We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Thermodynamics of Interfaces

Omid Moradi
Shahre-Qods Branch, Islamic Azad University,
Iran

1. Introduction

Thermodynamics is the branch of science that is concerned with the principles of energy transformation in *macroscopic* systems. Macroscopic properties of matter arise from the behavior of a very large number of molecules. Thermodynamics is based upon experiment and observation, summarized and generalized in the *Laws of Thermodynamics*. These laws are not derivable from any other principle: they are in fact improvable and therefore can be regarded as assumptions only; nevertheless their validity is accepted because exceptions have never been reported. These laws do not involve any postulates about atomic and molecular structure but are founded upon observation about the universe as it is, in terms of instrumental measurements. In order to represent the state of a gas or a liquid or a solid system, input data of average quantities such as temperature (T), pressure (P), volume (V), and concentration (c) are used. These averages reduce the enormous number of variables that one needs to start a discussion on the positions and momentums of billions of molecules. We use the thermodynamic variables to describe the state of a system, by forming a *state function*:

$$P = f(V, T, n) \tag{1}$$

This simply shows that there is a physical relationship between different quantities that one can measure in a gas system, so that gas pressure can be expressed as a function of gas volume, temperature and number of moles, n. In general, some relationships come from the specific properties of a material and some follow from physical laws that are independent of the material (such as the laws of thermodynamics). There are two different kinds of thermodynamic variables: *intensive variables* (those that do not depend on the size and amount of the system, like temperature, pressure, density, electrostatic potential, electric field, magnetic field and molar properties) and *extensive variables* (those that scale linearly with the size and amount of the system, like mass, volume, number of molecules, internal energy, enthalpy and entropy). Extensive variables are additive whereas intensive variables are not (Adamson, A.W. and Gast, A.P. 1997).

In thermodynamic terms, the object of a study is called the system, and the remainder of the universe, the surroundings. Amounts of the order of a mole of matter are typical in a system under consideration, although thermodynamics may remain applicable for considerably smaller quantities. The imaginary envelope, which encloses the system and separates it from its surroundings, is called the boundary of the system. This boundary may serve either to isolate the system from its surroundings, or to provide for interaction in specific ways

between the system and surroundings. In practice, if a reactor is used to carry out a chemical reaction, the walls of the reactor that are in contact with the thermo stated liquid medium around the reactor may be assumed to be the surroundings of the experimental system. For particles such as colloids, the medium in which they are immersed may act as the surroundings, provided nothing beyond this medium influences the particle. An isolated system is defined as a system to or from which there is no transport of matter and energy. When a system is isolated, it cannot be affected by its surroundings. The universe is assumed to be an isolated system. Nevertheless, changes may occur within the system that are detectable using measuring instruments such as thermometers, pressure gauges etc. However, such changes cannot continue indefinitely, and the system must eventually reach a final static condition of internal equilibrium. If a system is not isolated, its boundaries may permit exchange of matter or energy or both with its surroundings. A closed system is one for which only energy transfer is permitted, but no transfer of mass takes place across the boundaries, and the total mass of the system is constant. As an example, a gas confined in an impermeable cylinder under an impermeable piston is a closed system. For a closed system, this interacts with its surroundings; a final static condition may be reached such that the system is not only internally at equilibrium but also in external equilibrium with its surroundings. A system is in equilibrium if no further spontaneous changes take place at constant surroundings. Out of equilibrium, a system is under a certain stress, it is not relaxed, and it tends to equilibrate. However, in equilibrium, the system is fully relaxed. If a system is in equilibrium with its surroundings, its macroscopic properties are fixed, and the system can be defined as a given thermodynamic state. It should be noted that a thermodynamic state is completely different from a molecular state because only after the precise spatial distributions and velocities of all molecules present in a system are known can we define a molecular state of this system. An extremely large number of molecular states correspond to one thermodynamic state, and the application of statistical thermodynamics can form the link between them (Lyklema, J. 2005), (Dabrowski A., 2001).

