger is the pressure difference. Take  $H_2O$  for example,  $\sigma = 0.07197 \text{ N}\cdot\text{m}^{-1}$  at  $25^\circ\text{C}$ , for a water droplet with  $r = 10^{-6} \text{ m}$ ,

$$p^{(l)} - p^{(g)} = 2\sigma/r = (2 \times 0.07197 / 10^{-6}) \text{ Pa} = 144 \text{ kPa}$$

**Spherical Cavity (g) in Liquid (l)** Suppose the radius of the cavity is  $r$ ,  $V^{(g)} = 4\pi r^3/3$ ,  $dV^{(g)} = 4\pi r^2 dr = -dV^{(l)}$ ,  $dA_s = 8\pi r dr$ ,  $dA_s/dV^{(l)} = -2/r$ , substitution into Eq.(15-37) yields

$$p^{(l)} = p^{(g)} - 2\sigma/r \quad (15-40)$$

The pressure inside the cavity is greater than that of the liquid phase, the smaller the cavity, the larger is the pressure difference.

**Laplace Equation** Eqs.(15-37, 15-38, 15-39, 15-40) are all called Laplace equation.

**Capillary Rise or Depression** Using the Laplace equation, we can derive equations for capillary rise or depression the same as those derived by mechanical method,

$$\sigma = r(\rho^{(l)} - \rho^{(g)}) \frac{gh}{2} = R(\rho^{(l)} - \rho^{(g)}) \frac{gh}{2 \cos \theta} \quad (15-41)$$

where  $r$  is the radius of the meniscus formed by the wetting effect of the liquid inside the capillary,  $r = R/\cos \theta$ ,  $R$  is the radius of the capillary,  $\theta$

is the angle between the meniscus and the capillary wall called the **contact angle**,  $\rho^{(l)}$  and  $\rho^{(g)}$  are densities of liquid and gas, respectively,  $g$  is the accelerate gravity,  $h$  is the height of the liquid inside the capillary. Eq.(15-41) can be used to obtain interfacial (surface) tensions  $\sigma$  of liquids by measuring the height and the contact angle.

**Example** Use glass tube to touch a tiny amount of soap solution then blow a bubble with a radius of 1cm. Calculate the pressure difference between inside and outside the bubble.

**Solution:** Bubble in air is constructed by thin film with two surfaces inside and outside. Neglecting the thickness of the film we can consider that the radii of curvature of the two surfaces are the same. Therefore, the pressure difference calculated by Laplace equation should be simply doubled. For this soap solution,  $\sigma=0.0400\text{Nm}^{-1}$ .

$$\Delta p = 2 \times 2\sigma/r = 4 \times 0.0400\text{Nm}^{-1}/1 \times 10^{-2}\text{m} = 16.0\text{Pa}$$

## 15.5 Kelvin Equation

Pressure of the liquid with a curved surface is different from that with a planar surface. The chemical potential is therefore varied correspondingly, the saturated vapor pressure changes also. We will derive along this line.

### 1. Variation of Vapor Pressure with Liquid Pressure

When a pure liquid (l) and its pure vapor (g) reach equilibrium at a temperature  $T$ , if the interface is planar, the pressure of the liquid equals that of the vapor, it is the vapor pressure  $p^*$ , a characteristic property of the liquid. According to the phase-equilibrium condition, Eq.(15-33),

$$\mu^{(g)}(T, p^*) = \mu^{(l)}(T, p^*) \quad (15-42)$$

At the same temperature, if either there is an inert gas in the gas phase, or the interface is curved, the pressure of the liquid  $p^{(l)}$  does not equal that of the saturated vapor, the corresponding vapor pressure is not  $p^*$  again but changes to  $p^*$ . From Eq.(15-33), we can write

$$\mu^{(g)}(T, p^*) = \mu^{(l)}(T, p^{(l)}) \quad (15-43)$$

Subtract Eq.(15-42) from Eq.(15-43),

$$\mu^{(g)}(T, p^*) - \mu^{(g)}(T, p^*) = \mu^{(l)}(T, p^{(l)}) - \mu^{(l)}(T, p^*) \quad (15-44)$$

The isothermal pressure dependence of chemical potential can be estimated by Eq.(3-69)  $d\mu = V_m dp$ . Substitution into Eq.(15-44) yields

$$\int_{p^*}^{p^{(l)}} V_m^{(g)} dp^{(g)} = \int_{p^*}^{p^{(l)}} V_m^{(l)} dp^{(l)}$$

Suppose the vapor is an ideal-gas with the molar volume of the vapor  $V_m^{(g)} = RT/p^{(g)}$ , and  $V_m^{(l)}$  of the liquid does not change with pressure in the isothermal case, integration of the above equation yields

$$RT \ln \frac{p^{*'}}{p^*} = V_m^{(l)} (p^{(l)} - p^*) \quad (15-45)$$

We can see that the vapor pressure of the liquid  $p^{*'}$  increases as the pressure of the liquid  $p^{(l)}$  goes up.

## 2. Vapor Pressure of Liquid with Curved Surface, Kelvin Equation

**(1) Vapor Pressure of Liquid Droplet or Liquid in Capillary with Convex Meniscus** Consider a pure liquid droplet with a radius  $r$  in equilibrium with its vapor. The vapor pressure is  $p_r^*$ . From the Laplace equation (15-38),  $p^{(l)} = p^{(g)} + 2\sigma/r = p_r^* + 2\sigma/r$ . Applying Eq.(15-45) with  $p^{*'}$  replaced by  $p_r^*$ , and considering that in general,  $2\sigma/r \gg (p_r^* - p^*)$ , we obtain

$$RT \ln(p_r^*/p^*) = V_m^{(l)} (p_r^* + 2\sigma/r - p^*) \approx 2V_m^{(l)} \sigma/r = 2\sigma M / \rho r$$

$$\ln \frac{p_r^*}{p^*} = \frac{2\sigma M}{RT\rho r} \quad (15-46)$$

This is the Kelvin equation, where  $M$  is the molar mass of the liquid,  $\rho$  is the liquid density. The equation indicates that the vapor pressure  $p_r^*$  increases as the radius of the liquid droplet decreases. This result is also applicable to the convex meniscus of liquid in capillary. Table 15-4 lists calculated  $p_r^*/p^*$  for water droplets at 25°C by this equation. When  $r=1\mu\text{m}$ , vapor pressure increases only one thousandth. However, when  $r=1\text{nm}$ , vapor pressure raises about two fold.

## (2) Vapor Pressure of Liquid in Capillary with Concave Meniscus

Consider a pure liquid in capillary, it rises and forms a concave meniscus with a radius  $r$ . Similar to the section (1), we can derive,

$$\ln \frac{p_r^*}{p^*} = -\frac{2\sigma M}{RT\rho r} \quad (15-47)$$

This is also a Kelvin equation. The vapor pressure of a liquid in

capillary with a concave meniscus is less than that of a planar liquid at the same temperature. The smaller the radius of the concave meniscus, the lower the vapor pressure is.

Table 15-4 Calculated  $p_r^*/p^*$  at 25°C for water droplets

$r/\text{m}$	$10^{-6}$	$10^{-7}$	$10^{-8}$	$10^{-9}$
$p_r^*/p^*$	1.001	1.011	1.111	2.88

(3) **Applicable Limits of the Kelvin Equation** Kelvin equation is a thermodynamic relation, in the case of  $2\sigma/r \gg |p_r^* - p^*|$ , the correctness is without doubt. The problem is when the radius of curvature is very small, whether the interfacial tension still remains the same as that in the ordinary situation. On the other hand, is the Laplace equation still valid in this case? This controversy has not reached final conclusion.

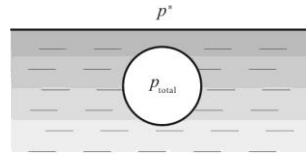


Figure 15-7 Cavity in planar liquid

(4) **Cavity in Liquid** Figure 15-7 shows a cavity with a radius  $r$  just under the planar surface of a liquid, the liquid reaches equilibrium with its vapor. The vapor pressure of a planar liquid is  $p^*$ , it equals the pressure of the liquid  $p^{(l)}$ . Now the question is how much the vapor pressure inside the cavity is? Can we use Eq.(15-47) to estimate it? From the derivation of Eqs.(15-45) we can see that the effect of the curved surface on the vapor pressure of liquid lies virtually in the effect of the pressure of the liquid. In Figure 15-7, although the surface of the cavity is curved, because the position of the cavity is just beneath the planar surface, the pressure at the curved surface is virtually the same as that of the planar liquid, therefore, the chemical potential keeps unchanged, the vapor pressure inside the cavity is the same as that of the planar liquid,  $p_r^* = p^* = p^{(l)}$ . Eq.(15-47) can not be used for this cavity. As for the total pressure inside the cavity, from the Laplace equation (15-38),  $p^{(g)} = p_{\text{total}} = p^{(l)} + 2\sigma/r = p^* + 2\sigma/r$ , therefore, besides the pressure of saturated vapor  $p^*$ , there must be some other gas existing with a pressure of  $2\sigma/r$ . If there is no other gas, the cavity would not be stable.

(5) **Melting Point of Tiny Crystal** Eq.(15-46) can also be used to estimate the vapor pressure of tiny crystals. When the scale of the crystal decreases, the vapor pressure rises similarly, the melting point lowers correspondingly. The normal melting point of gold is 1336K, while it lowers to 1000K when the diameter of gold particle is 4nm.

### 3. Meta-stable State

The existence of meta-stable states adheres to the difficulties

accompanying the creation of new phases, which will be discussed briefly.

(1) **Supersaturated Vapor** Pressure of the saturated vapor equals the vapor pressure of the liquid  $p^*$ . However, when the vapor condenses, the new phase just emerging is tiny liquid droplets. Suppose the radius of those droplets is  $r$ , the corresponding vapor pressure is  $p_r^*$ , from the Kelvin equation (15-46),  $p_r^* > p^*$ , indicating that the vapor with a pressure  $p^*$  does not saturate with those tiny droplets, they could not emerge. Increase the pressure isothermally beyond  $p_r^*$ , the condensation can then appear. This vapor with a pressure exceeding  $p^*$  is called a supersaturated vapor. Although the corresponding chemical potential can match with that of those tiny droplets, it is greater than that of the planar liquid. Therefore, the supersaturated vapor is in the meta-stable state.

Particles such as dusts in vapor can serve as cores of condensation favoring the formation of liquid droplets with larger radius, making the start of condensation at a smaller supersaturated level. In artificial rainfall, people use AgI particles spraying in the clouds as the condensation cores for supersaturated water vapor. Ions can also serve as condensation cores. The Wilson cloud chamber for studying fundamental particles is built based on this principle.

(2) **Superheated Liquid** Suppose the boiling point of a liquid under a constant external pressure  $p_{\text{ext}}$  is  $T_b$ . During boiling, normally, the vapor pressure  $p^*$  equals  $p_{\text{ext}}$ . However, when boil starts, the gas phase just formed is tiny cavities. Suppose the radius of those cavities is  $r$ . From the Laplace equation (15-40), the pressure of the stable cavities should be  $2\sigma/r$  greater than the pressure of the liquid (the external pressure  $p_{\text{ext}}$ ). But, as discussed in 15.5.2(4) above, the vapor pressure inside those cavities is the same as that of the planar liquid, equals  $p^*$  or  $p_{\text{ext}}$ . Therefore, the cavities can not form, the boiling can not happen. If the temperature under constant  $p_{\text{ext}}$  is raised, the vapor pressure of the planar liquid  $p^*$  will surpass  $p_{\text{ext}}$ ,  $p^* > p_{\text{ext}}$ , the pressure of the vapor inside the cavities  $p_r^* = p^*$  is also greater than  $p_{\text{ext}}$ . On the other hand, the surface tension  $\sigma$  will be lowered because of rising temperature. If the equation  $p_r^* = p_{\text{ext}} + 2\sigma/r$  is satisfied, cavities can then stably exist, boiling can then start. This liquid with a temperature surpass  $T_b$

is called a superheated liquid. It is in a meta-stable state.

The superheating of liquid during distillation always causes bumping. To prevent, we usually add some zeolites, bisque, or glass capillary with one end sealed, they can provide small cavities serving as cores of gasification, making the boiling start at a lower superheating level. The other choice is lowering the pressure, and then some cavities may appear in the interior of the superheated liquid. The bubble chamber used in studying fundamental particles is constructed based on this principle.

(3) **Super-cooled Liquid** Suppose the melting point of a liquid under a constant external pressure  $p_{\text{ext}}$  is  $T_f$ . When solidifying starts, the solid phase just formed is tiny crystals. From the Kelvin equation (15-46) which can also be applied to tiny crystals, their vapor pressure or chemical potential is greater than those ordinary crystals at the same temperature. Solidifying can not take place. Further lowering the temperature, vapor pressures of liquid and solid both diminish, but that of the solid diminishes more. When the vapor pressure or chemical potential approaches that of the tiny crystals, the latter can exist, solidifying then happens. This liquid with a temperature lower than  $T_f$  is called a super-cooled liquid. It is in a meta-stable state.

Extra pure water could maintain a liquid state without freezing even cooled to  $-40^\circ\text{C}$ . During re-crystallization for purifying materials, to avoid super-cooling, usually some tiny crystals of the same material as seeds are added. They play the role of cores for solidification, the crystallization or solidification can then take place for liquid with minor super-cooling.

(4) **Supersaturated Solution** When a solution precipitates or crystallizes, the solute solid just appeared is tiny crystals. Similarly, a solution with a concentration higher than the solubility is a supersaturated solution. It is in a meta-stable state.

In crystallization operation, if the degree of super-saturation is too large, the crystals formed will be too small to be favorable for further filtration and washing. For obtaining larger crystals, we usually add seeds when the degree of super-saturation is not too large. The crystals crystallized from the solution are always non-homogeneous in size. If raising the temperature a

little, the solution will be unsaturated for the smaller crystals, but still super-saturated for the larger crystals. Lengthening the time of heat preservation, the smaller crystals gradually dissolve while the larger crystals grow further, the particles gradually approach homogeneous. This operation is called the **aging**.

**Example** A water droplet with a radius of  $10^{-8}\text{m}$ , what is the temperature rise that has the same effect as the vapor pressure increase for this droplet at  $25^\circ\text{C}$ . The density of water is  $0.998 \times 10^3 \text{kg} \cdot \text{m}^{-3}$ , molar enthalpy of vaporization is  $44.01 \text{kJ} \cdot \text{mol}^{-1}$ .

**Solution:** According to the Kelvin equation (15-46),

$$\ln \frac{p_r^*}{p^*} = \frac{2\sigma M}{RT\rho r} = \frac{2 \times 0.07197 \times 18.02 \times 10^{-3}}{8.3145 \times 298.15 \times 0.998 \times 10^3 \times 1 \times 10^{-8}} = 0.1048$$

From the Claperon-Clausius equation (2-127),  $\ln(p_2^*/p_1^*) = (\Delta_{\text{vap}}H_m/R)(1/T_1 - 1/T_2)$

$$\frac{1}{T_2} = \frac{1}{T_1} - \frac{R \ln(p_2^*/p_1^*)}{\Delta_{\text{vap}}H_m} = \left( \frac{1}{298.15} - \frac{8.3145 \times 0.1048}{44.01 \times 10^3} \right) \text{K}^{-1} = 3.3342 \times 10^{-3} \text{K}^{-1}$$

$T_2 = 299.92 \text{K} \quad \Delta T = T_2 - T_1 = 1.77 \text{K}$

## 15.6 Gibbs Isotherm

### 1. Gibbs Isotherm

**Derivation** We start from the Gibbs-Duhem equation (15-17), since  $V^{(\sigma)} = 0$ , we have

$$0 = S^{(\sigma)}dT^{(\sigma)} + A_s d\sigma + \sum_i n_i^{(\sigma)} d\mu_i^{(\sigma)} \quad (15-48)$$

In isothermal case,  $S^{(\sigma)}dT^{(\sigma)}$  term also disappears. When a bulk phase and an interfacial phase reach equilibrium, from the phase-equilibrium condition Eq.(15-33),  $\mu_i^{(\sigma)} = \mu_i$ , chemical potential is invariable with respect to different phases. Further if we apply the definition of the unit interfacial excess (adsorption), Eq.(15-6),  $\Gamma_i = n_i^{(\sigma)}/A_s$ , Eq.(15-48) can be rearranged as

$$-d\sigma = \sum_i (n_i^{(\sigma)}/A_s) d\mu_i = \sum_i \Gamma_i d\mu_i \quad (15-49)$$

If adopting the Gibbs unit interfacial excess (adsorption)  $\Gamma_i^{(1)}$ ,  $\Gamma_i^{(1)} = 0$ ,

$$-d\sigma = \sum_{i \neq 1} \Gamma_i^{(1)} d\mu_i \quad (15-50)$$

For binaries, Eqs.(15-49, 15-50) can be rewritten respectively as

$$-d\sigma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \quad (15-51)$$

$$-d\sigma = \Gamma_2^{(1)} d\mu_2, \quad \Gamma_2^{(1)} = -(\partial\sigma/\partial\mu_2)_T \quad (15-52)$$

Eqs.(15-49, 15-50, 15-51, 15-52) are the Gibbs isotherms or the **Gibbs**

**adsorption isotherms.** They relate the unit interfacial excess (adsorption) with the rate of the interfacial-tension change with respect to chemical potential.