2. Energy, work and heat

2.1 The first law of thermodynamics
Generally, when a system passes through a process it exchanges energy U with its environment. The energy change in the system ΔU may result from performing work w on the system or letting the system perform work, and from exchanging heat q between the system and the environment

$$\Delta U = q + w \tag{2}$$

The heat and the work supplied to a system are withdrawn from the environment, such that, according to the first law of thermodynamics

$$\Delta U_{system} + \Delta U_{environment} = 0 \tag{3}$$

The First Law of thermodynamics states that the energy content of the universe (or any other isolated system) is constant. In other words, energy can neither be created nor annihilated. It implies the impossibility of designing a perpetuum mobile, a machine that performs work without the input of energy from the environment. The First Law also implies that for a system passing from initial state 1 to final state 2 the energy change

$\Delta_{1\to 2}U$ does not depend on the path taken to go from 1 to 2. A direct consequence of that conclusion is that U is a function of state: when the macroscopic state of a system is fully specified with respect to composition, temperature, pressure, and so on (the so-called state variables), its energy is fixed. This is not the case for the exchanged heat and work. These quantities do depend on the path of the process. For an infinitesimal small change of the energy of the system

$$\Delta U = \partial q + \partial w \tag{4}$$

For w and, hence, ∂w, various types of work may be considered, such as mechanical work resulting from compression or expansion
of the system, electrical work, interfacial work associated with expanding or reducing the interfacial area between two phases, and chemical work due to the exchange of matter between system and environment. All types of work are expressed as $\int X dY$, where X and Y are state variables. X is an intensive property (independent of the extension of the system) and Y the corresponding extensive property (it scales with the extension of the system). Examples of such combinations of intensive and extensive properties are pressure p and volume V, interfacial tension γ and interfacial area A, electric potential Ψ and electric charge Q, the chemical potential μ_i of component i, and the number of moles n_i of component i. As a rule, X varies with Y but for an infinitesimal small change of Y, X is approximately constant. Hence, we may write

$$dU = \partial q - pdV + \gamma dA + \psi dQ + \sum_i \mu_i dn_i \tag{5}$$

The terms of type XdY in Eq. above represent mechanical (volume), interfacial, electric, and chemical works, respectively. $\sum_i$ implies summation over all components in the system. It is obvious that for homogeneous systems the γdA term is not relevant.

2.2 The second law of thermodynamics: entropy

According to the First Law of thermodynamics the energy content of the universe is constant. It follows that any change in the energy of a system is accompanied by an equal, but opposite, change in the energy of the environment. At first sight, this law of energy conservation seems to present good news: if the total amount of energy is kept constant why then should we be frugal in using it? The bad news is that all processes always go in a certain direction, a direction in which the energy that is available for performing work continuously decreases.
Entropy, S, is the central notion in the Second Law. The entropy of a system is a measure of the number of ways the energy can be stored in that system. In view of the foregoing, any spontaneous process goes along with an entropy increase in the universe that is, ΔS > 0. If as a result of a process the entropy of a system decreases, the entropy of the environment must increase in order to satisfy the requirement ΔS > 0 (Levine, I.N., 1990).
Based on statistical mechanics, the entropy of a system, at constant U and V can be expressed by Boltzmann's law

$$S_{u,v} = k_B \ln w \tag{6}$$

where w is the number of states accessible to the system and k_B is Boltzmann's constant. For a given state w is fixed and, hence, so is S. It follows that S is a function of state. It furthermore follows that S is an extensive property: for a system comprising two subsystems (a and b) w= w_a + w_b and therefore, because of, S = S_a+ S_b. The entropy change in a system undergoing a process $1 \rightarrow 2$ is thermodynamically formulated in terms of the heat ∂q taken up by that system and the temperature T at which the heat uptake occurs(sraelachvili, J. 1991):

$$\Delta S \geq \int_1^2 \frac{\partial q}{T} \tag{7}$$

Because the temperature may change during the heat transfer is written in differential form (Pitzer, K.S. and Brewer L. 1961).

2.3 Reversible processes

In contrast to the entropy, heat is not a function of state. For the heat change it matters whether a process $1 \rightarrow 2$ is carried out reversibly or irreversibly. For a reversible process, that is, a process in which the system is always fully relaxed

$$\Delta S = \int_1^2 \frac{\partial q_{rev.}}{T} \tag{8}$$

Infinitesimal small changes imply infinitesimal small deviations from equilibrium and, therefore, reversibility. The term ∂q in (5) may then be replaced by TdS, which gives

$$dU = Tds - pdV + \gamma dA + \psi dQ + \sum_i \mu_i dn_i \tag{9}$$

where all terms of the right-hand side are now of the form XdY. Equation (9) allows the intensive variables X to be expressed as differential quotients, such as, for instance,

$$\gamma = (\frac{\partial U}{\partial A})_{S,V,Q,ni,s} \tag{10}$$

where the subscripts indicate the properties that are kept constant. In other words, the interfacial tension equals the energy increment of the system resulting from the reversible extension of the interface by one unit area under the conditions of constant entropy, volume, electric charge, and composition. The required conditions make this definition very impractical, if not in operational. If the interface is extended it is very difficult to keep variables such as entropy and volume constant.

The other intensive variables may be expressed similarly as the change in energy per unit extensive property, under the appropriate conditions (Tempkin M. I. and Pyzhev V., 1940).