**Adopt Concentration** In studying adsorption, we always adopt the concentration (the amount-of-substance concentration)  $c_2$  to represent the chemical potential for the solute of the bulk phase. The chemical potential is then expressed by Eq.(3-129) in 3.12.4 as  $\mu_2 = \mu_{c,2}^{**} + RT \ln a_{c,2}$ , where  $a_{c,2}$  is the activity in terms of the reference state IV,  $a_{c,2} = c_2 \gamma_{c,2} / c^*$ ,  $\gamma_{c,2}$  is the corresponding activity factor,  $c^* = 1 \text{ mol} \cdot \text{dm}^{-3}$ . Isothermally, we have  $d\mu_2 = RT d \ln a_{c,2}$ . Substitution into Eq.(15-52) yields

$$\Gamma_2^{(1)} = -\frac{1}{RT} \left( \frac{\partial \sigma}{\partial \ln a_{c,2}} \right)_T = -\frac{a_{c,2}}{RT} \left( \frac{\partial \sigma}{\partial a_{c,2}} \right)_T \quad (15-53)$$

For dilute solutions,  $\gamma_{c,2} \approx 1$ , activity  $a_{c,2}$  can be simply replaced by concentration, we then have

$$\Gamma_2^{(1)} \approx -\frac{c_2}{RT} \left( \frac{\partial \sigma}{\partial c_2} \right)_T \quad (15-54)$$

Eqs.(15-53, 15-54) are also the Gibbs isotherms. They express general relations among the unit interfacial excess (adsorption), temperature, bulk concentration and the rate of interfacial-tension change with respect to bulk concentration.

**Application of Gibbs Isotherm** By experiment or by constructing model, we have relations between  $\sigma$  and  $c_2$  at a certain temperature. We can then calculate  $\Gamma_2^{(1)}$  by the Gibbs isotherm. On the contrary, if we have relations between  $\Gamma_2^{(1)}$  and  $c_2$ , we can estimate  $\sigma$ . In principle, Eqs.(15-53, 15-54) can be used for any interface, but mainly for gas-liquid and liquid-liquid interfaces.

**Experimental Test for Gibbs Isotherm** In 1930, McBain J W used a fast moving blade to scrape a sample film with a surface area of  $310 \text{ cm}^2$  and a thickness of  $0.05 \sim 0.10 \text{ mm}$  from the solution surface. He analyzed the amount of solvent and solute, the obtained  $\Gamma_2^{(1)}$  fairly agrees with that calculated by Eq.(15-54). This result positively verified the Gibbs isotherm. After 1950s, some other authors adopted tracer atoms and did the similar job.



**Example 1** In the range of dilute solutions, generally, the linear relation  $\sigma^* - \sigma = bc_2$  exists between the gas-liquid surface tension and the bulk concentration. Derive the relation between the unit interfacial adsorption and the concentration.

**Solution:**  $(\partial\sigma/\partial c_2)_T = -b$ , substitution into Eq.(15-54) yields

$$\Gamma_2^{(1)} = -c_2 (\partial\sigma/\partial c_2)_T / RT = bc_2 / RT.$$

It shows that in the range of dilute solution,  $\Gamma_2^{(1)}$  is proportional to  $c_2$ .

**Example 2** At higher concentration, the following semi-empirical equation can well express the relation between the gas-liquid interfacial (surface) tension and the bulk concentration:  $\sigma^* - \sigma = A + B \ln c_2$ ,  $A$  and  $B$  are constants. Derive the relation among the adsorption, temperature and concentration.

**Solution:**  $(\partial\sigma/\partial c_2) = -B/c_2$ , substitution into Eq.(15-54) yields

$$\Gamma_2^{(1)} = -c_2 (-B/c_2) / RT = B/RT, \quad \Gamma_2^{(1)} \text{ approaches a limit independent of } c_2.$$

## 2. Positive Adsorption and Negative Adsorption

When a substance dissolves in a liquid (water), with increasing concentration, as shown in Figure 15-8, the interfacial (surface) tension exhibits different changes depending on the nature of the substance.

(1) Curve A:  $\sigma$  increases,  $(\partial\sigma/\partial c_2)_T > 0$ .

From Eq.(15-54),  $\Gamma_2^{(1)} < 0$ , it is a negative adsorption. Inorganic salts NaCl, Na<sub>2</sub>SO<sub>4</sub>, KOH, NH<sub>4</sub>Cl, KNO<sub>3</sub>, poly-hydroxyl compounds cane sugar and mannitol in water belong to this case.

(2) Curve B:  $\sigma$  decreases,  $(\partial\sigma/\partial c_2)_T < 0$ .

From Eq.(15-54),  $\Gamma_2^{(1)} > 0$ , it is a positive

adsorption. Alcohols, aldehydes, ketones, carboxylic acids and esters in water fall to this category. These substances are called **surface active substances** because they can depress the surface tension  $\sigma$ .

(3) Curve C:  $\sigma$  sharply declines, the initial slope is highly negative indicating a large adsorption at low concentration. Aqueous solutions of soap, alkali salts of normal organic acids with more than 8 carbon atoms, high carbon normal alkyl sulfate and benzene sulfonate are examples. These substances are called **surfactants**, refer to 15.9.1.

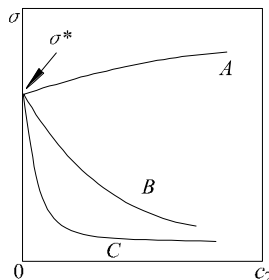


Figure 15-8 Relations between  $\sigma$  and  $c_2$  in isothermal condition.

Figure 15-9 depicts variations of gas-liquid interfacial tensions with the liquid concentration for aqueous solutions of butyric acid and NaCl. Figure 15-10 shows the corresponding calculated relations between  $\Gamma_2^{(1)}$  and  $c_2$  by Eq.(15-54), they are called the **adsorption isotherms**.

## 15.7 Wetting

**Various Kinds of Wetting and Spreading** When a drop of liquid is put on the solid surface, because of the different properties, sometime it may spread out, which is called the **spreading wetting**, or it may adhere on the surface forming a convex-lens like, called the **adhesive wetting**. They are all wetting phenomena. If the liquid does not adhere and keeps a shape of ellipsoid, it is called the **non-wetting**. If a solid can be wetted by a liquid, then dip the solid completely into the liquid, it is called the **dip wetting**. If dropping a liquid onto the surface of another liquid which is insoluble to or partial soluble in the former liquid, sometimes it spread out, which is called the **spreading**, or forming a convexo-convex lens like, called the **non-spreading**. All the above types are shown in Figure 15-11. We can see that the spreading and the non-spreading between two liquids are very similar to the spreading wetting and the non-wetting between liquid and solid.

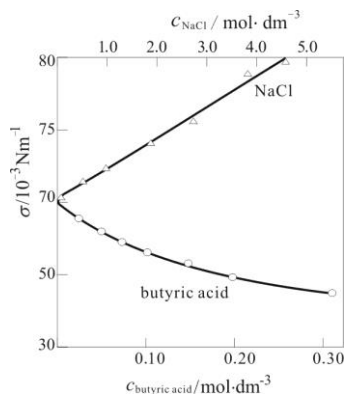


Figure 15-9 Surface tension varies with composition for aqueous solutions of butyric acid and NaCl.

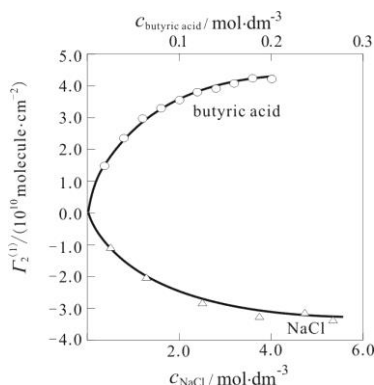


Figure 15-10 Adsorption isotherms for aqueous solutions of butyric acid and NaCl.

Chattoraj D K, Birdi K S. Adsorption and the Gibbs Surface Excess. Plenum press: New York. 1984, p41.

## 1. Spreading Coefficient

**Definition** The spreading process of a liquid drop on a solid (or another liquid) surface under isothermal and isobaric condition is shown in Figure 15-12. During this process, the original gas-solid interface disappears. A liquid-solid interface and a gas-liquid interface are newly created. If the surface area of the solid is  $A_s$ , the surface of the liquid drop is very small that can be neglected, the change of Gibbs function is

$$\Delta G = A_s (\sigma_{l,s} + \sigma_{g,l} - \sigma_{g,s}) \quad (15-55)$$

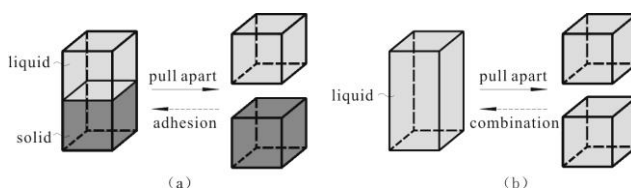


Figure 15-13 Adhesive work and cohesive work

The spreading coefficient  $\phi$  of a liquid on a solid is then defined as: (can be extended to a liquid on another liquid)

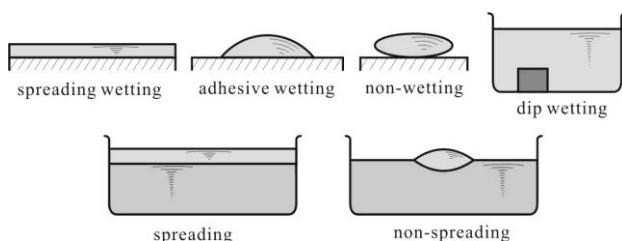


Figure 15-11 Various kinds of wetting and spreading

$$\phi \stackrel{\text{def}}{=} -(\sigma_{l,s} + \sigma_{g,l} - \sigma_{g,s}) = -\Delta G/A_s \quad (15-56)$$

Because  $\sigma_{l,s}$  and  $\sigma_{g,s}$  are difficult to measure experimentally, the spreading coefficient  $\phi$  can not be estimated directly from this equation. However,  $\sigma_{g,l}$  and  $\sigma_{(I),l(II)}$  are measurable, therefore, the spreading coefficient can be calculated to judge the spreading between a liquid I and a liquid II.



Figure 15-12 Spreading wetting process

### Physical

**Meaning of the Spreading Coefficient** By definition, only when  $\phi$  is

positive,  $\Delta G$  is correspondingly negative, spreading can then happen. To reveal the physical meaning, rewrite Eq. (15-56),

$$\varphi = (\sigma_{g,l} + \sigma_{g,s} - \sigma_{l,s}) - 2\sigma_{g,l} \quad (15-57)$$

The first term on the right side,  $\sigma_{g,l} + \sigma_{g,s} - \sigma_{l,s}$ , is the Gibbs function change per unit area for the system after pulling apart a liquid-solid interface creating a new gas-liquid interface and a new gas-solid interface, referring to Figure 15-13(a). It is the reversible work consumed to pull apart a liquid-solid interface

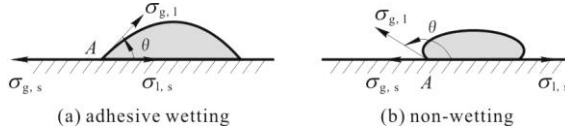


Figure 15-14 Wetting and contact angle

that can be used to evaluate the adhesive force of a liquid to a solid, therefore, called the **adhesive work**  $W_a$ ,

$$W_a = \sigma_{g,l} + \sigma_{g,s} - \sigma_{l,s} \quad (15-58)$$

The second tem on the right side,  $2\sigma_{g,l}$ , is the Gibbs function change per unit area for the system when breaking a liquid column creating two new gas-liquid interfaces, referring to Figure 15-13(b). It is the reversible work consumed to break a liquid column that can be used to evaluate the cohesive force inside a liquid itself, therefore, called the **cohesive work**  $W_c$ ,

$$W_c = 2\sigma_{g,l} \quad (15-59)$$

Substitution of Eqs.(15-58, 15-59) into Eq.(15-57) yields

$$\varphi = W_a - W_c \quad (15-60)$$

The equation indicates that only when the adhesive work  $W_a$  is greater than the cohesive work  $W_c$ , a liquid can then spread on a solid.

## 2. Contact Angle and Young's Equation

**Contact Angle** When  $\varphi$  is negative,  $\Delta G$  is positive, spreading could not happen, we will have the adhesive wetting or the non-wetting. Referring to Figure 15-14, at the common boundary where the three phases, gas, liquid and solid meet, i.e., point A (a loop surrounding the liquid drop) in the figure, there are three interfacial tensions interacted. Among them,  $\sigma_{g,s}$  tends to spread the liquid drop,  $\sigma_{l,s}$  tends to contract the drop, while for  $\sigma_{g,l}$ , it will either contract or spread the drop depending on whether it is adhesive wetting or non-wetting. Contact angle is then defined by the angle between vectors  $\sigma_{g,l}$  and  $\sigma_{l,s}$ .

**Young's Equation** From Figure 15-14, the following equation named after Young T can be established at equilibrium,

$$\sigma_{g,s} = \sigma_{l,s} + \sigma_{g,l} \cos \theta \quad (15-61)$$

$$\cos \theta = (\sigma_{g,s} - \sigma_{l,s}) / \sigma_{g,l} \quad (15-62)$$

Analyzing this equation, we can distinguish the following two cases:

(1)  $\sigma_{g,s} > \sigma_{l,s}$ ,  $\cos \theta > 0$ ,  $\theta < 90^\circ$ . Adhesive wetting will happen, see Figure 15-14(a). When  $\theta = 0^\circ$ , corresponds to a complete wetting.

(2)  $\sigma_{g,s} < \sigma_{l,s}$ ,  $\cos \theta < 0$ ,  $\theta > 90^\circ$ . Non-wetting will appear, see Figure 15-14(b). When  $\theta = 180^\circ$ , corresponds to a complete non-wetting.

**Calculating Spreading Coefficient** Combining Eq.(15-58) and the Young's equation (15-62), we obtain the adhesive work,

$$W_a = \sigma_{g,l} (1 + \cos \theta) \quad (15-63)$$

On the other hand, from Eqs.(15-60) and (15-59), we have an equation for calculating the spreading coefficient from the experimental contact angle,

$$\varphi = \sigma_{g,l} (\cos \theta - 1) \quad (15-64)$$

The spreading coefficient  $\varphi$  obtained in this case is always  $\leq 0$ .

## II. Characteristic Properties of Interfacial Equilibria

### 15.8 Gas-Liquid and Liquid-Liquid Interfaces

**Interfacial Tension** It is the most fundamental characteristic property of gas-liquid and liquid-liquid interfaces. From data of the interfacial tension and its temperature and (bulk) concentration dependence, we can calculate the specific enthalpy of interfaces, estimate the pressure difference between the two sides of a curved interface, calculate the vapor pressure of liquids with curved surface, study various meta-stable phenomena, evaluate the unit interfacial excess or adsorption, and investigate the characteristics of spreading and wetting. As usual, there are three resources of the data: experimental, semi-empirical and theoretical methods.

#### 1. Experimental Methods for Interfacial Tensions

Mostly used methods are: **capillary rising, maximum bubble pressure, drop weight, hanging ring, Wilhelmy slide, pendant drop**, etc.

## 2. Semi-Empirical Methods for Interfacial Tensions

### (1) Interfacial (Surface) Tension between Pure Liquid and Gas

**Parachor Method** In 1923, Macleod D B proposed an equation,

$$\sigma^{1/4} = [p](\rho^{(l)} - \rho^{(g)}) \quad (15-65)$$

$\rho^{(l)}$  and  $\rho^{(g)}$  are densities of liquid and gas, respectively.  $[p]$  is a characteristic parameter for substance independent of temperature, which is called the parachor. It depends on the molecular volume, therefore, having a certain additive performance. A group contribution method has been developed that can estimate  $[p]$  from the molecular structure then calculate  $\sigma$  by the above equation. This method is especially suitable for molecules with hydrogen bonding. The error is usually less than 5%, too.

**Corresponding-State Method** Dimensionless (dimension 1) group  $\sigma/p_c^{2/3}(RT_c)^{1/3}$  is expressed as a generalized function of reduced temperature  $T_r$ . This method is suitable for non-hydrogen bonding liquids. The error is usually less than 5%, too.