2.4 Maxwell relations

At equilibrium, implying that the intensive variables are constant throughout the system, (9) may be integrated, which yields

$$U = TdS - pV + \gamma A + \psi Q + \sum_i \mu_i n_i \tag{11}$$

To avoid impractical conditions when expressing intensive variables as differential quotients as, for example auxiliary functions are introduced. These are the enthalpy H, defined as

$$H \equiv U + pV \tag{12}$$

the Helmholtz energy

$$A \equiv U - TS \tag{13}$$

and the Gibbs energy

$$G \equiv U + pV - TS = H - TS = A + pV \tag{14}$$

Since U is a function of state, and p, V, T, and S are state variables, H, A, and G are also functions of state. The corresponding differentials are

$$dH = TdS + Vdp + \gamma dA + \psi dQ + \sum_i \mu_i dn_i \tag{15}$$

$$dA = -SdT - pdV + \gamma dA + \psi dQ + \sum_i \mu_i dn_i \tag{16}$$

$$dG = -SdT + Vdp + \gamma dA + \psi dQ + \sum_i \mu_i dn_i \tag{17}$$

Expressing γ, Ψ, or μ_i as a differential quotient requires constancy of S and V, S and p, T and V, and T and p, when using the differentials dU, dH, dA, and dG, respectively. In most cases the conditions of constant T and V or constant T and p are most practical. It is noted that for heating or cooling a system at constant p, the heat exchange between the system and its environment is equal to the enthalpy exchange. Hence, for the heat capacity, at constant p,

$$C_p = (\frac{\partial q}{dT})_p = (\frac{dH}{dT})_p \tag{18}$$

In general, for a function of state f that is completely determined by variables x and y, df = Adx + Bdy. Cross-differentiation in df gives $(\partial A / \partial y)_x = (\partial B / \partial x)_y$, known as a Maxwell relation. Similarly, cross-differentiation in dU, dH, dA, and dG yields a wide variety of Maxwell relations between differential quotients. For instance, by cross-differentiation in dG we find, (Lyklema, L. 1991), (Pitzer, K.S. and Brewer L. 1961).

$$(\frac{\partial \gamma}{\partial T})_{p,A,Q,n_i,s} = -(\frac{\partial S}{\partial A})_{T,p,Q,n_i,s} \tag{19}$$

2.5 Molar properties and partial molar properties

Molar properties, indicated by a lowercase symbol, are defined as an extensive property Y per mole of material: y = Y/n. Since they are expressed per mole, molar quantities are intensive.

For a single component system Y is a function of T; p; . . . ; n. Many extensive quantities vary linearly with n, but for some (e.g., the entropy) the variation with n is not proportional. In the latter case y is still a function of n. In a two-, three- or multi-component system (i.e., a mixture), the contribution of each component to the functions of state, say, the energy of the

system cannot be assigned unambiguously. This is because the energy of the system is not simply the sum of the energies of the constituting components but includes the interaction energies between the components as well. It is impossible to specify which part of the total interaction energy belongs to component i. For that reason partial molar quantities y_i are introduced. They are defined as the change in the extensive quantity Y pertaining to the whole system due to the addition of one mole of n_i under otherwise constant conditions. Because by adding component i the composition of the mixture and, hence, the interactions between the components are affected, y_i is defined as the differential quotient (Prausnitz, J.M., and et al. 1999).

$$y_i \equiv \left(\frac{\partial Y}{\partial n_i}\right)_{T,p,\ldots,n\,j\neq 1} \tag{20}$$

The partial molar quantities are operational; that is, they can be measured. Now $Y_{T,p,\ldots n_{i,s}}$ can be obtained as $\sum_i n_i y_i$ A partial molar quantity often encountered is the partial molar Gibbs energy (Aveyard, R. and Haydon, D.A., 1973),

$$g_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,p,\ldots,n\,j\neq i} \tag{21}$$

According to (17)

$$g_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,p,\ldots,n\,j\neq i} = \mu_i \tag{22}$$

that is, at constant $_{T,p,\ldots,n\,j\neq i}$,the chemical potential of component *i* in a mixture equals its partial molar Gibbs energy.

By cross-differentiation in (17) the temperature- and pressure-dependence of μ_i can be derived as

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\ldots,n_{i,s}} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,p,\ldots,n\,j\neq i} = -s_i \tag{23}$$

With

$$\mu_i = g_i \equiv H_i - Ts_i \tag{24}$$

it can be deduced that

$$\left(\frac{\partial (\mu_i / T)}{\partial T}\right)_{p,\ldots n_{i,s}} = -\frac{H}{T^2} \tag{25}$$

The pressure-dependence of mi is also obtained from (17):

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\ldots,n_{i,s}} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,\ldots n\,j\neq i} \equiv v_i \tag{26}$$

For an ideal gas

$$v_i = \frac{RT}{p_i} \tag{27}$$

in which R is the universal gas constant. Combining (26) and (27) gives, after integration, an expression for $\mu_i(p_i)$ in an ideal gas

$$\mu_i = \mu_i^0 + RT \ln p_i \tag{28}$$

where μ_i^0 is an integration constant that is independent of p_i; $\mu_i^0 \equiv \mu_i(p_i = 1)$, its value depending on the units in which p_i is expressed. Similarly, without giving the derivation here, it is mentioned that for the chemical potential of component i in an ideal solution

$$\mu_i = \mu_i^0 + RT \ln c_i \tag{29}$$

where c_i is the concentration of i in the solution. In more general terms, for an ideal mixture

$$\mu_i = \mu_i^0 + RT \ln X_i \tag{30}$$

where X_i is the mole fraction of i in the mixture, defined as $X_i \equiv n_i / \sum_i n_i$. Note that the value of μ_i^0 is the one obtained for m_i by extrapolating to X_i=1 assuming ideality of the mixture. This value deviates from the real value of μ_i for pure i, because in the case of pure i the ''mixture'' is as far as possible from ideal. As said μ_i and μ_i^0 are defined per unit X_i, c_i, and p_i, respectively, and their values are therefore independent of the configurations of i in the mixture. They do depend on the interactions between i and the other components and therefore on the types of substances in the mixture. Because X_i, c_i, and p_i are expressed in different units, the values for μ_i and μ_i^0 differ (Keller J.U., 2005)

The $RT \ln X_i$ term in Eq. (30) or, for that matter, the $RT \ln c_i$ and $RT \ln p_i$ terms in (28) and (29) do not contain any variable pertaining to the types of substances in the mixture. Hence, these terms are generic. Interpretation of the $RT \ln X_i$ term follows from

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\dots n_i,s} = \frac{\partial \mu_i^0}{\partial T} + R \ln X_i \tag{31}$$

which, because of (23), gives

$$s_i = s_i^0 - R \ln X_i \tag{32}$$

The partial molar entropy of i is composed of a part s_i^0, which is independent of the configurations of i in the mixture but dependent on the interactions of i with the other components, and a part $R \ln X_i$, which takes into account the possible configurations of i. It follows that the $RT \ln X_i$ (or $RT \ln c_i$ or $RT \ln p_i$) term in the expressions for μ_i stems from the configurationally possibilities as well.

3. Basic thermodynamics of interfaces

For an open system of variable surface area, the Gibbs free energy must depend on composition, temperature, T, pressure, p, and the total surface area, A:

$$G = G(T, p, A, n_1, n_2, \ldots n_k)$$ (33)

From this function it follows that:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \left(\frac{\partial G}{\partial p}\right)_{p,n_j} dp + \left(\frac{\partial G}{\partial A}\right)_{T,p,n_i} dA + \sum_{i=1}^{i=k} \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} dn_i$$ (34)

The first two partial differentials refer to constant composition, so we my use the general definitions:

$$G = H - TS = U + PV - TS$$ (35)

To obtain

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,n_j}$$ (36)

and

$$V = -\left(\frac{\partial G}{\partial p}\right)_{p,n_i}$$ (37)

Insertion of these relations into (35) gives us the fundamental result

$$dG = -SdT + Vdp + \gamma dA + \sum_{i=1}^{i=k} \mu_i dn_i$$ (38)

where the chemical potential μ_i is defined as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j}$$ (39)

and the surface energy γ as:

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,p,n_j}$$ (40)

The chemical potential is defined as the increase in free energy of a system on adding an infinitesimal amount of a component (per unit number of molecules of that component added) when T, p and the composition of all other components are held constant. Clearly, from this definition, if a component 'i' in phase A has a higher chemical potential than in phase B (that is, $\mu_i^A > \mu_i^B$) then the total free energy will be lowered if molecules are transferred from phase A to B and this will occur in a spontaneous process until the

chemical potentials equalize, at equilibrium. It is easy to see from this why the chemical potential is so useful in mixtures and solutions in matter transfer (open) processes (Norde, W., 2003). This is especially clear when it is understood that mi is a simple function of concentration, that is:

$$\mu_i = \mu_i^0 + kT \ln C_i \tag{41}$$

for dilute mixtures, where mi o is the standard chemical potential of component 'i', usually 1 M for solutes and 1 atm for gas mixtures. This equation is based on the entropy associated with a component in a mixture and is at the heart of why we generally plot measurable changes in any particular solution property against the log of the solute concentration, rather than using a linear scale. Generally, only substantial changes in concentration or pressure produce significant changes in the properties of the mixture. (For example, consider the use of the pH scale.) (Koopal L.K., and et al. 1994).