### (2) Interfacial (Surface) Tension between Liquid Mixture and Gas

**Butler Equation** Usually we use the activity to express the non-ideality of liquid mixtures. If the reference state I is adopted, from Eqs.(3-99, 3-102) in 3.10,  $\mu_i = \mu_i^* + RT \ln a_i$ ,  $a_i = x_i \gamma_i$ . For an interfacial phase, we have to use the interfacial chemical potential  $\mu_i^{(\sigma)'}$  defined by Eq.(15-35), that of the reference state is correspondingly  $\mu_i^{*(\sigma)'}$  defined as:

$$\mu_i^{*(\sigma)'} \stackrel{\text{def}}{=} \mu_i^{*(\sigma)} + \sigma_i^* A_{si}^* \quad (15-66)$$

where  $\sigma_i^*$  is the interfacial (surface) tension of the pure liquid  $i$ ,  $A_{si}^*$  is the molar interfacial area of the pure component  $i$ . We can then write:

$$\mu_i^{(\sigma)'} = \mu_i^{*(\sigma)'} + RT \ln a_i^{(\sigma)} = \mu_i^{*(\sigma)'} + RT \ln (x_i^{(\sigma)} \gamma_i^{(\sigma)}) \quad (15-67)$$

Substitution of Eq.(15-35)  $\mu_i^{(\sigma)'} \stackrel{\text{def}}{=} \mu_i^{(\sigma)} + \sigma A_{si}$  and Eq.(15-66) yields

$$\mu_i^{(\sigma)} + \sigma A_{si} = \mu_i^{*(\sigma)} + \sigma_i^* A_{si}^* + RT \ln (x_i^{(\sigma)} \gamma_i^{(\sigma)}) \quad (15-68)$$

When an interfacial phase reaches equilibrium with a liquid phase  $\alpha$ , in terms of the phase-equilibrium condition, Eq.(15-33),  $\mu_i^{(\alpha)} = \mu_i^{(\sigma)}$ . Suppose  $A_{si} \approx A_{si}^*$ , and noticing that the two phases have the same reference state,

$\mu_i^{*(\sigma)} = \mu_i^{*(\alpha)}$ , by substituting  $\mu_i^{(\alpha)} = \mu_i^{*(\alpha)} + RT \ln x_i^{(\alpha)} \gamma_i^{(\alpha)}$  of the  $\alpha$  phase and Eq.(15-68) into  $\mu_i^{(\alpha)} = \mu_i^{(\sigma)}$ , we obtain:

$$RT \ln x_i^{(\alpha)} \gamma_i^{(\alpha)} = RT \ln x_i^{(\sigma)} \gamma_i^{(\sigma)} + A_{si}^* (\sigma_i^* - \sigma)$$

or 
$$\sigma = \sigma_i^* + \frac{RT}{A_{si}^*} \ln \frac{x_i^{(\sigma)} \gamma_i^{(\sigma)}}{x_i^{(\alpha)} \gamma_i^{(\alpha)}} \quad (15-69)$$

This equation was derived by Butler J A V in 1932, which connects the interfacial tension of liquid mixtures with that of the pure components and enables predicting  $\sigma$  from  $\sigma_i^*$ . In application, mixture models are needed.

(3) **Liquid-Liquid Interfacial Tension** In 1957, Jirifalco L F and Good R J proposed an equation for estimating the interfacial tension  $\sigma_{\alpha\beta}$  between a liquid phase  $\alpha$  and a liquid phase  $\beta$ ,

$$\sigma_{\alpha\beta} = \sigma_\alpha + \sigma_\beta - 2\xi(\sigma_\alpha \sigma_\beta)^{1/2} \quad (15-70)$$

$\sigma_\alpha$  and  $\sigma_\beta$  are the corresponding gas-liquid surface tensions for  $\alpha$  and  $\beta$  phases, respectively,  $\xi$  is an empirical parameter about 0.5~1.15.

### 3. Theoretical Studies for Interfacial Tensions

**Statistical-Mechanics Method** Taking the canonical ensemble for example, from Eq.(13-14)  $A = -kT \ln Z$ ,  $Z$  is the canonical partition function. Substitution into Eq.(15-20)  $\sigma = \left( \partial A^{(\sigma)} / \partial A_s \right)_{T,V,n_j}$  yields

$$\sigma = \left( \frac{\partial A^{(\sigma)}}{\partial A_s} \right)_{T,V,n_j} = -kT \left( \frac{\partial \ln Z}{\partial A_s} \right)_{T,V,n_j} \quad (15-71)$$

Adopting a certain intermolecular-force model, this equation can give  $\sigma$  in principle. Specifically, we can use the integral-equation method based on distribution functions.

**Computer Molecular Simulation** We usually adopt MC and MD methods and numerical values of  $\sigma$  can be obtained.

**Examples** Figure 15-15 shows the result of the density distribution in an interfacial layer for a Lennard-Jones fluid. The ordinate  $\rho$  is the density expressed by volume fraction, the zero of the abscissa can be considered approximately the center of the interfacial layer,  $z$  is the distance to the center,  $\varepsilon$  and  $d$  are the energy and size parameters, respectively, of the Lennard-Jones potential function. The figure shows a continuous change from high density to low density, where the zigzag line is obtained by

computer simulation, the curve is the calculated result by YBG, an integral-equation theory. Figure 15-16 shows the energy-parameter dependence of  $\sigma$ . The larger  $\varepsilon$ , the stronger intermolecular interactions, the higher  $\sigma$  is.

## 15.9 Surfactants and Surface Films

### 1. Surfactants

The surface active substances that can notably depress the interfacial tensions of the water-gas and water-oil interfaces by adding only a small amount are called surfactants. Referring to the curve *C* in Figure 15-8, the interfacial (surface) tension sharply decreases at very low concentration, and quickly approaches a constant value as the concentration further increases. The terminology oil used here is in a general sense for those non-polar and weak polar substances such as hydrocarbons. Due to the low density, even

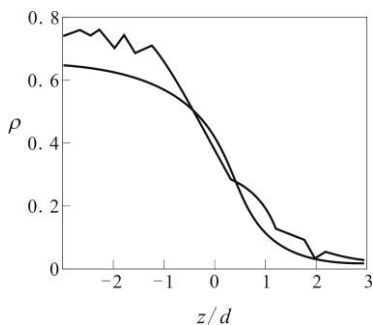


Figure 15-15 Density distribution in interfacial layer.  $kT/\varepsilon=0.918$ . Zigzag line: Simulation: Chapela G A et al. J Chem Soc Faraday Trans, 1977, II73:1133. Curve: YBG integral equation, Fischer J, Methfessel M. Phys Rev, 1980, A22:2836.

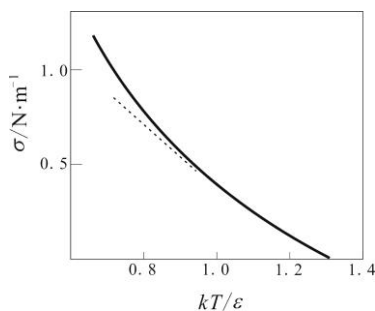


Figure 15-16 Variation of gas-liquid interfacial tension with  $kT/\varepsilon$ . Solid line: Simulation: Miyazaki et al. J Chem Phys. 1976, 64:3364. Dotted line: YBG integral equation, Fischer J, Methfessel M. Phys Rev, 1980, A22:2836.

containing some polar contents, gas phase falls to the same category as oil. Surfactants are usually composed of both a lipophilic group and a hydrophilic group. Because of the dual character, the surfactant molecules quickly assemble in the interface with the lipophilic group pointing to the oil or gas phase and the hydrophilic group to the water phase, they occupy the interface almost completely causing the interfacial tension to sharply depress and to approach a constant limit. Whether naturally or unnaturally (laboratory) synthesized, surfactants usually contain a long carbon chain



with more than 8 carbon atoms as the lipophilic group, and those charged species served as the hydrophilic group such as carboxylate, sulfonate, phosphate anions, quarternary ammonium cation, amphoteric ions such as amino acid, also some polar groups such as hydroxyl, ether groups. Figure 15-17 depicts structures of soap and lecithin clearly showing their lipophilic and hydrophilic parts. The strength of the lipophilic and hydrophilic groups for surfactants is usually evaluated by the HLB values, refer to 18.11.

## 2. Micelles and Critical Micelle Concentration

**Micelles and Interfacial Monomolecular Films** Figure 15-18(a) depicts intuitively changes by adding surfactant continuously into water. (1)

In a very dilute solution, no marked difference from the ordinary solutions is observed. (2) As the concentration slightly increases, surfactant molecules quickly assemble onto the solution surface, resulting in a notable decrease of the amount of water molecules in the interfacial layer, the surface tension sharply depresses

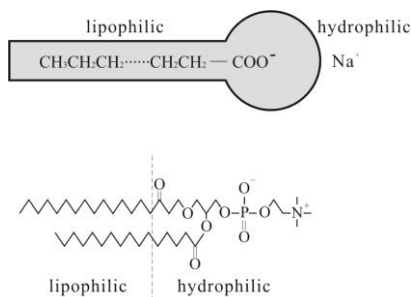


Figure 15-17 Structures of soap (upper) and lecithin (lower)

correspondingly. At the same time, surfactant molecules in the bulk water are also assembled two or three together, the assemblies are called the **micelles**. (3) As the concentration further increases, sufficient amount of surfactant molecules assemble crowdedly on the solution surface, they orient and arrange forming a monomolecular film. The properties of the surface notably change. This corresponds to the turn point in the curve *C* in Figure 15-8. On the other hand, the spherical micelles start forming in the bulk. (4) If the concentration increases again, surfactant molecules in bulk solution will assemble further to several tenths up to several hundreds forming many spherical micelles with different sizes, even forming rod-like micelles and lamellar micelles as shown in Figure 15-18(b).

**Critical Micelle Concentration** The minimum concentration of the surfactant for the formation of spherical micelles is called the critical micelle concentration, abbreviated as cmc. It corresponds to the concentration at the turning point of the Curve *C* in Figure 15-8. Approximately, it is also the minimum concentration when the monomolecular layer is formed.

**Solubilization** When the concentration of surfactant surpasses cmc, some water-insoluble substances can enter the micelles in the bulk solution

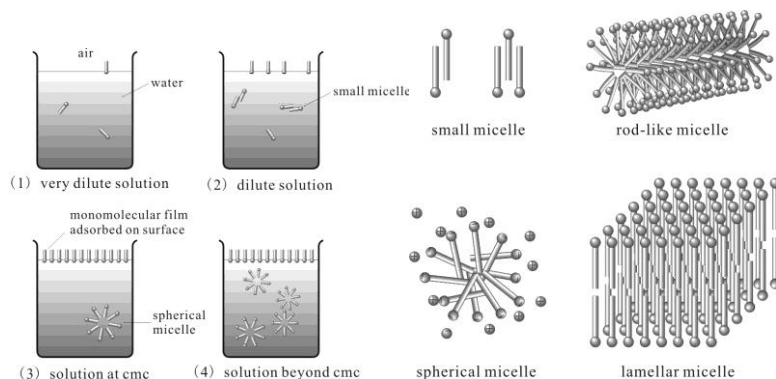


Figure 15-18 (a) States of the surfactant molecules in different concentrations

Figure 15-18 (b) Sketch representation of various forms of micelles

resulting in the enhancement of their solubility. This phenomenon is called the solubilization. It is possible that the micelles further grow up to form super micro liquid drops with oil encapsulated, the size of them may reach several nm up to several tenths of nm.

Emulsions, micro-emulsions and foams are also closely related to the surfactants in the interface, refer to Chapter 18 Colloids.

### 3. Surfactant and Wetting

**Wetting Function of Solid** A solid that can be wetted by liquid is called the **lyophilic solid**, that can not be wetted is called the **lyophobic solid**. The wetting function of solid depends on the structure. The most common liquid is water. Those polar solids such as quartz, silicates are hydrophilic. Most non-polar solids such as paraffin wax, leaves of the plants and graphite are hydrophobic. Using suitable surfactants (wetting agents) can notably modify the wetting function of the solid surface. From the

Young's equation (15-62) we can see that varying the interfacial tensions  $\sigma$  of the relevant interfaces in the studied system, the contact angle  $\theta$  can be changed, therefore, changing the wetting situation of the system.

### Examples

(1) By using methyl silane chloride to increase the contact angle  $\theta$ , papers and textiles can turn to be hydrophobic, they can be wetted by hydrocarbons such as benzene and paraffin oil. The latter can go through freely while the water is prevented. By combining filter papers treated and untreated, the oil water mixtures can be separated.

(2) The inner wall of pipes of the copper condenser can turn to hydrophobic after being treated with a small amount of dithio-octadecane ( $C_{18}H_{37}S \cdot SC_{18}H_{37}$ ). Water vapor forms tiny droplets during condensation rolling down along the wall making the most part of the wall uncovered by the liquid film, therefore, the heat efficiency is greatly enhanced (about ten fold).

(3) Foam flotation can improve the quality of mineral ore. The basic principle is treating the milled crude ore with the ore-dressing agent making the surface of ore particles hydrophobic (greater  $\theta$ ). The exposed part of the small particles in the gas phase is therefore increased as shown in Figure 15-19. Further, we add the bubbling agent into the tank, stir and aerate, those hydrophobic ore particles adhere on the bubbles and rise to the liquid surface, after collection, foam breaking, the quality of the mineral ore is improved. The silts mingled in the ore are mainly silicates. They are hydrophilic, therefore, remain in the bottom of the tank to be removed.

(4) Adding suitable amount of surfactant into pesticides can strengthen their wetting function towards plants or insects then enhance the efficiency.

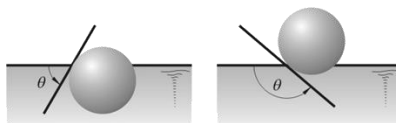


Figure 15-19 Contact angle and the position of solid particle on liquid surface

(5) Adding OT (dioctyl sodium sulfosuccinate) and other surfactants into photographic latex before coating in film manufacture process can improve the wetting function of the latex to film base then raise the coating speed.

#### 4. Insoluble Monomolecular Films

When dropping a tiny amount of surfactant (dissolved in a solvent) with very small solubility in water on the water surface, the surfactant spreads to form an interfacial film (membrane) which is an insoluble monomolecular film. The carbon chain of the lipophilic group of these surfactants is usually long, for example, hexadecanoic acid (palmitic acid) with a 15 C chain, oleic acid which is unsaturated and with a 17 C chain, tetradecanol with a 14 C chain,  $\alpha$ -hydroxyl tetracosanoic acid with a 24 C chain, as well as cholesterol, lecithin, polyvinyl acetate, poly benzoic esters, etc. The formation of insoluble monomolecular film is one of the foundations of self-organization, referring to 10.12 Super Molecules.

(1)  $\pi$ - $A_s$  Relations  $\pi$  is the spreading pressure. A monomolecular film can be considered as a two-dimensional fluid. Similar to the isothermal  $p$ - $V$  relation for a three-dimensional fluid, we have the isothermal  $\pi$ - $A_s$  relation as a characteristic property for a two-dimensional monomolecular film. Figure 15-20 is a sketch of a film balance for measuring  $\pi$ - $A_s$  relations. A barrier (float) is located in between the monomolecular film and the pure water, the force bore per unit length of the barrier is the difference between the interfacial (surface) tension of pure water  $\sigma^*$  and that of the monomolecular film  $\sigma$ . By definition of Eq.(15-3),  $\pi = \sigma^* - \sigma$ , that is the spreading pressure. To keep the interfacial area unchanged, an external force should be applied, the external force per unit length has the same magnitude as  $\pi$  but with an opposite direction. It can be measured by a pressure sensor. Measuring  $\pi$  corresponding to

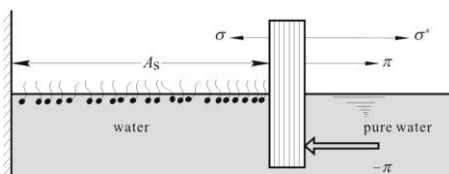
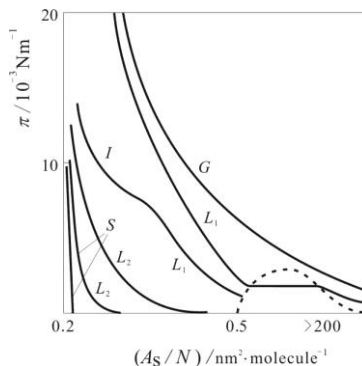


Figure 15-20 Sketch of a film balance

different  $A_s$ , we obtain  $\pi$ - $A_s$  relation. Figure 15-21 depicts different types of  $\pi$ - $A_s$  relation. There are similarities between  $\pi$ - $A_s$  diagram and  $p$ - $V$  diagram of fluids. For example, the part surrounded by dash line is a two-phase coexistence region.

**Solid Film** The  $S$  line on the left-most side in the figure is very steep indicating that the film is nearly incompressible called a solid film. Long chain aliphatic acids and alcohols belong to this type. The intersection of the  $S$  line (or its prolonged line) and the abscissa at  $\pi=0$  is about  $0.2 \text{ nm}^2\cdot\text{molecule}^{-1}$ , it is the cross section area of the molecular chain. The cross section area determined by the crystal structure of aliphatic acids is  $0.185 \text{ nm}^2\cdot\text{molecule}^{-1}$  indicating that the molecules in the monomolecular solid films are nearly tightly arranged.

Figure 15-21 Various types of  $\pi$ - $A_s$  relation

**Liquid Condensed Film** For the  $L_2$  line, it exhibits a little greater compressibility than that of the  $S$  line. In this case, the water molecules might be mixed with the hydrophilic terminals of the surfactant molecules resulting in larger polar heads that could be interlocked during compression, therefore, enhance the compressibility. The corresponding film is therefore called a liquid condensed film. The second line on the left side in the figure shows a transition from  $S$  to  $L_2$ . Cholesterols, hydroxyl aliphatic acids belong to this type.

**Liquid Expanded Film**  $L_1$  line in the figure is similar to a typical  $p$ - $V$  plot for a fluid. Molecules in the film might be partly inclined or lie down on the surface resulting in greater compressibility. The intersection of the prolonged  $L_1$  line and the abscissa at  $\pi=0$  is a little larger than  $0.5 \text{ nm}^2\cdot\text{molecule}^{-1}$ , far apart from the tightly arrangement. It is possible that a liquid-gas phase change appears when  $\pi$  is low enough as shown by the horizontal segment of the line. The corresponding film is then called a liquid expanded film. Pentadecanol is an example. On the left side of  $L_1$ , there is a line where the curve rises up as usual ( $L_1$ ) with increasing  $\pi$ , then the curve subsides again ( $I$ ) indicating a possible structure collapse. Figure 15-22 shows results for pentadecanoic acid at a temperature range of  $17.9^\circ\text{C}$  to  $35.2^\circ\text{C}$ , indicating a transition from type  $L_1$  to type  $L_2$ .

**Gaseous Film** For the  $G_1$  line on the right side, molecules

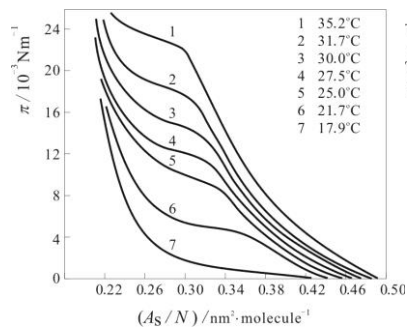


Figure 15-22  $\pi$ - $A_s$  relations for pentadecanoic acid  
Boyd G E. J Phys Chem, 1958, 62: 536.

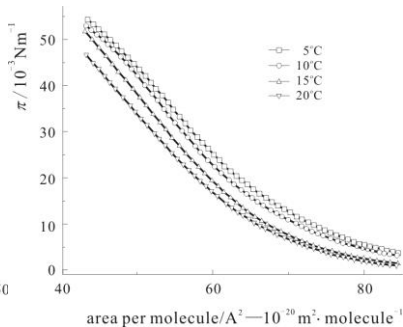


Figure 15-23  $\pi$ - $A_s$  for 17PyOx film with negative  
thermal expansion. Zhou M et al. to be published

completely lie down on the surface with a behavior similar to gas. The corresponding film is therefore called a gaseous film. Many surfactants including proteins and some polymers at a low spreading pressure belong to this type.

**Abnormal Case** In general, the film exhibits a positive thermal expansion as shown in Figure 15-22. The higher the temperature, the larger spreading pressure will be at a constant surface area. Recently, a very rare abnormal case was found that on the contrary, the lower spreading pressure is exhibited with increasing temperature. Figure 15-23 depicts this abnormal phenomena for a film made of N',N'-bis (4-heptadecylpyridin-2-yl) oxamide hydrochloride (17PyOx), a novel gemini surfactant, containing pyridine headgroups and an oxamide spacer. The figure shows clearly a negative thermal expansion for the film. The reason might lie in the fact that the film forms network due to hydrogen bonding. As the temperatures increases, part of the hydrogen bonding breaks resulting in the shrinkage of the film.

**Equation of State for Monomolecular Film** Semi-empirical method is usually used to construct equations of state for monomolecular films, i.e., the  $\pi A_{sm} T$  relations (similar to  $pVT$  relations for fluids),  $A_{sm}$  is the molar interfacial area. For example, analogy to the ideal-gas equation and the van der Waals equation, we have

$$\pi A_{sm} = RT \quad (15-72)$$

$$\left( \pi + \frac{a}{A_{\text{sm}}^2} \right) (A_{\text{sm}} - b) = RT \quad (15-73)$$

For theoretical studying, the statistical-mechanics method is usually adopted.

**Application** A well-known example is applying the insoluble film on the water surface to prevent reservoirs and lakes from evaporation.

(2) **LB Film** Langmuir I in 1920 and Blodgett K B in 1935, early and late respectively, realized depositing multi-layer monomolecular films on glass or metal surfaces, known as the LB film. Due to the demand in the field of micro-electronic materials and non-linear optical materials, LB film

has recently attracted great

interests. A sketch of the

preparation method is shown

in Figure 15-24.

A glass plate is

slowly immersed into the water surface covered with monomolecular film (such as barium stearate), on the plate, a monomolecular film with the lipophilic group pointing to the glass plate (type A) is then formed. If the glass plate immersed in water is slowly pulled out, a monomolecular film with the hydrophilic group pointing to the plate (type B) can be observed. Repeat the procedure, materials with a thickness of hundreds of layers can be prepared, i.e., the LB film. If the deposit sequence is AAA..., it is called a X film, if in turn as ABAB..., it is called a Y film, while BBB... is called a Z film.

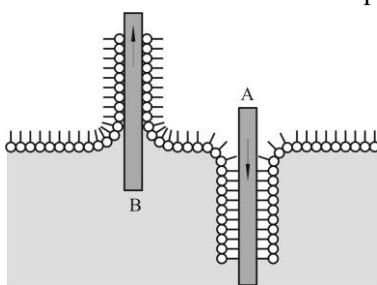


Figure 15-24 Preparation of LB film

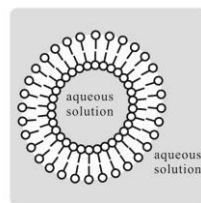


Figure 15-25 Vesicle

(3) **Bi-layer Membranes and Vesicles** Substances with a structure similar to lecithin shown in Figure 15-17 are easy to form a lamellar structure shown in Figure 15-19, which is called bi-layer membranes (films). They are formed by two monomolecular films with two lipophilic groups contacted together. With a special preparation method, we can have vesicles shown in Figure 15-25. The two surfaces inside and outside the vesicle wall

are both composed of hydrophilic groups, therefore, inside and outside the vesicle can all be aqueous solutions but can dissolve different solutes. This vesicle is a very good model for bio cells.

#### (4) Surface Structure of Films     The scanning tunneling microscopy

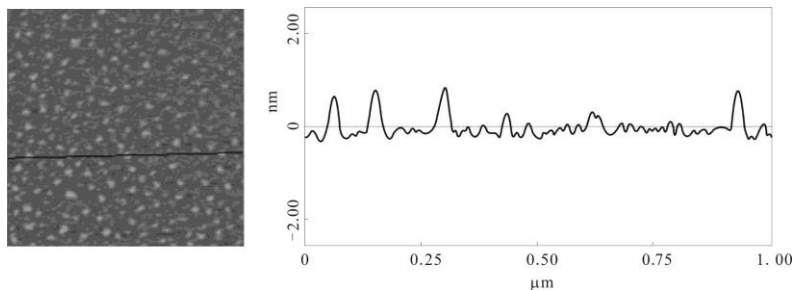


Figure 15-26 AFM image of a LB film by 18-Ar-18,2Br<sup>-1</sup>, the right picture corresponds to the height distribution along the straight line in left picture with a scale of nm.

Chen Q B, Liang X, Wang S, Xu S, Liu H, Hu Y. J Colloid Interface Sci. 2007, 314: 651.

(STM) introduced in 9.6.3, or the atomic force microscopy (AFM) developed on the basis of STM can be adopted to study the surface structure of films. The latter, the AFM, can provide the surface morphologies by measuring the weak repulsion force between the measuring tip and the surface. Figure 15-26 is an AFM image of a LB film which is formed by a Gemini surfactant on water at  $\pi=20$  mN/m, then transferred as a sample. The chemical formula of the surfactant is [C<sub>18</sub>H<sub>37</sub>(CH<sub>3</sub>)<sub>2</sub>-N<sup>+</sup>-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-N<sup>+</sup>-(CH<sub>3</sub>)<sub>2</sub>C<sub>18</sub>H<sub>37</sub>], 2Br<sup>-1</sup> abbreviated as 18-Ar-18, 2Br<sup>-1</sup>, it has two hydrophilic groups connected by a spacer Ar (C<sub>6</sub>H<sub>4</sub>) followed by two hydrophobic tails. The figure vividly shows the distribution of rod-like micelles on the planar substrate.

## 15.10 Adsorptions on Solid Surface

The most fundamental characteristic property of gas-solid and liquid-solid interfaces is the unit interfacial adsorption and its variation with temperature, pressure and bulk concentration. From these sorts of information, the interfacial tension not easy to be directly determined can be estimated.

### 1. Adsorption and Amount of Adsorption

**Adsorption Phenomena** Adding some active carbon into bromine



vapor or aqueous iodine solution, the color of the vapor and solution pales indicating the gradually enrichment of bromine and iodine on the surface of active carbon. This concerns the adsorption of gas on gas-solid or solute on liquid-solid interfaces. The solid substance with adsorption effect is called an **adsorbent**. The adsorbed substance is called an **adsorbate**.

**Gibbs Unit interfacial Adsorption** In gas-solid and liquid-solid systems, substances in gas or liquid phase generally do not enter the bulk of the solid phase, the definition of the Gibbs unit interfacial adsorption (here the adsorption means the amount of adsorption) Eq.(15-7) becomes

$$\Gamma_2^{(1)} = \Gamma_2 - \Gamma_1 c_2^{(l,g)} / c_1^{(l,g)} \quad (15-74)$$

**Gas-Solid Adsorption** Because densities of the gas and the interfacial layer differ seriously, the latter is close to that of liquid, the position of the boundary between the gas phase and the interfacial layer is not sensitive, therefore, in general, it is not necessarily to use the Gibbs unit interfacial adsorption  $\Gamma_i^{(1)}$ , instead, we can directly use the unit interfacial adsorption  $\Gamma_i$ ,  $\Gamma_i = n_i^{(\sigma)} / A_s$ . For convenience, we can use the volume of the adsorbed gas at standard condition  $V(\text{STP})$  and the mass of the adsorbent

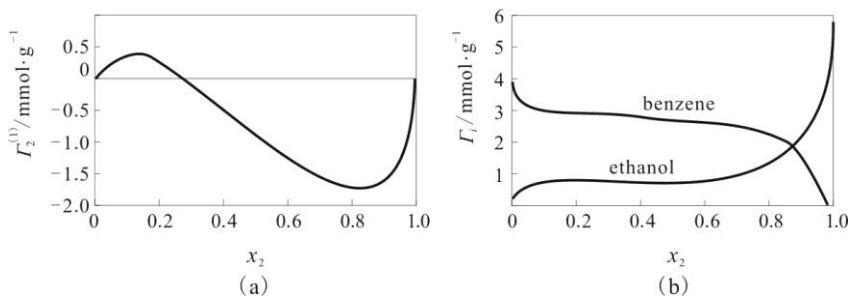


Figure 15-27 Adsorption of Benzene(1)-ethanol(2) on charcoal at 20°C  
Bartell F E, Sloan C K. JACS, 1929, 51:1643. Kipling J J, Tester D A. J Chem Soc, 1952, 20: 4123.

$m$  to replace  $n_i^{(\sigma)}$  and  $A_s$ , respectively.  $\Gamma_i$  can then be expressed as:

$$\Gamma_i = n_i^{(\sigma)} / A_s, \quad \Gamma_i = V(i, \text{STP}) / A_s \quad (15-75)$$

$$\Gamma_i = n_i^{(\sigma)} / m, \quad \Gamma_i = V(i, \text{STP}) / m \quad (15-76)$$

**Liquid-Solid Adsorption** Because densities of the liquid phase and the interfacial layer do not differ seriously, we have to carefully distinguish  $\Gamma_i^{(1)}$  and  $\Gamma_i$ . Figure 15-27 depicts variations of the amount of adsorption of benzene(1)-ethanol(2) on charcoal with the bulk liquid composition. Where

(a) is the Gibbs unit interfacial adsorption  $\Gamma_2^{(1)}$ , benzene is regarded as a solvent. The figure shows that at low  $x_2$ ,  $\Gamma_2^{(1)} > 0$ , it is positive adsorption for ethanol. As  $x_2$  increases, gradually  $\Gamma_2^{(1)} < 0$ , turns to negative adsorption. (b) is the unit interfacial adsorption  $\Gamma_1$  and  $\Gamma_2$ , both benzene and ethanol exist in the interfacial layer. When  $x_2$  is low,  $x_2^{(\sigma)} = \Gamma_2 / (\Gamma_1 + \Gamma_2)$  in the interfacial layer calculated by  $\Gamma_1$  and  $\Gamma_2$  is greater than  $x_2$  indicating a positive adsorption for ethanol. As  $x_2$  rises,  $x_2^{(\sigma)}$  is less than  $x_2$ , it is then negative adsorption for ethanol. Clearly, adopting  $\Gamma_i^{(1)}$  is more intuitive.

**Surface Coverage  $\theta$**  It is defined as:

$$\theta \stackrel{\text{def}}{=} \Gamma / \Gamma_{\infty} \quad (15-77)$$

$\Gamma_{\infty}$  is the amount of adsorption when covered with a monomolecular layer.

The adsorption might be multi-layer if  $\theta$  greater than 1.

## 2. Variation of Adsorption with Temperature and Pressure

We focus on  $\Gamma T p$  relations for the gas-solid adsorption and also give a little attention to  $\Gamma T b$  relations for the liquid-solid adsorption,  $b$  is the morality of liquid phase. In the latter, the effect of pressure can be neglected.

**Adsorption Isotherm** The  $\Gamma \sim p$  relation in Figure 15-28 for the gas-solid adsorption and the  $\Gamma \sim b$  relation in Figure 15-29 for the liquid-solid adsorption at constant temperature are called the adsorption isotherm.

**Adsorption Isobar** The  $\Gamma \sim T$  relation in Figure 15-30 for the gas-solid adsorption at constant pressure is called the adsorption isobar.

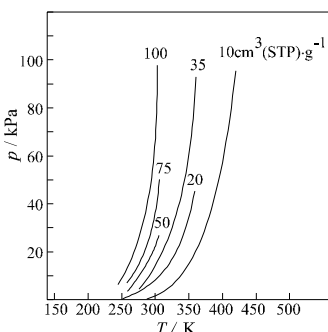
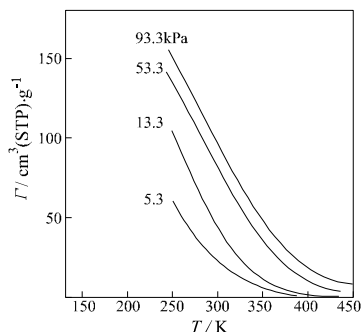


Figure 15-30 Adsorption isobar of  $\text{NH}_3$  on charcoal. Figure 15-31 Adsorption isostere of  $\text{NH}_3$  on charcoal.

**Adsorption Isostere** The  $T \sim p$  relation in Figure 15-31 for the gas-solid adsorption and the  $T \sim b$  relation for the liquid-solid adsorption at constant amount of adsorption are called the adsorption isostere.

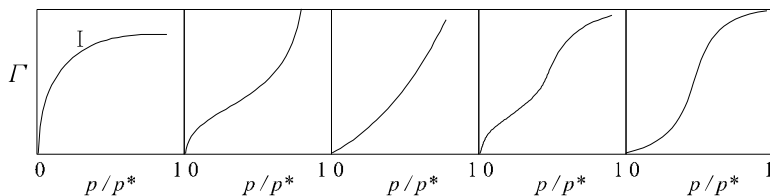


Figure 15-32 Five types of adsorption isotherms.

**Types of Isotherms** There are five types of isotherms for the gas-solid adsorption shown in Figure 15-32, where abscissa is the related pressure  $p/p^*$ ,  $p^*$  is the vapor pressure of the adsorbate at system temperature. Type I is also called the Langmuir type. Adsorptions of  $\text{NH}_3$  on blood charcoal and  $\text{O}_2$  on silica gel at low temperature are examples. Type II is more common, it is usually called the S type isotherm.  $\text{N}_2$  on silica gel and

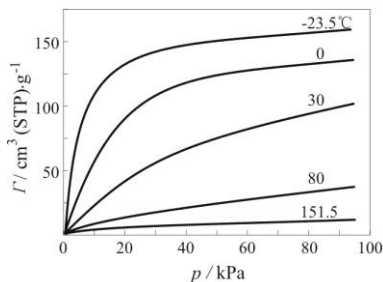


Figure 15-28 Adsorption isotherm of  $\text{NH}_3$  on charcoal. Brunauer S. The Adsorption of Gases and Vapors. Princeton University Press: Princeton. 1945, p14.