3.1 Thermodynamics for closed systems

The First Law of Thermodynamics is the law of conservation of energy; it simply requires that the total quantity of energy be the same both before and after the conversion. In other words, the total energy of any system and its surroundings is conserved. It does not place any restriction on the conversion of energy from one form to another. The interchange of heat and work is also considered in this first law. In principle, the internal energy of any system can be changed, by heating or doing work on the system. The First Law of Thermodynamics requires that for a closed (but not isolated) system, the energy changes of the system be exactly compensated by energy changes in the surroundings. Energy can be exchanged between such a system and its surroundings in two forms: heat and work. Heat and work have the same units (joule, J) and they are ways of transferring energy from one entity to another. A quantity of heat, Q, represents an amount of energy in transit between a system and its surroundings, and is not a property of the system. Heat flows from higher to lower temperature systems. Work, W, is the energy in transit between a system and its surroundings, resulting from the displacement of external force acting on the system. Like heat, a quantity of work represents an amount of energy and is not a property of the system. Temperature is a property of a system while heat and work refer to a process. It is important to realize the difference between temperature, heat capacity and heat: temperature, T, is a property which is equal when heat is no longer conducted between bodies in thermal contact and can be determined with suitable instruments (thermometers) having a reference system depending on a material property (for example, mercury thermometers show the density differences of liquid mercury metal with temperature in a capillary column in order to visualize and measure the change of temperature). Suppose any closed system (thus having a constant mass) undergoes a process by which it passes from an initial state to a final state. If the only interaction with its surroundings is in the form of transfers of heat, Q, and work, W, then only the internal energy, U, can be changed, and the First Law of Thermodynamics is expressed mathematically as (Lyklema, J. ;2005 & Keller J.U.;2005)

$$\Delta U = U_{final} - U_{initial} = Q + W \tag{42}$$

where Q and W are quantities inclusive of sign so that when the heat transfers from the system or work is done by the system, we use negative values in Equation (11). Processes

where heat should be given to the system (or absorbed by the system) (Q > 0) are called endothermic and processes where heat is taken from the system (or released from the system) (Q < 0) are called exothermic. The total work performed on the system is W. There are many different ways that energy can be stored in a body by doing work on it: volumetrically by compressing it; elastically by straining it; electrostatically by charging it; by polarizing it in an electric field E; by magnetizing it in a magnetic field H; and chemically, by changing its composition to increase its chemical potential. In interface science, the formation of a new surface area is also another form of doing work. Each example is a different type of work – they all have the form that the (differential) work performed is the change in some extensive variable of the system multiplied by an intensive variable. In thermodynamics, the most studied work type is pressure–volume work, W_{PV}, on gases performed by compressing or expanding the gas confined in a cylinder under a piston. All other work types can be categorized by a single term, *non-pressure–volume work*, W_{non-PV}. Then, *W* is expressed as the sum of the pressure–volume work, W_{PV}, and the non pressure–volume work, W_{non-PV}, when many types of work are operative in a process (Miladinovic N., Weatherley L.R. 2008).

Equation (11) states that the internal energy, ΔU depends only on the initial and final states and in no way on the path followed between them. In this form, heat can be defined as *the work-free transfer of internal energy from one system to another*. Equation (11) applies both to *reversible* and *irreversible* processes. A *reversible process* is an infinitely slow process during which departure from equilibrium is always infinitesimally small. In addition, such processes can be reversed at any moment by infinitesimal changes in the surroundings (in external conditions) causing it to retrace the initial path in the opposite direction. A reversible process proceeds so that the system is never displaced more than differentially from an equilibrium state. An *irreversible process* is a process where the departure from equilibrium cannot be reversed by changes in the surroundings. For a differential change, Equation (11) is often used in the differential form (Scatchard, G. 1976), (Zeldowitsch J., 1934):

$$dU = \partial W + \partial Q \qquad (43)$$

for reversible processes involving infinitesimal changes only. The internal energy, *U* is a function of the measurable quantities of the system such as temperature, volume, and pressure, which are all state functions like internal energy itself. The differential d*U is* an exact differential similar to d*T*, d*V*, and d*P*; so we can always integrate $\left[\int_1^2 f(U)dU \right]$ expression.