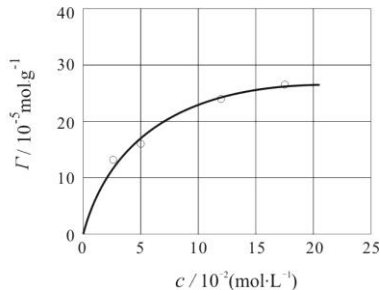


Figure 15-29 Adsorption isotherm of lauric acid adsorbed from  $\text{CCl}_4$  on carbon black. Smith H A, Hurley R B. J Phys Chem, 1949, 53:1409.

on Fe catalyst at low temperature (78K) are examples. Type III distinguishes itself from the type II by its concave-upward shape.  $\text{Br}_2$  on silica gel at 352K is an example. Type IV is similar to the type II except that the adsorption approaches saturation when the related pressure is close to 1. Benzene on iron oxide at 323K is an example. Type V is similar to the type III except that the adsorption approaches saturation when the related pressure is close to 1. Water vapor on charcoal at 373K is an example. Types of the liquid-solid adsorption are more or less similar to those of the gas-solid adsorption.

**Phase Change in Interfacial Layer** Similar to fluids, phase change sometimes can be observed in the interfacial layer during adsorption. Figure

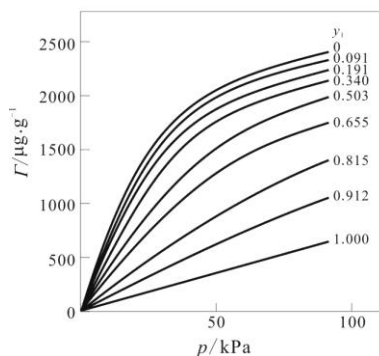


Figure 15-34 Adsorption isotherms of ethane(1)-propane(2) mixture on carbon black at 25°C.

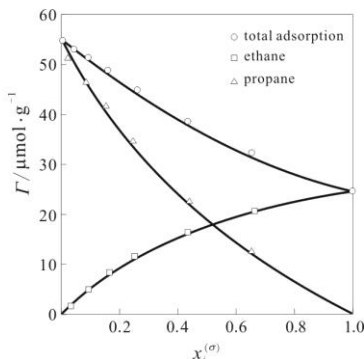


Figure 15-35 Adsorptions of various substances vary with compositions of interfacial layer corresponding to Figure 15-34 at 25°C, 43.3kPa.

Friederich R O, Mullins J C. Ind Eng Chem Fundam, 1972, 11(4): 439.

15-33 depicts isotherms of Kr adsorbed on NaBr solid plotted as the surface coverage  $\theta$  with respect to  $p$  at different temperatures. At low temperatures, nearly vertical lines appear corresponding to a gas-liquid phase change. Inside the dash line of the figure is a two-phase region; the vertex of it is the critical point of the interfacial layer.

**Adsorption Isotherm for Gas Mixture** It is the  $\Gamma \sim p$  relation at constant temperature and constant gas phase composition  $y_i$ ,  $\Gamma$  is the total amount of adsorption. Figure 15-34 shows adsorption isotherms of ethane-propane mixtures on carbon black. Figure 15-35 is the corresponding relations  $\Gamma_i \sim x_i^{(\sigma)}$  for various components at constant temperature and pressure,  $x_i^{(\sigma)}$  is the composition in the interfacial layer.

**Enthalpy of Adsorption** Generally, adsorption is exothermic. Similar to gas-liquid equilibrium where we can calculate the enthalpy of vaporization from the variation of vapor pressure with temperature, by using

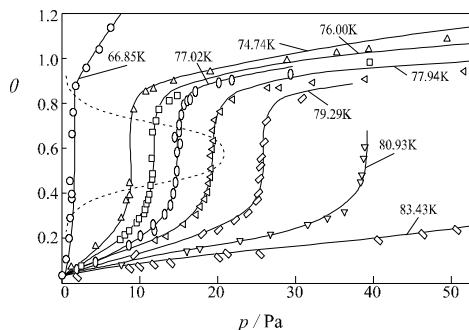


Figure 15-33 Adsorption isotherms of Kr on NaBr. Azarnoff D A, Curran G L. JACS. 1957, 79:2969

the Clapeyron-Clausius equation (2-126), we can also obtain the enthalpy of adsorption  $\Delta_{\text{ads}} H_m$  from  $T$ - $p$  relations of the adsorption isosteres. Figure 15-36 depicts variation of the enthalpy of adsorption for He on  $\text{TiO}_2$  with the adsorption amount. The absolute value of the enthalpy of adsorption decreases as the adsorption amount increases. The change is especially

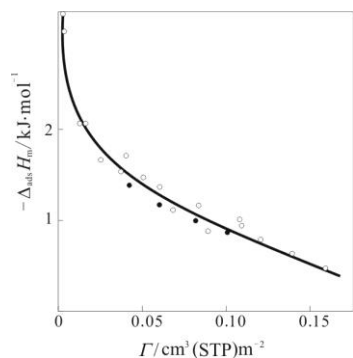


Figure 15-36 Enthalpy of adsorption of He on  $\text{TiO}_2$  surface varies with the amount of adsorption.

○—calorimetry data at 14.5K

●—calculated by isosteres at 17.1K

Steele W A, Aston J G. J Am Chem Soc, 1957, 79:2393

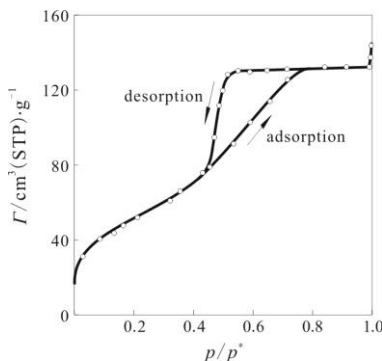


Figure 15-37 Adsorption and desorption of  $\text{N}_2$  on Si-Al cracking catalyst.

Van Nordstrand R A, Kreger W, Ries H E.

J Phys Chem, 1951, 55:621.

striking at the beginning of adsorption, this is usually caused by the surface heterogeneity, adsorption prefers those sites with higher activity; the enthalpy of adsorption is therefore more negative.

### 3. Adsorption Hysteresis

After gas is adsorbed on some adsorbents, if lowering the pressure to allow desorption, hysteresis phenomena could happen. Figure 15-37 shows the adsorption and desorption isotherms for  $\text{N}_2$  on a Si-Al cracking catalyst. As the desorption just begins, the two curves still coincide. When  $p/p^*$  is less than 0.8, the hysteresis starts, the desorption isotherm leaves that of the adsorption. When  $p/p^*$  is less than 0.5, the hysteresis comes to an end, the two isotherms coincide again. The nature of the phenomena is quite complicated.

### 4. Physical Adsorption and Chemical Adsorption

**Physical Adsorption** It is mainly caused by van der Waals forces similar to gas liquification and can be regarded as surface condensation. Generally, no selectivity is observed. The easier to be liquefied, the more the

gas is to be adsorbed. The adsorption could be monolayer or multilayer, but is generally the latter. It is “reversible”; the desorbed species is the same as the adsorbate. The enthalpy of adsorption is close to that of condensation. Rates of adsorption and desorption are high; equilibrium is easier to attain.

**Chemical Adsorption** It is characterized by the chemical bond formation on the solid surface during the adsorption and can be regarded as a surface chemical reaction. Notable selectivity is generally observed. It always forms monomolecular layer. It is mostly “irreversible”; the desorbed species is often different from the adsorbate. For instance, after adsorption of  $O_2$  on charcoal, the desorbed species contains CO and  $CO_2$ . The enthalpy of adsorption is in general higher (more negative) than  $-80\text{kJ}\cdot\text{mol}^{-1}$ ; the order of magnitude is approximately the same as that of chemical reactions. Rates of adsorption and desorption are usually small; equilibrium is not easy to attain at low temperatures.

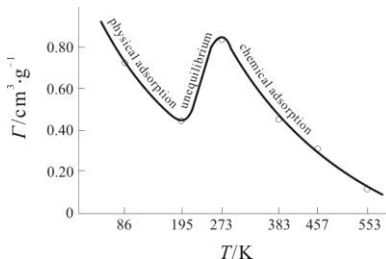


Figure 15-38 Adsorption isobar (20kPa) of CO on Pt. Taylor H S, McKinney P V. J Am Chem Soc, 1931, 53 (10): 3604

**Physical and Chemical Adsorptions Could Happen either Sequentially or Simultaneously** Figure 15-38 shows the adsorption isobar of CO on Pt. At a low temperature, it is a physical adsorption, the amount of adsorption decreases with increasing temperature. Between  $-100^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ , chemical adsorption starts, but does not attain equilibrium, therefore, the amount of adsorption increases with rising temperature. Above  $0^{\circ}\text{C}$ , chemical adsorption reaches equilibrium, the amount of adsorption decreases again as the temperature further increases. This is an example of sequentially happening. In some cases, physical and chemical adsorptions can happen simultaneously. For instance, adsorption of  $O_2$  on metals can have three types existing simultaneously: chemical adsorption with atomic O adsorbed, physical adsorption with molecular  $O_2$  adsorbed, besides, there are some molecular  $O_2$  adsorbed on oxygen atoms.

## 5. Temperature-Swing and Pressure-Swing Adsorptions

In industry, adsorption operation is mostly adopting the temperature-swing style. Referring to Figure 15-39, where two isotherms at two different temperatures are depicted. Usually adsorption and desorption take place at lower and higher temperatures  $T_1$  and  $T_2$ , respectively. Because of the bad heat transfer function of the solid adsorbent, energy utilization and operation efficiency are highly limited. Since 1960s, the pressure-swing adsorption develops, see Figure 15-39, adsorption and desorption take place at the same temperature but respectively at higher pressure and lower pressure  $p_1$  and  $p_2$ . The efficiency is greatly enhanced. Economic analysis indicates that the cost of pressure-swing adsorption in manufacturing liquid nitrogen is even much lower than that of the cryogenic separation.

## 15.11 Semi-Empirical and Theoretical Methods in Gas-Solid Adsorptions

### 1. Experimental Methods

In principle, there are two methods for adsorption measurements: the **volumetric method**, measuring the change of the gas volume before and after the adsorption, and the **gravitational method**, measuring the change of the weight of the adsorbent before and after the adsorption.

### 2. Semi-Empirical Models

#### (1) Freundlich Equation

$$\Gamma = k p^{1/l}$$

This is an empirical equation named after Freundlich H. It is widely used for data correlation.  $k$  and  $l$  are empirical parameters. Plot of  $\lg\{\Gamma\}$  against  $\lg\{p\}$  should be straight line. However, deviation always occurs in wider range.

#### (2) Langmuir Adsorption Isotherm

**Adsorption Model** Langmuir I proposed in 1916 that the force field of atoms on solid surface is unsaturated that can adsorb gas or solute molecules colliding to the surface. After adsorbing a layer of molecules, the

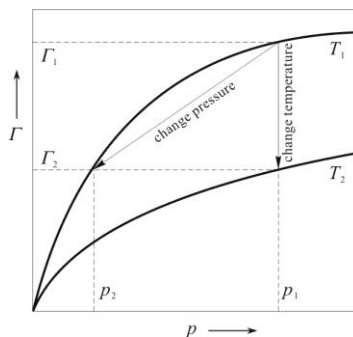


Figure 15-39 Temperature-swing and pressure-swing adsorptions

force field is saturated. Therefore, adsorption layer is a monomolecular layer. Further suppose that the solid surface is homogeneous and no interactions occur between adsorbed molecules.

**Derivation** Suppose at a moment, the surface coverage of adsorbed molecules on solid surface is  $\theta$  defined by Eq.(15-77), the area fraction of the uncovered surface is correspondingly  $1-\theta$ . From the kinetic theory of gas, the number of molecules striking a unit surface in a unit time is proportional to the gas pressure  $p$ . Expressions for the rates of adsorption and desorption of gas,  $v_2$  and  $v_1$ , can then be respectively written as follows:

$$v_2 = k_2 p(1-\theta) \quad , \quad v_1 = k_1 \theta \quad (15-79)$$

where  $k_2$  and  $k_1$  are rate constants for the adsorption and the desorption, respectively. When reaching equilibrium,  $v_2 = v_1$ , we have

$$\theta = \frac{k_2 p}{k_1 + k_2 p} = \frac{bp}{1 + bp} \quad (15-80)$$

where  $b=k_2/k_1$ , is called the **adsorption coefficient**. Substitution of Eq.(15-77)  $\theta = \Gamma / \Gamma_\infty$  yields

$$\Gamma = \Gamma_\infty \frac{bp}{1 + bp} \quad (15-81)$$

Eqs.(15-80, 15-81) are the Langmuir adsorption isotherm.  $\Gamma_\infty$  and  $b$  are two characteristic parameters of the adsorption system.

**Features** Generally, chemical adsorption or physical adsorption in micro pores builds a monomolecular layer; the Langmuir model is especially suitable. Eq.(15-81) can well explain the type I adsorption in Figure 15-32. At a low pressure,  $bp$  is much smaller than 1,  $1+bp \approx 1$ ,  $\Gamma = \Gamma_\infty bp$ ,  $\Gamma$  is proportional to  $p$  (this is also a form of Henry's law). At a high pressure,  $bp$  is much greater than 1,  $1+bp \approx bp$ ,  $\Gamma = \Gamma_\infty$ , indicating that the adsorbent surface is completely covered by a monomolecular layer of adsorbate.  $\Gamma_\infty$  is called the **monomolecular saturated adsorption**. Rearrange Eq.(15-81) to

$$\frac{p}{\Gamma} = \frac{1}{\Gamma_\infty b} + \frac{p}{\Gamma_\infty} \quad (15-82)$$

Plotting  $p/\Gamma$  against  $p$  should be a straight line. This Eq.(15-82) was just the empirical equation found by Langmuir from experiment before he established his model. Using the slope and the intersection with the ordinate of the straight line,  $b$  and  $\Gamma_\infty$  can be obtained.



(3) **Frumkin-Srukin Adsorption Isotherm** The adsorption coefficient  $b$  of Eq.(15-80) corresponds to the adsorption equilibrium constant. It has the following relation with the enthalpy of adsorption  $\Delta_{\text{ads}} H_m$ ,

$$b = A_0 \exp(-\Delta_{\text{ads}} H_m / RT) \quad (15-83)$$

As it is pointed out in 15.10.2, due to the surface heterogeneity of the adsorbent, the absolute value of the enthalpy of adsorption diminishes as the surface coverage increases. In 1935, Frumkin and Srukin (Фрумкин А Н, Слукин А) proposed that there is a linear relation between the enthalpy of adsorption and the surface coverage with two parameters  $\Delta H_0$  and  $\beta$ ,

$$\Delta_{\text{ads}} H_m = \Delta H_0 (1 - \beta \theta) \quad (15-84)$$

Substitution of Eqs(15-83, 15-84) into Eq.(15-80) yields

$$Ap = [\theta / (1 - \theta)] \exp(-\beta \Delta H_0 \theta / RT) \quad (15-85)$$

where  $A = A_0 \exp[-\Delta H_0 / RT]$ . Taking logarithms for the two sides of the equation, and omitting  $\ln[\theta / (1 - \theta)]$  at moderate pressure, we obtain

$$\theta = -\frac{RT}{\beta \Delta H_0} \ln Ap \quad (15-86)$$

This is the Frumkin-Srukin adsorption isotherm widely used in chemical adsorption on non-homogeneous surface.