3.2 Derivation of the gibbs adsorption isotherm

Let us consider the interface between two phases, say between a liquid and a vapor, where a solute (i) is dissolved in the liquid phase. The real concentration gradient of solute near the interface may look like Figure 10.1. When the solute increases in concentration near the surface (e.g. a surfactant) there must be a surface excess of solute n_i^δ, compared with the bulk value continued right up to the interface. We can define a surface excess concentration (in units of moles per unit area) as:

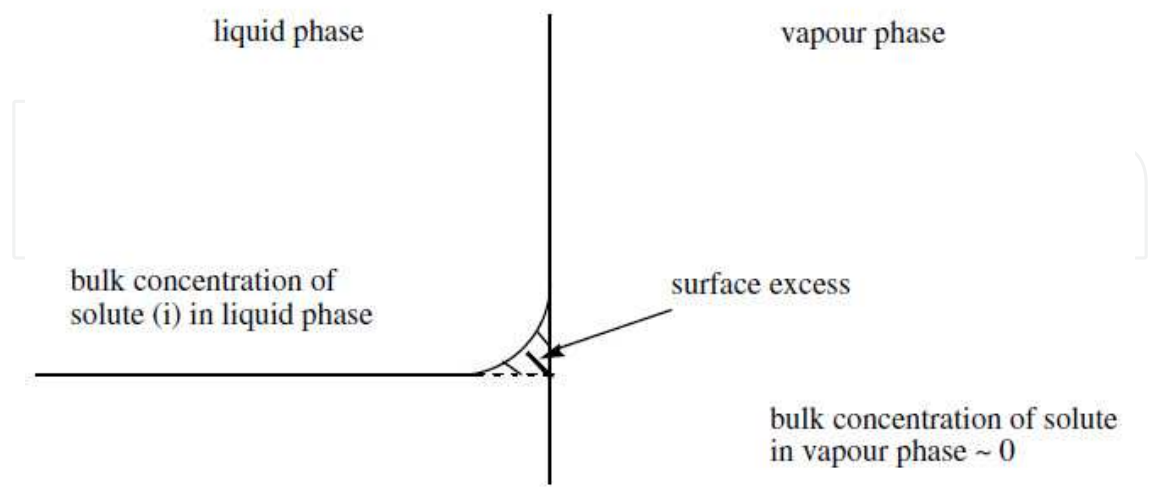$$\Gamma_i = \frac{n_i^{\delta}}{A} \tag{44}$$

Fig. 1. Diagram of the variation in solute concentration at an interface between two phases.
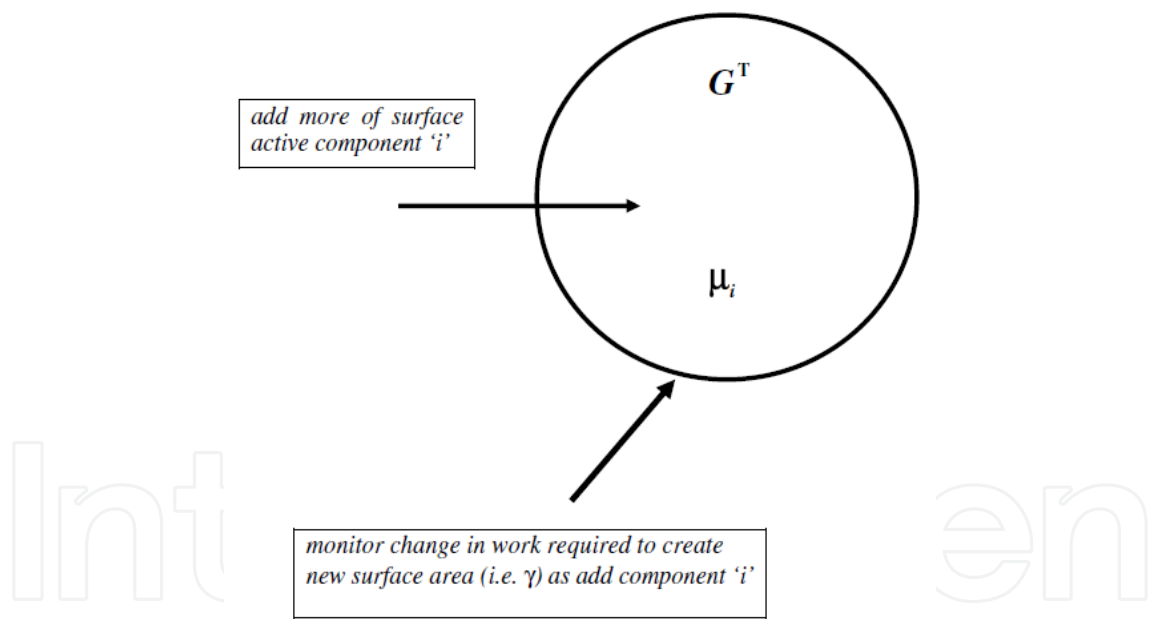