(4) **BET Adsorption Isotherm** In 1938, Brunauer S, Emmett P H and Teller E proposed the idea of multi-layer adsorption, referring to Figure 15-40. The model considers: The first layer is formed by the intermolecular force between solid and gas, but the adsorbed molecules still have attraction with the gas. Because of this intermolecular force between the adsorbate molecules, the second layer, third layer, ... can form on the first adsorption layer sequentially, similar to the gas condensation. Treat each layer with the Langmuir model, and sum up the adsorption of all layers, BET adsorption isotherm is finally derived which is suitable for the physical adsorption,

$$\Gamma = \Gamma_{\infty} \frac{cp}{(p^* - p)[1 + (c - 1)p/p^*]} \quad (15-87)$$

where  $c$  is the characteristic parameter concerning the enthalpy of adsorption

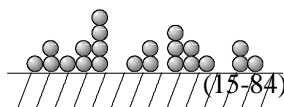


Figure 15-40 Multi-layer adsorption model

of the first layer and the enthalpy of condensation,  $p^*$  is the vapor pressure of the adsorbate. BET adsorption isotherm can well express the middle part of all the five types of adsorption isotherms especially for the S style of type II, best in the range of  $p/p^*=0.05-0.35$ . Isotherms of N<sub>2</sub> and Ar on silica gel

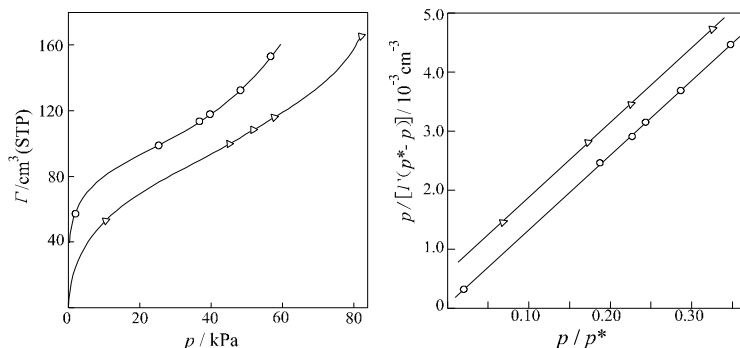


Figure 15-41 Adsorption isotherms of two gases on 0.606g silica gel. o- N<sub>2</sub>, -195.8°C; Δ- Ar, -183°C.

Brunauer S, Emmett P H. JACS, 1937, 59:2682;

Brunauer S, Emmett P H, Teller E. JACS, 1938, 60:309.

Figure 15-42 BET diagram for Figure 15-41.

shown in Figure 15-41 are examples. Rearranging Eq.(15-87),

$$\frac{p}{\Gamma(p^* - p)} = \frac{1}{\Gamma_{\infty}c} + \frac{c-1}{\Gamma_{\infty}c} \cdot \frac{p}{p^*} \quad (15-88)$$

Plot  $p/[\Gamma(p^* - p)]$  against  $p/p^*$ , a straight line can be obtained,  $c$  and  $\Gamma_{\infty}$  can be calculated by the slop and the intersection with the ordinate.  $\Gamma$  in equation can be expressed by any of Eqs.(15-75, 15-76), or by the mass of the adsorbate. Figure 15-42 is plotted by the data of Figure 15-41 showing good linear relations.

**Improvement** If setting a limit for the number of adsorption layers, we can derive a new BET equation with three parameters. The application range extends to  $p/p^*=0.60$ . Further improvement should consider the heterogeneity of the solid surface, the interactions between molecules in the same layer, and the capillary condensation.

**Applications** The most popular application is to determine the specific surface area of adsorbents and catalysts. From the  $\Gamma_{\infty}$  value obtained, we can calculate the number of molecules fully covered a monomolecular layer. Giving the area occupied by a single molecule, the interfacial (surface) area is then obtained.

**Example** Adsorption of methanol vapor on silica white at 40.0°C was measured by gravitational method. Data are listed in the table where  $\Gamma$  is expressed by mass. The mass of the adsorbent  $m=0.2326\text{g}$ ,  $p^*=35.09\text{kPa}$ , the area occupied by a single methanol molecule  $A_m=0.25\text{nm}^2\cdot\text{molecule}^{-1}$ . Calculate specific area of the silica white sample.

$p/\text{kPa}$	$p/p^*$	$\Gamma \times 10^3/\text{g}$	$p/[\Gamma(p^* - p)]/\text{g}^{-1}$
1.653	0.0472	5.70	8.7
3.706	0.106	8.05	14.8
5.805	0.165	9.10	21.8
7.551	0.215	9.85	27.8

**Solution:** According to Eq.(15-88), plotting  $p/[\Gamma(p^* - p)]/\text{g}^{-1}$  against  $p/p^*$ , a straight line is obtained with  $\text{slope}=118$ ,  $\text{intersection}=2.5$ ,

$$\Gamma_\infty/\text{g} = (\text{slope} + \text{intersection})^{-1} = (118 + 2.5)^{-1} = 0.00829$$

For methanol,  $M=32.0\text{g}\cdot\text{mol}^{-1}$ ,  $A_m=0.25\text{nm}^2\cdot\text{molecule}^{-1}$ , the total area of silica white is

$$A_s = (\Gamma_\infty/M)LA_m = (0.00829/32.0) \times 6.022 \times 10^{23} \times 0.25 \times 10^{-18} \text{m}^2 = 39\text{m}^2$$

The specific area,  $A_{s0} = A_s/m = 39\text{m}^2/0.2326\text{g} = 1.7 \times 10^2 \text{m}^2\text{g}^{-1}$

(5) **Capillary Model** Fine gaps of a porous adsorbent can be modeled as capillary tubes with various big and small radii. Easily liquefiable vapor can not only be adsorbed on the surface as multi-layers, but also be condensed as a liquid in the capillary gaps (tubes). The latter is called the **capillary condensation phenomena**.

If a liquid can be well wetted on the inner surface of a solid capillary tube, the meniscus formed should be concave. From the Kelvin equation (15-47), the vapor pressure of the concave surface  $p_r^*$  is lower than that of the planar surface  $p^*$ . Therefore, the vapor unsaturated to the planar liquid could be saturated to the concaved liquid in the capillary tube and be condensed. For a given pressure of the vapor, suppose a zero contact angle, the radius of meniscus equals that of the capillary tube, from Eq.(15-47), we can calculate the radius  $r_i$  of the capillary tube in which the vapor with a pressure  $p_i$  starts condensation. Obviously, vapor with a pressure  $p_i$  can be condensed in all those micro pores with radius smaller than  $r_i$ . As the pressure of the vapor gradually increases, the larger micro pores will be filled up, the amount of adsorption will be quickly increased. As shown in Figure 15-32, for all types except type I, isotherms quickly bend upward after  $p/p^*$  is greater than 0.4.

**Applications** With the Kelvin equation, the pore distribution of porous materials can be obtained from the adsorption or the desorption

isotherms. Besides, if the shape of a micro pore is bottle like with a narrow neck, adsorption starts from the bottom with a larger radius requiring higher pressure, desorption starts from the bottle neck with a smaller radius requiring a lower pressure. This might be one of the reasons for the adsorption hysteresis.

**(6) Interpretations for Five Types of Adsorption Isotherm**    In the five types of adsorption isotherm shown in Figure 15-32, type I is the Langmuir type with a monomolecular layer formed. Chemical adsorption is generally this type. For the physical adsorption on an adsorbent composed of micro pores with radius below 2~3nm, although the multi-layer adsorption and capillary condensation could happen at lower relative pressure resulting in a sharp increase of adsorption as the relative pressure increases, the micro pores quickly fill up, the adsorption no longer increases and approaches saturation, therefore, it displays as the type I. This tells us that the type I adsorption isotherm is not necessarily only for chemical adsorption, physical adsorption is also possible. For the type II, the adsorbent generally possesses micro pores with radius greater than 5 nm. From the beginning to  $p/p^*=0.1$ , adsorption is monomolecular layer, consequently, the multi-layer adsorption starts, after  $p/p^*=0.4$ , the capillary condensation happens, because no high limit for the radius of pores, the adsorption sharply increases with pressure, the ordinary condensation prevails finally. For the type IV, the adsorbent possesses micro pores with radius between 2 nm to 20 nm. When the relative pressure approaches 1, the large pores fill up, the adsorption approaches saturation. For types III and V, the adsorption force between adsorbent and adsorbate is weak, the adsorption at the beginning is small, as the relative pressure further increases, the adsorption quickly enhances due to the multi-layer adsorption and capillary condensation; the isotherms are therefore concave upward. The difference between the type III and the type V is similar to that between the type II and the type IV when the relative pressure approaches 1.

**(7) Ideal Adsorption Solution Model (IAS)**    For the adsorption of gas mixture, Myers A L and Prausnitz J M proposed in 1965 that the mixture in the adsorption layer can be treated as an ideal mixture (solution).

For a practical example of adsorption of the ethane-propane mixture as shown in Figure 15-35, this model can well correlate the experimental data. Further we can treat non-ideal mixtures by adopting the activity-factor correlation equations, also the interfacial equations of state.

### 3. Theoretical Method

Theoretical study for the characteristic properties of interfacial adsorption requires statistical mechanics. For instance, the parameter  $b$  of the Langmuir adsorption isotherm Eq. (15-81) corresponds to adsorption equilibrium constant. We can derive for it an expression,

$$b = (Vq_{0a}/kTq_{0g})e^{-\Delta\epsilon_a/kT} \quad (15-89)$$

where  $q_{0a}$  is the molecular partition function of adsorbed molecules. It represents the total characteristics of distribution of adsorbed molecules on various rotational, vibrational and electronic energy levels (no translational energy).  $q_{0g}$  is the molecular partition function of gas phase.  $\Delta\epsilon_a = \epsilon_{0a} - \epsilon_{0g}$  is the adsorption energy of one molecule.

## III. Rate Processes in Interfaces

### 15.12 Dynamic Interfacial Tension

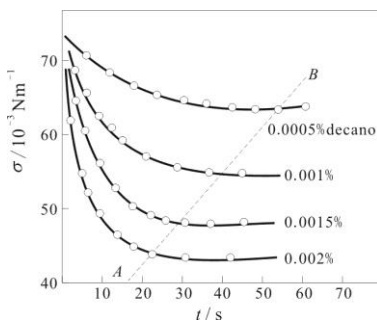


Figure 15-43 Dynamic interfacial tensions of aqueous decanol. Addison C C, Hutchinson S K. J Chem Soc, 1949, 17:3387.

**Dynamic Interfacial (Surface) Tension** As a fresh interface just creates, in a certain period, the interface might deviate from equilibrium, and the interfacial (surface) tension could be different from that in equilibrium and will vary with time. Figure 15-43 shows the experimental results for aqueous decanol. At the very beginning, the interfacial tension closes to that of the pure water, then gradually depresses as the time elapses and finally reaches the equilibrium value accorded with the Gibbs equation. The time needed for reaching equilibrium depends on the concentration of the solution as shown by the dashed line in the figure. The reason for these phenomena lies in the fact that the diffusion of surface active molecules

from the bulk to the surface costs time. The smaller the solute concentration, the longer time is needed, on the other hand, the larger the diffusion coefficients of the solute molecules or ions, the shorter time is consumed for reaching equilibrium. The tensions per unit length acting in the non-equilibrium interface (surface) are called the dynamic interfacial (surface) tensions. The above phenomena do not happen in pure substances. In many practical processes such as evaporation, distillation, absorption and extraction, because of the evaporation of solvent or the dissolution of air on the solution surface, or the chemical reaction between gas and solute on the surface, or because the solute is too slow to diffuse to the newly created surface during the gas bubbling, all of those will induce the phenomena on the interface that the interfacial tension will deviate from that in equilibrium, and all those processes will then be affected.

**Marangoni Effect** The effect named after Marangoni C G M concerns with the movement of bulk substances motivated by the interfacial-tension gradient existing in the interfacial layer. It has important influences in transport processes.

**Interfacial Viscosity** In the interfacial layer, if a flow-rate gradient exists, the layer might exhibit stickiness or viscosity, the corresponding characteristic parameter is called the interfacial viscosity. It is an important parameter in studying monomolecular films and the spreading of fluids.

## 15.13 Chemical Reactions in Surface Films

Many reactions proceed concerning monomolecular surface films. The most common ones are reactions between the substances in film and those in bulk. For examples, hydrolysis of vinyl stearate film, oxidation of oleic acid

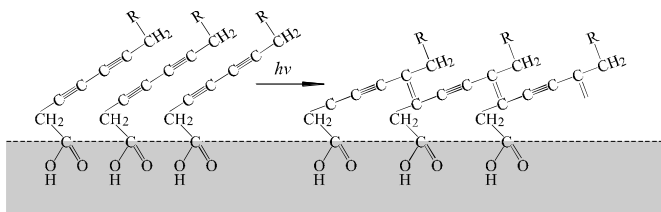


Figure 15-44 Photo-polymerization of long chain diacetylene carboxylic acid  
 Day D and Lando J B. *Macromolecules*, 1980, 13:1478;  
 Day D and Ringsdorf. *J Polym Sci Polym Lett Ed*, 1978, 16:205

film by  $\text{KMnO}_4$  in solution, lactonization of hydroxyl stearic acid film, hydrolysis of dicetyl succinate film in alkaline solution, etc. These reactions are mostly first order, they can be controlled to proceed at the condition of a constant spreading pressure (similar to a constant pressure) or a constant surface area (similar to a constant volume). Kinetics can be studied by measuring the change of physical properties of films, such as interfacial area, spreading pressure, film electric potential, film viscosity, infrared absorption, ultraviolet absorption, tracers, etc. Film reactions also have different types such as consecutive, parallel and opposite. The above hydrolysis of dicetyl succinate film is a consecutive reaction; it forms mono cetyl ester and succinic acid sequentially. The most attractive fact for the reactions in monomolecular films lies in that by adjusting the spreading pressure, molecules in the interface can be oriented in different levels. Figure 15-44 is a sketch of the photo-polymerization of a long chain diacetylene carboxylic acid. Because of the orientation of molecules in interface, a very neat zipper-like polymerization occurs. This is difficult to realize in ordinary solutions.

## 15.14 Heterogeneous Catalysis

**Heterogeneous Catalytic Reactions** The distinguishing feature of heterogeneous catalytic reactions is that the reactants and the catalyst exist in two phases, respectively. Reactions occur at the interface, the surface characteristics of catalysts play a key role.

**Chemical Adsorption** Generally, at least one of the reactants is chemically adsorbed on the catalyst surface, therefore, the electron distribution in that molecule changes correspondingly. A suitable and moderate strength of the chemical adsorption is favorable to the catalytic reactions. Too strong chemical adsorption will be harmful, for instance, far-infrared spectrum indicates that CO forms a stable  $\text{O}\equiv\text{C}-\text{M}$  on the Pt catalyst, therefore, it is a poison.

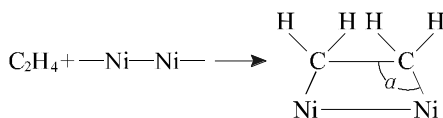
**Surface Heterogeneity** Generally, the catalyst surface is inhomogeneous, only a small part of it possesses catalytic activities, called the **active center**. Different sites may have different activities.

## 1. Metal Catalysts

There are two factors, the electronic factor and the geometric factor that decide the catalytic activities of metal catalysts.

(1) **Electronic Factor** The adsorption ability of metals depends on the electronic structure of the metal. Atoms of alkaline metal possess simple valence electron shell (s electrons). In a solid state, these valence electrons form a half filled energy band and play a role of the active electron donor. Therefore, alkaline metals are strong reductive agents. They can strongly adsorb electron acceptors forming stable compounds, as a result, very rare to be a catalyst. Transition metals are characterized by their unpaired d electrons. Chemical adsorption on them has moderate strength, therefore, exhibit good catalytic functions. For examples, for the dehydrogenation of paraffines and naphthenes, the hydrogenation of olefins and aromatics, Pt, Pd, Ni and those in group VIII with suitable amount of unpaired d electrons are good catalysts. Ag and Au of group IB have bad activity because the d orbital is filled. Although the d orbital of Cu is filled, d electrons are easily excited to s orbital at a higher temperature resulting in unpaired d electrons. Therefore, Cu can be used as a hydrogenation catalyst at a higher temperature.

(2) **Geometric Factor** For metal catalysts, the structure of the active center on surface and its geometric correspondence with the reactants should also be considered. Taking hydrogenation of ethylene on Ni catalyst for example, the chemical adsorption of ethylene on surface can be expressed as the adsorption on two Ni atoms, called a **dual-sites adsorption**,



The bond length of C–C is 0.154nm, after adsorption, C–Ni distance is 0.182nm. There are mainly two types of spacing on different crystal planes for metal Ni, 0.248nm and 0.352nm, correspondingly, two bond angles,  $\alpha = 105^\circ$  and  $123^\circ$ , respectively. The four  $\text{sp}^3$  hybrid orbitals of C atom form a tetrahedron with a bond angle of  $109^\circ 28'$  close to  $105^\circ$  but quite different from  $123^\circ$ . Therefore, a greater tension exists in the later case of adsorption



bond, corresponding to the formation of an active activated complex on the surface. In experiment, two different Ni films were prepared. An oriented film constructed solely by (100) crystal plane with a spacing of 0.352nm and a non-oriented film where each of the (110), (100) and (111) planes occupies 1/3. Hydrogenation of ethylene on the two films proved that the activity of the oriented film is five fold greater than that on the non-oriented film.

## 2. Semi-conductor Catalysts

Many oxides and sulfides of transition metals are semi-conductors. Those n-type and p-type, the conduction of them is bore by free electrons and cavities with positive charge, respectively, play the role of electron donor and acceptor in chemical adsorption, which are closely related to the catalytic activities. If the chemical adsorption of a gas on the oxide leads to the enhancement of the charge load resulting in a progressive increase of the electric conductance of the semi-conductor, chemical adsorption is then easier to happen. This is called the **cumulative adsorption**. On the contrary, if it leads to the depression of the charge load and decrease of electric conductance, chemical adsorption is then harder to happen. This is called the **attenuate adsorption**. For instance, for the decomposition of  $N_2O$  to  $N_2$  and  $O_2$ , adsorbed  $N_2O$  forms  $N_2O^-$  anion that consumes electrons or increases cavities. Therefore, p-type semi-conductors  $Cu_2O$ ,  $CoO$ ,  $NiO$ ,  $CuO$ ,  $CdO$ ,  $Cr_2O_3$  and  $Fe_2O_3$  are good catalysts, while  $ZnO$  is a n-type semi-conductor with the lowest activity. Because the conductivity of semi-conductors can be

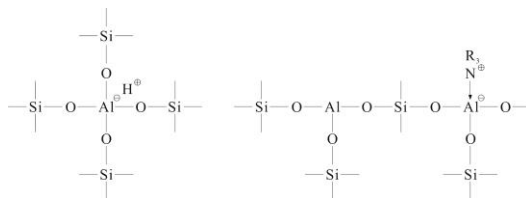


Figure 15-45 Brønsted acid center. Figure 15-46 Lewis acid center.

effectively adjusted by adding impurities, this could be one of the reasons that tiny amount of additives (promoter or poison) can raise or depress catalytic activities in a great extent.

## 3. Insulator Catalysts

This kind of catalyst has few transportable free electrons or cavities, therefore, with a very low electric conductance, but can form acid or base centers with certain structures on the surface playing the role of active centers to promote acid base catalytic reactions. Commonly used are  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and aluminum silicate. The latter is an excellent cracking catalyst; its surface has probably two types of acid center: One is the **Brönsted acid center**. As shown in Figure 15-45, where part of  $\text{Si}^{4+}$  ions is replaced by  $\text{Al}^{3+}$  ions resulting in an excess of negative charge. To keep electro-neutrality, a proton  $\text{H}^+$  is adsorbed and served as a protonic acid center called the Brönsted acid center. The other is the **Lewis acid center**. It is a generalized acid as shown in Figure 15-46. Part of  $\text{Si-O}$  is replaced by  $\text{Al}^{3+}$  ions that can adsorb substances with lone-pair electrons such as amines  $\text{R}_3\text{N}$  because of the strong ability to attract electron pairs. The strength of the acid center can be adjusted by changing the Si-Al ratio or by ion exchange.

**Zeolites** Zeolites are a family of aluminosilicates usually called **molecular sieves** due to the ability to selectively sort molecules based primarily on the size of the micro pores and tunnels. They have an open structure that can accommodate various cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  which are rather loosely held and can readily be exchanged by others. More than 150 types have been synthesized and 48 naturally occurring are known. Zeolites are widely used as cracking, isomerization and alkylation catalysts in petrochemical industry. Besides micro pores, recently, zeolites with meso and macro pores have been synthesized and attract more attention.

## 15.15 Heterogeneous Catalytic Kinetics

### Fundamental Steps for Heterogeneous Catalytic Reactions

Generally, there are five steps:

- (1) Reactants in the bulk phase diffuse to the surface of the catalyst.
- (2) Chemical adsorption for some reactants.
- (3) Surface reactions, including reaction between adsorbed molecules, isomerization or dissociation of adsorbed molecules, reaction between adsorbed and bulk molecules.
- (4) Products desorb from the surface of the catalyst.

(5) Desorbed molecules diffuse to the bulk phase.

Figure 15-47 is a sketch of the potential energy changes for a heterogeneous catalytic reaction and the corresponding gas phase non-catalytic reaction indicating that the heterogeneous catalytic reaction changes the reaction

Table 15-5 Comparison between activation energies of catalytic reaction and non-catalytic reaction

Decomposition reactant	Catalyst	$E_a / (\text{kJ} \cdot \text{mol}^{-1})$	
		Catalytic	Non-catalytic
HI	Au	105	183
	Pt	58	
N <sub>2</sub> O	Au	121	245
	Pt	136	
NH <sub>3</sub>	W	163	>335
	Os	197	
CH <sub>4</sub>	Pt	230~251	~335

path, lowers the activation energy, therefore, notably accelerates the reaction. Table 15-5 is a comparison between the activation energies with or without a catalyst. The rates of heterogeneous catalytic reactions are also closely related to the mass transfer and heat transfer processes.

**Construction of Kinetic Equation** Because reactions are carried out on the surface of the catalyst, reaction rate  $v$  is usually expressed by the variation rate of the amount of substance with respect to time at unit surface area or unit mass of the catalyst. Besides the reaction rate coefficient, the kinetic equation should include only those measurable variables such as bulk concentrations or partial pressures for reactants and products. We could use the steady state approximation; however, the derived results are usually complex. Most commonly, we use the method of controlling-step approximation.

### 1. Diffusion Control

For a reaction  $A \rightarrow P$ , if it is a reactant A diffusion control, reaction rate  $v$  equals the diffusion flux  $j_A$  of the reactant A from the bulk to the surface,  $v=j_A$ . From the Ficks law Eq.(6-1), supposing a constant concentration gradient, we obtain the rate equation for diffusion control,

$$v = j_A = -D \frac{dc_A}{dx} = -\frac{D}{\delta} (c_A^{(\text{surface})} - c_A^{(\alpha)}) = k_d (c_A^{(\alpha)} - c_A^{(\text{surface})}) \approx k_d c_A^{(\alpha)} \quad (15-90)$$

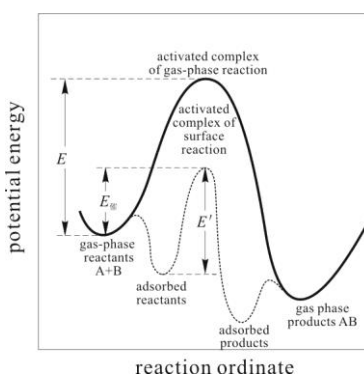


Figure 15-47 Potential diagram for gas phase non-catalytic reaction (solid) and surface reaction on catalyst (dash).

where the superscript  $\alpha$  denotes bulk phase,  $D$  is the diffusion coefficient,  $k_d$  is the **diffusion rate constant**,  $k_d = D/\delta$ ,  $\delta$  is the thickness of the diffusion layer. The characteristic of diffusion control is  $k_d \ll k$ ,  $k$  is the rate constant for adsorption, desorption or surface reaction. Because  $c_A^{(\text{surface})}$  is generally very small that can be neglected, the equation is formally the same as a first order equation. Diffusion activation energy is generally small; therefore, the temperature effect can usually be neglected. Besides, increasing the linear flow velocity of the reaction flux can diminish the thickness of diffusion layer and enhance  $k_d$  then increase the reaction rate.

**External Diffusion and Internal Diffusion** The phenomena that the reactants transport from the bulk to the external surface of the catalyst or the products transport from the external surface of the catalyst to the bulk are called the external diffusion. The phenomena that the reactants transport along the catalyst void to the internal surface of the catalyst or the products transport leaving the internal surface along the catalyst void to outside are called the internal diffusion. The internal diffusion distinguishes itself from others by the fact that it proceeds in parallel with the reaction. When the reactants move along the pore channel into the depth of the particle, catalytic reactions take place at the same time as the reactant molecules continuously collide the pore wall, similar to a parallel reaction. Besides, when the pore diameter matches the mean free path, the **Knudson diffusion** will take place, it is determined by the collisions between molecules and pore wall, collisions between molecules reduce to the second place. When the internal diffusion controls, because the diffusion and reaction have to be treated simultaneously, the apparent activation energy for the total catalytic reaction is about one half of the reaction activation energy. Crushing the catalyst particles can always improve the internal diffusion by shortening the pore channels.

## 2. Adsorption or Desorption Control

For a reaction  $A \rightarrow P$ , besides the diffusion steps of reactants and products, the elementary reactions including the adsorption of reactant A, the surface reaction and the desorption of product P, they can be expressed as



where S represents the adsorption center on the catalyst surface,  $k_{\text{ads}(A)}$ ,  $k_{\text{ads}(P)}$ ,  $k_{\text{des}(A)}$ ,  $k_{\text{des}(P)}$  are the adsorption and desorption rate constants for the reactant A and product P,  $k_{\text{s+}}$  and  $k_{\text{s-}}$  are the rate constants for the positive and reverse reactions, respectively. For simplicity, we suppose that the catalyst surface is homogeneous, there are no interactions between adsorbed molecules and the Langmuir adsorption model can be applied. Among the above rate constants and the adsorption coefficients  $b_A$  and  $b_P$  for A and P, the equilibrium constant  $K_s$  for surface reaction, and the equilibrium constant  $K_p$  for gas phase reaction  $A \rightarrow P$ , there are the following relations:

$$b_A = \frac{k_{\text{ads}(A)}}{k_{\text{des}(A)}}, \quad b_P = \frac{k_{\text{ads}(P)}}{k_{\text{des}(P)}}, \quad K_s = \frac{k_{\text{s+}}}{k_{\text{s-}}}, \quad K_p = K_s \frac{b_A}{b_P} \quad (15-91)$$

### Adsorption of Reactant A is Rate-Control Step

Suppose the

surface coverage of A and P is  $\theta_A$  and  $\theta_P$ , respectively, the uncovered fraction is  $1 - \theta_A - \theta_P$ ,  $v$  is the difference between adsorption rate and desorption rate,

$$v = k_{\text{ads}(A)} p_A (1 - \theta_A - \theta_P) - k_{\text{des}(A)} \theta_A \quad (15-92)$$

We consider that the surface reaction is in equilibrium, correspondingly,

$$K_s = \theta_P / \theta_A \quad (15-93)$$

Desorption of the product P can also be considered in equilibrium, the adsorption rate equals desorption rates for product P,

$$k_{\text{ads}(P)} p_P (1 - \theta_A - \theta_P) = k_{\text{des}(P)} \theta_P$$

$$\theta_P = b_P p_P (1 - \theta_A) / (1 + b_P p_P) \quad (15-94)$$

Combining Eqs. (15-91, 15-93, 15-94),  $\theta_A$  and  $\theta_P$  can be solved as follows:

$$\theta_A = \frac{b_A p_P / K_p}{1 + b_A p_P / K_p + b_P p_P}, \quad \theta_P = \frac{b_P p_P}{1 + b_A p_P / K_p + b_P p_P} \quad (15-95)$$

Substitution into Eq.(15-92) yields the reaction rate equation,

$$v = \frac{k_{\text{ads}(A)} (p_A - p_P / K_p)}{1 + b_A p_P / K_p + b_P p_P} \quad (15-96)$$

Altogether four parameters appear in the equation, among them,  $b_A$  and  $b_P$  can be obtained independently from the adsorption equilibrium experiment,  $K_p$  can be calculated by using the thermodynamic method in Chap. 5, therefore, there is only one kinetic parameter  $k_{\text{ads}(A)}$  that should be reduced

from the kinetic experimental data. At the beginning stage,  $p_p \rightarrow 0$ ,

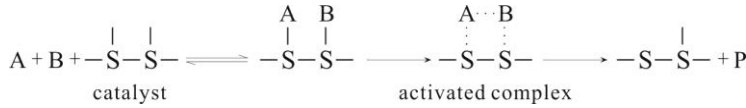
$$v = k_{\text{ads(A)}} p_A \quad (15-97)$$

Apparent reaction order is 1, apparent activation energy is the adsorption activation energy.

### 3. Surface Reaction Control

For a reaction  $A + B \rightarrow P$ , there are two possible mechanisms:

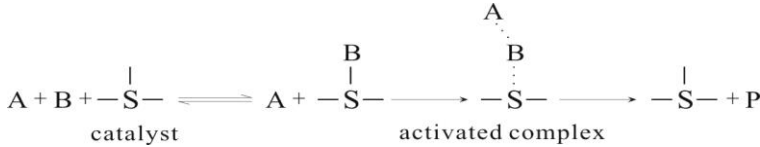
(1) **Langmuir-Hinshelwood Mechanism** This mechanism supposes that the reaction occurs between adsorbed reactant molecules A



and B,

Neglecting the reverse reaction,  $k_s = k_{s+}$ , we obtain

$$v = k_s \theta_A \theta_B = \frac{k'_s p_A p_B}{(1 + b_A p_A + b_B p_B)^2}, \quad k'_s = k_s b_A b_B \quad (15-98)$$



(2) **Rideal Mechanism** This mechanism supposes that the reaction occurs between the molecule A in gas phase and the adsorbed molecule B.

Also neglecting the reverse reaction,  $k_s = k_{s+}$ , we have

$$v = k_s p_A \theta_B = \frac{k'_s p_A p_B}{1 + b_A p_A + b_B p_B}, \quad k'_s = k_s b_B \quad (15-99)$$

Most heterogeneous catalytic reactions follow the Langmuir-Hinshelwood mechanism, there are three typical cases:

(a) **A and B are Both Weak Adsorption.**

$1 + b_A p_A + b_B p_B \approx 1$ , Eq. (15-98) changes to a second-order rate equation,

$$v = k'_s p_A p_B \quad (15-100)$$

(b) **A is a Weak Adsorption, B is a Moderate Adsorption.**

$1 + b_A p_A + b_B p_B \approx 1 + b_B p_B$ , Eq. (15-98) changes to

$$v = \frac{k_s b_A b_B p_A p_B}{(1 + b_B p_B)^2} = k'_s \frac{p_A p_B}{(1 + b_B p_B)^2} \quad (15-101)$$

If  $p_B$  keeps unchanged, reaction is first order to A. On the contrary, if  $p_A$  keeps unchanged,  $v$  accelerates at first as increasing  $p_B$ , reaches maximum at  $p_B=1/b_B$ , then slows down with increasing  $p_B$ , indicating that B finally retards the reaction. For instance, the water gas reaction on Pt wire at 1000°C,  $H_2+CO_2 \rightarrow CO+H_2O$ , when keeping  $p_{H_2}=1.3 \times 10^4$  Pa, reaction rate varies with the pressure of  $CO_2$ , maximum appears at  $p_{CO_2} = 3 \times 10^4$  Pa, as shown in Figure 15-48.

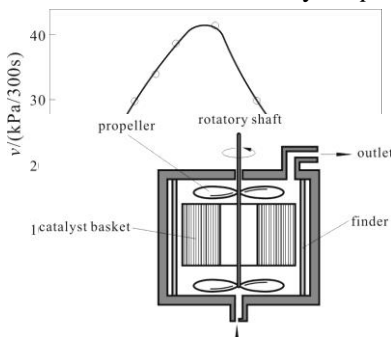


Fig. 15-48. The relative rate of  $H_2 + CO_2$  reaction versus the pressure of  $CO_2$ .  
Prichard, Figure 15-48, *Rotary Basket Reactor*, Soc. Trans., 1925, 127: 806

(c) A is a Weak Adsorption, B is a Strong Adsorption.

$$v = k'_s p_A / p_B, \quad k'_s = k_s b_A / b_B \quad (15-102)$$

B retards the reaction.

Parameters  $k_s$  or  $k'_s$  in above equations should be determined by reduction of the experimental kinetic data.

#### 4. Experimental Method

**Kinetic Experiment** Usually, the diffusion influence is first to be eliminated. In studying the kinetics of adsorption or surface reaction, the flow velocity should be increased until the reaction rate keeps constant to remove the influence of external diffusion. On the other hand, we reduce the particle size of the catalyst until the rate unchanged to eliminate the internal diffusion effect. Then we carry out the experiment in a tube reactor or a tank reactor based on the ordinary chemical kinetics method. Figure 15-49 is a rotary basket reactor. Catalyst of very fine particles contained in the basket rotates at a high speed, effects of internal and external diffusions are all removed. Besides, no concentration gradient occurs in the catalyst bed. This is a continuous tank reactor or a differential reactor, which is popularly used in laboratory to measure directly the reaction rates.

**Theoretical Study in Heterogeneous Catalysis** Close attentions have been paid for the surface electronic and geometrical state and the structure of the active center of the catalysts. Identification of the

intermediates and their configurations, and reaction mechanisms have also attracted the scientists. LEED, Auger spectroscopy, XPD, STM, AFM and FEM are important means in experiment. In theoretical studies, quantum mechanics and solid state physics are mainly used. To realize the prediction of the kinetic performance of heterogeneous catalysis, a great amount of work is needed.