Fig. 2. Diagrammatic illustration of the change in surface energy caused by the addition of a solute.

where A is the interfacial area (note that Γ_i may be either positive or negative). Let us now examine the effect of adsorption on the interfacial energy (γ). If a solute 'i' is positively adsorbed with a surface density of Γ_i, we would expect the surface energy to decrease on increasing the bulk concentration of this component (and vice versa). This situation is illustrated in Figure 10.2, where the total free energy of the system GT and mi are both increased by addition of component i but because this component is favourably adsorbed at the surface (only relative to the solvent, since both have a higher energy state at the surface),

the work required to create new surface (i.e. γ) is reduced. Thus, although the total free energy of the system increases with the creation of new surface, this process is made easier as the chemical potential of the selectively adsorbed component increases (i.e. with concentration). This reduction in surface energy must be directly related to the change in chemical potential of the solute and to the amount adsorbed and is therefore given by the simple relationship (Zeldowitsch J., 1934):

$$d\gamma = -\Gamma_i d\mu_i \tag{45}$$

or, for the case of several components,

$$d\gamma = -\sum_i \Gamma_i d\mu_i \tag{46}$$

The change in m_i is caused by the change in bulk solute concentration. This is the Gibbs surface tension equation. Basically, these equations describe the fact that increasing the chemical potential of the adsorbing species reduces the energy required to produce new surface (i.e. γ). This, of course, is the principal action of surfactants, which will be discussed in more detail in a later section. Using this result let us now consider a solution of two components

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \tag{47}$$

and hence the adsorption excess for one of the components is given by

$$\Gamma_1 = -\left(\frac{\partial \gamma}{\partial \mu_1}\right)_{T,\mu_2} \tag{48}$$

Thus, in principle, we could determine the adsorption excess of one of the components from surface tension measurements, if we could vary m_1 independently of μ_2. But the latter appears not to be possible, because the chemical potentials are dependent on the concentration of each component. However, for dilute solutions the change in μ for the solvent is negligible compared with that of the solute. Hence, the change for the solvent can be ignored and we obtain the simple result that

$$d\gamma = -\Gamma_1 d\mu_1 \tag{49}$$

Now, since $\mu_1 = \mu_2 + RT \ln c_1$, differentiation with respect to c_1 gives

$$\left(\frac{\partial \mu_1}{\partial c_1}\right)_T = RT\left(\frac{\partial \ln c_1}{\partial c_1}\right)_T = \frac{RT}{c_1} \tag{50}$$

Then substitution in (49) leads to the result:

$$\Gamma_1 = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln c_1}\right)_T = \frac{c_1}{RT}\left(\frac{\partial \gamma}{\partial c_1}\right)_T \tag{51}$$

This is the important Gibbs adsorption isotherm. (Note that for concentrated solutions the activity should be used in this equation.) An experimental measurement of γ over a range of concentrations allows us to plot γ against $\ln c_1$ and hence obtain Γ_1, the adsorption density at

the surface. The validity of this fundamental equation of adsorption has been proven by comparison with direct adsorption measurements. The method is best applied to liquid/vapor and liquid/liquid interfaces, where surface energies can easily be measured. However, care must be taken to allow equilibrium adsorption of the solute (which may be slow) during measurement.

Finally, it should be noted that (51) was derived for the case of a single adsorbing solute (e.g. a non-ionic surfactant). However, for ionic surfactants such as CTAB, two species (CTA$^+$ and Br$^-$) adsorb at the interface. In this case the equation becomes(Murrell, J.N. and Jenkins, A.D. 1994), (Ng J.C.Y., and et al. 2002):

$$\Gamma_1 = -\frac{1}{2RT}\left(\frac{\partial\gamma}{\partial\ln c_1}\right)_{TT} \tag{52}$$

because the bulk chemical potentials of both ions change with concentration of the surfactant.