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### Brief History

Studies of the interfacial phenomena started from mechanics. Early in 19th century, the idea of the interfacial tension was created. In 1905, Young T of England (also referring to Chap. 9) defined the interfacial tension in elastic film from the view point of mechanics, and extended to systems containing solid. He derived the celebrated Young's equation which relates the gas-liquid, liquid-solid, gas-solid interfacial tensions with the contact angle. In 1806, Laplace P S of France derived an equation relating the pressure difference between the two sides of a curved interface, which can describe the phenomena of rising and depressing of liquid in capillary. In 1869, Dupra A studied wetting and adhesion, and related the adhesive work and cohesive work with the interfacial tensions. The founder of thermodynamics of interfaces is Gibbs J W of the USA (also referring to Chap. 3, 4, 5, 13), the framework of chemical thermodynamics he established also includes the contributions of interfaces. Considering the difficulty of setting the thickness of interface, he proposed the Gibbs interfacial phase model with zero thickness. The model has been used up to present. The generalized equations relating  $\bar{I}_i$  and  $\sigma$  with the variation of bulk concentration derived from Gibbs-Duhem equation is called the Gibbs isotherm. Another scientist who made great contribution is Kelvin L of England (also referring to Chap. 2). In 1859, he connected the heat accompanied by the interfacial expansion with the variation of interfacial tension with respect to temperature. In 1871, he derived an equation named after him which describes the variation of vapor pressure with the radius of the curved interface. In 1916, Langmuir I, a US chemist (also referring to Chap. 10), proposed an adsorption isotherm in his name.

In 1893, van der Waals J D of the Netherland (also referring to Chap. 1) recognized that the density in the interfacial layer is continuously distributed. Applying the idea of the local free energy (Helmholtz function), combining with the van der Waals equation and introducing semi-empirical revisions, he studied theoretically the relation between the interfacial tension and parameters of the equation of state and found that the latter depends on intermolecular forces. Van der Waals' study could be viewed as the prelude of the statistical mechanical studying for interfacial phenomena. After 1950s, essential progresses have been obtained in that field. Buff F P and Kirkwood J G of the USA adopted the grand canonical ensemble and the density functional method, Harasima A of Japan applied the canonical ensemble, and carried out studies similar to that of van der Waals, but with more firm theoretical basis. On the other hand, experimental



work using LEED, XPD, STM for solid surfaces has been developed. Deeper understanding on the surface structures and the configurations of molecules has been obtained. Quantum mechanics studies have gone further and in depth progressively. Ertl G, a German chemist, has contributed original research on the solid surface at the molecular level. His work helps people to the better understanding of why iron gets rusty, and the basic principle of fuel cells, solid catalysts, and the car tail gas purification equipment. He won the Nobel Prize of

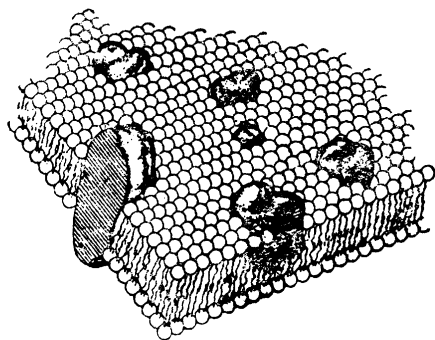


Figure 15-50 Cell membrane

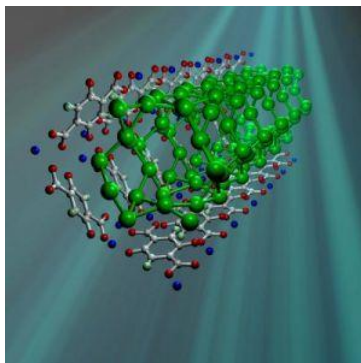


Figure 15-51 Adsorption of deuterium in MOF-74, Gray-C, blue-Zn, green- $^2\text{H}$   
Liu Y et al. Langmuir. 2008, 24: 4772

chemistry in 2007.

## Concluding Remarks

Studies of interfacial phenomena have been increasingly growing. Not only those adsorption and heterogeneous catalytic techniques are widely used in chemical and petroleum industries, also are in other fields such as food, medicine, dyeing and finishing, new energy resources exploration, environmental, materials and biochemical technology, all of them cannot be managed without the application of the interfacial phenomena. For the life science, interfacial phenomena have special meanings. Taking a cell for example as shown in Figure 15-50, the structure of the cell membrane is virtually a bi-layer formed by phospholipid and those proteins such as enzymes, coenzymes and coloring matters buried in it. For the material science, interfacial phenomena also play an important role. Various new materials continuously emerge. Recently, it was reported that a new material called MOF-74 (Metal Organic Frameworks) can adsorb deuterium at ordinary pressure. At liquid  $\text{N}_2$  temperature, the density of  $^2\text{H}$  adsorbed even higher than that of solid  $^2\text{H}$ . The material has a tube-like structure composed of C and Zn with Zn located in the inner wall as shown in Figure 15-51. One gram of the sample has a surface area as large as about two basket-ball playground. Inelastic neutron scattering reveals the occupancy of different binding sites, hydrogen molecules are observed to fully occupy the strongest binding site before populating other adsorption sites. The material has the potential for hydrogen storage.

This chapter is the first one of the Part V, Extension. The special point is its comprehensive discussion. Not only it includes both equilibria and rates, for each of them, it discusses general principles and characteristic properties, the latter

needs experimental, semi-empirical and theoretical methods. For theoretical studying, it concerns levels deeper than thermodynamics and kinetics, i.e., statistical mechanics and quantum mechanics. Because of the limitation of a fundamental course, also because of the practical situation of the developments, for many sides especially the theoretical parts, we can only touch a little. However, as a complete structure of the knowledge, we have to obtain an all-side understanding. Comparison is always proved to be useful. For example, we have focused on gas-solid adsorption, for liquid-solid adsorption we can also know something in comparison with the former.

For thermodynamics and kinetics, in principle, interfaces have no new fundamentals. The special point is emphasizing on the interfacial tension and the unit interfacial excess or adsorption. They concern the generalized force and displacement. The approaches for treatment have mainly two kinds: One is defining a new chemical potential such as the interfacial chemical potential in this Chapter, and the electrochemical potential that will be introduced in Chapter 17. The other is defining new thermodynamic functions, such as a new enthalpy, which is often used in the cases concerning external field. There is no fundamental difference between these two approaches. You can choose at will.

It is helpful to compare those directly measurable state functions and the corresponding intensive properties for an ordinary bulk phase and an interfacial phase. For example, they can be arranged as follows:

Bulk phase:  $T, p, V, n_i, i=1\sim K; T, p, x_i (b_i, c_i)$

Interface:  $T, \sigma, A_s, n_i^{(\sigma)}, i=1\sim K; T, \sigma, \Gamma_i (\Gamma x_i^{(\sigma)})$

We can clearly see their correspondence. Another example is to compare an ordinary gas-liquid equilibrium and an interfacial equilibrium, the content of their studies can be arranged as follows:

Vapor-liquid equilibrium: Studies variation of  $y_i$  of the gas phase with  $T, p$  and  $x_i$  of the liquid phase.

Fluid-fluid interfacial equilibrium: Studies variation of  $\sigma$  with  $T, p$  and  $x_i$  of the bulk phase.

Fluid-solid interfacial equilibrium: Studies variation of  $\Gamma_i$  with  $T, p$  and  $x_i$  of the bulk phase.

where  $\sigma$  and  $\Gamma_i$  are correlated by Gibbs-Duhem equation. However, because the thickness of interface is only several molecules, the experimental techniques and the theoretical studies are more difficult than those of the bulk. The corresponding researches are relatively delayed compared to that of bulk.

Interfacial phenomena are a very active research field in physical chemistry.

## General Problems

1. Is it true that the contracted tension in interface is the interfacial tension?
2. Since  $\Gamma_2^{(1)}$  is  $\Gamma_2$  at  $\Gamma_1=0$ , is  $\Gamma_2^{(1)}$  dependent on the position of the interfacial phase?
3. How do we define the interfacial tension?
4. From Eq.(15-20)  $\sigma = (\partial H^{(\sigma)} / \partial A_s)_{S, p, n_j}$  and Eq.(15-21)  $H_A = (\partial H^{(\sigma)} / \partial A_s)_{T, p, n_j}$ , is it right that  $\sigma$  is also the specific interfacial enthalpy?
5. Are the equilibrium conditions completely the same when the systems are with

and without interfacial phase?

6. There are two water drops with different radii in a closed container, what phenomenon will happen when they are laid for a long period?

7. The vapor pressure of liquid with a concaved surface is lower than that of the planar liquid. Give your comments.

8. As shown in Figure 15-52, at the two terminals of a glass tube, there are two soap bubbles with different radii. Open the cock to connect the two sides, what are the changes of the sizes of the two bubbles? What is the situation when reaches equilibrium? What is the pressure difference inside and outside the bubble in air with a radius  $r$ ?

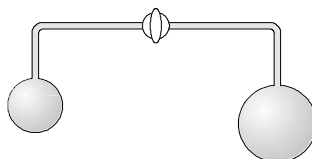


Figure 15-52

9. As shown in Figure 15-53, there are three glass tubes a, b and c with the same inner radius. Inserting "a" vertically into water, the meniscus with a radius of  $r$  inside the tube rises to a height of  $h$ . If inserting "b" and "c" vertically into water also as shown in the figure, what are the radius and height of the meniscus?

10. As shown in Figure 15-54, there are two capillaries filled with two different liquids. If heating the right side, how do those liquids move?

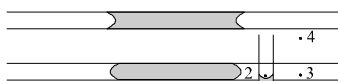


Figure 15-54

11. A glass capillary is inserted into water and the meniscus rises as shown in Figure 15-55. If the water vapor on the meniscus is in equilibrium with the liquid water, what is the sequence of the pressures of water vapor from low to high at the four points as shown in the figure. (Points 2 and 3 are at the same height.)



Figure 15-55

12. Gibbs isotherm is a kind of Gibbs-Duhem equation. Please give comments.

13. When a liquid I spreads on a liquid II, how do we obtain spreading coefficient from experiment?

14. Compare the  $\pi$ - $A_s$  relation of a monomolecular film and the  $p$ - $V$  relation of a fluid. What are the similarities and dissimilarities?

15. Figures 15-27, 15-29 and 15-30 give adsorption isotherms, isobars and isosteres. Draw a sketch of a three-dimensional  $\Gamma$ - $T$ - $p$  phase diagram, and mark those isotherms, isobars and isosteres.

16. How do we obtain the enthalpy of adsorption from experimental adsorption data?

17. Suggesting that the enthalpy of adsorption has an exponential relation with the surface coverage, derive the Freundlich equation.

18. What is the principle for measuring the surface area and the pore radius distribution of adsorbents and catalysts by adsorption?

19. What are the applicable ranges of various semi-empirical adsorption isotherms and models?

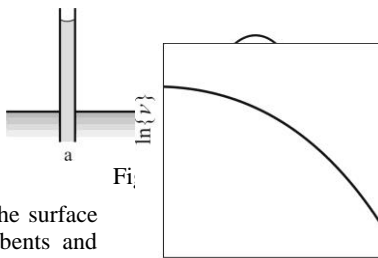


Figure 15-56

20. Figure 15-56 shows generally the variation of the heterogeneous catalytic reaction rate with temperature. Interpret it.

## Numerical Problems

1. Disperse  $1 \text{ cm}^3$  of oil into water forming an emulsion of oil drops with a radius of  $1 \mu\text{m}$ . The interfacial tension of oil-water interface is  $62 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$ . Estimate the minimum work required.

2. The surface tension of water at 298K is  $\sigma = 72.0 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$ ,  $(\partial \sigma / \partial T)_{p, A_s} = -0.157 \times 10^{-3} \text{ N} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ . When reversibly increase the surface area of water for  $1 \text{ m}^2$  at 298 K and 0.1 MPa, calculate  $W$ ,  $Q$ ,  $\Delta H^{(\sigma)}$ ,  $\Delta S^{(\sigma)}$  and  $\Delta G^{(\sigma)}$ .

3. Benzene vapor condenses to fog with a radius of  $1 \mu\text{m}$  for liquid drops at 293 K. Calculate the pressure difference inside and outside the drop interface and the percentage of vapor-pressure rising for the drops comparing to the planar liquid. The density of liquid benzene at 293K is  $0.879 \text{ g} \cdot \text{cm}^{-3}$ , surface tension  $\sigma = 28.9 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$ .

4. Calculate the unit interfacial adsorption  $\Gamma_2^{(1)}$  of an aqueous ethanol with a concentration  $c = 0.5 \text{ mol} \cdot \text{dm}^{-3}$ . The relation between the surface tension of aqueous ethanol and  $c$  at 298K is

$$\frac{\sigma}{\text{N} \cdot \text{m}^{-1}} = 72 \times 10^{-3} - 0.50 \times 10^{-6} \frac{c}{\text{mol} \cdot \text{m}^{-3}} + 0.20 \times 10^{-9} \left( \frac{c}{\text{mol} \cdot \text{m}^{-3}} \right)^2$$

5. The surface tension of aqueous butyric acid at 292K can be expressed as  $\sigma = \sigma^* - a \ln(1 + bc)$ ,  $\sigma^*$  is the surface tension of pure water,  $a$  and  $b$  are parameters. (1) Derive the relation between  $\Gamma_2^{(1)}$  and  $c$ . (2) Knowing that  $a = 13.1 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$ ,  $b = 19.6 \times 10^{-3} \text{ mol}^{-1} \cdot \text{m}^3$ , calculate  $\Gamma_2^{(1)}$  when  $c = 0.2 \text{ mol} \cdot \text{dm}^{-3}$ .

6. Surface tensions of ethanol and mercury at 293 K are  $22.0 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$  and  $471.6 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$ , respectively. The interfacial tension of ethanol and mercury is  $364.3 \times 10^{-3} \text{ N} \cdot \text{m}^{-1}$ . Can the ethanol spread on the mercury?

7. Adsorption of  $\text{O}_2$  on a catalyst at 473 K was studied. When the pressures of  $\text{O}_2$  are 0.1MPa and 1MPa, the amounts of  $\text{O}_2$  adsorbed on 1g of catalyst are  $2.5 \text{ cm}^3(\text{STP})$  and  $4.2 \text{ cm}^3(\text{STP})$ , respectively. Langmuir isotherm can be used in this case. Calculate the equilibrium pressure of  $\text{O}_2$  when  $\Gamma$  is one half of  $\Gamma_\infty$ .

8. When the surface of a silica gel is covered by a monomolecular layer of  $\text{N}_2$ , the corresponding volume of  $\text{N}_2$  adsorbed is  $129 \text{ cm}^3(\text{STP})$  per 1g of gel. The area occupied by one molecule  $\text{N}_2$  is  $0.162 \text{ nm}^2$ . Calculate the specific area of this gel.

9. The adsorption amounts of  $\text{N}_2(\text{STP})$  on 1g of a catalyst at different equilibrium pressure are measured at 77.2 K as shown in the table:

$p / \text{kPa}$	8.70	13.64	22.11	29.93	38.91
$V / \text{cm}^3$	115.6	126.3	150.7	166.4	184.4

Calculate the specific area of the catalyst by the BET isotherm. The vapor pressure of  $\text{N}_2$  at 77.2 K is 99.10 kPa. The area occupied by a  $\text{N}_2$  molecule is  $0.162 \text{ nm}^2$ .

10. The decomposition of  $\text{N}_2\text{O}$  on Au at 1173 K was measured as shown in the table. ( $x$  is the ratio of  $\text{N}_2\text{O}$  decomposed with respect to that at the beginning.)

$t / \text{min}$	15	30	65	80	120	$\infty$
$x$	0.17	0.32	0.57	0.65	0.78	1.00

Knowing that  $\text{N}_2\text{O}$  on Au is a weak adsorption, the adsorption of products can be

neglected. Calculate the rate coefficient  $k$  of the decomposition reaction.

11. The raw material ethylene chloride for the manufacture of polyethylene chloride can be obtained by a catalytic reaction of acetylene and HCl on  $\text{HgCl}_2(\text{s})$ , the reaction is:  
 $\text{C}_2\text{H}_2 + \text{HCl} \longrightarrow \text{C}_2\text{H}_3\text{Cl}$

The reaction mechanism is:  $\text{HCl} + \text{HgCl}_2 \xrightleftharpoons[k_{-1}]{k_1} \text{HgCl}_2 \cdot \text{HCl}$  ①

$\text{C}_2\text{H}_2 + \text{HgCl}_2 \cdot \text{HCl} \xrightarrow{k_2} \text{HgCl}_2 \cdot \text{C}_2\text{H}_3\text{Cl}$  ②

$\text{HgCl}_2 \cdot \text{C}_2\text{H}_3\text{Cl} \xrightarrow{k_3} \text{HgCl}_2 + \text{C}_2\text{H}_3\text{Cl}$  ③

where ① and ③ proceed very fast making the adsorption and the desorption of HCl on catalyst keeping equilibrium. Desorption of the product  $\text{C}_2\text{H}_3\text{Cl}$  is also very fast, therefore, reaction ② is the rate control step. If the Langmuir isotherm can be used for describing the adsorption of HCl on  $\text{HgCl}_2(\text{s})$ ,

(1) Write the reaction rate equation for  $\text{C}_2\text{H}_2 + \text{HCl} \longrightarrow \text{C}_2\text{H}_3\text{Cl}$ .

(2) Under what condition the reaction is first order?