4. Fundamentals of pure component adsorption equilibrium

Adsorption equilibria information is the most important piece of information in understanding an adsorption process. No matter how many components are present in the system, the adsorption equilibria of pure components are the essential ingredient for the understanding of how many those components can be accommodated by a solid adsorbent. With this information, it can be used in the study of adsorption kinetics of a single component, adsorption equilibria of multicomponent systems, and then adsorption kinetics of multicomponent systems. In this section, we present the fundamentals of pure component equilibria. Various fundamental equations are shown, and to start with the proceeding we will present the most basic theory in adsorption: the Langmuir theory (1918). This theory allows us to understand the monolayer surface adsorption on an ideal surface. By an ideal surface here, we mean that the energy fluctuation on this surface is periodic and the magnitude of this fluctuation is larger than the thermal energy of a molecule (kT), and hence the troughs of the energy fluctuation are acting as the adsorption sites. If the distance between the two neighboring troughs is much larger than the diameter of the adsorbate molecule, the adsorption process is called localised and each adsorbate molecule will occupy one site. Also, the depth of all troughs of the ideal surface are the same, that is the adsorption heat released upon adsorption on each site is the same no matter what the loading is. After the Langmuir theory, we will present the Gibbs thermodynamics approach. This approach treats the adsorbed phase as a single entity, and Gibbs adapted the classical thermodynamics of the bulk phase and applied it to the adsorbed phase. In doing this the concept of volume in the bulk phase is replaced by the area, and the pressure is replaced by the so-called spreading pressure. By assuming some forms of thermal equation of state relating the number of mole of adsorbate, the area and the spreading pressure (analogue of equations of state in the gas phase) and using them in the Gibbs equation, a number of fundamental equations can be derived, such as the linear isotherm, etc (Mohan D., Pittman Jr C.U. 2006).

Following the Gibbs approach, we will show the vacancy solution theory developed by Suwanayuen and Danner in 1980. Basically in this approach the system is assumed to consist of two solutions. One is the gas phase and the other is the adsorbed phase. The

difference between these two phases is the density. One is denser than the other. In the context of this theory, the vacancy solution is composed of adsorbate and vacancies. The latter is an imaginary entity defined as a vacuum space which can be regarded as the solvent of the system. Next, we will discuss one of the recent equations introduced by Nitta and his co-workers. This theory based on statistical thermodynamics has some features similar to the Langmuir theory, and it encompasses the Langmuir equation as a special case. Basically it assumes a localized monolayer adsorption with the allowance that one adsorbate molecule can occupy more than one adsorption site. Interaction among adsorbed molecules is also allowed for in their theory. As a special case, when the number of adsorption sites occupied by one adsorbate molecule is one, their theory is reduced to the Fowler-Guggenheim equation, and further if there is no adsorbate-adsorbate interaction this will reduce to the Langmuir equation. Another model of Nitta and co-workers allowing for the mobility of adsorbed molecules is also presented in this section.
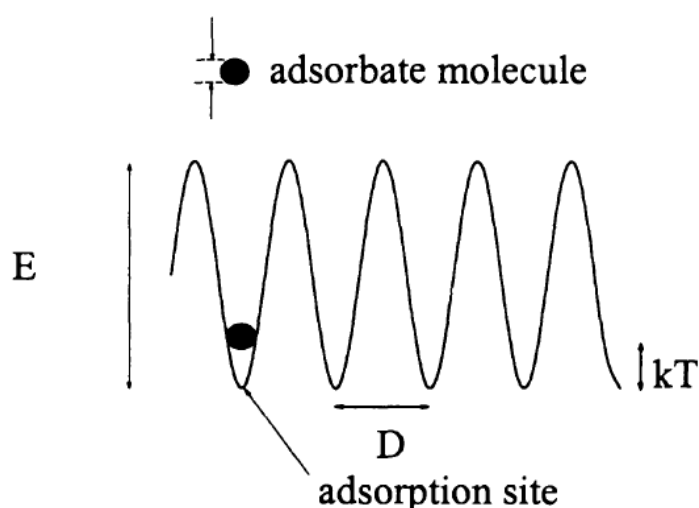

Fig. 3. Surface energy fluctuations

4.1 Langmuir equation

Langmuir (1918) was the first to propose a coherent theory of adsorption onto a flat surface based on a kinetic viewpoint, that is there is a continual process of bombardment of molecules onto the surface and a corresponding evaporation (desorption) of molecules from the surface to maintain zero rate of accumulation at the surface at equilibrium. The assumptions of the Langmuir model are:

4.1.1 Surface is homogeneous, that is adsorption energy is constant over all sites
4.1.2 Adsorption on surface is localized, that is adsorbed atoms or molecules are adsorbed at definite, localized sites
4.1.3 Each site can accommodate only one molecule or atom

The Langmuir theory is based on a kinetic principle, that is the rate of adsorption (which is the striking rate at the surface multiplied by a sticking coefficient, sometimes called the accommodation coefficient) is equal to the rate of desorption from the surface. The rate of striking the surface, in mole per unit time and unit area, obtained from the kinetic theory of gas is:

$$R_s = \frac{P}{\sqrt{2\pi M R_g T}} \qquad (53)$$

To give the reader a feel about the magnitude of this bombardment rate of molecule, we tabulate below this rate at three pressures

P (Torr)	R_s (molecules/cm²/sec)
760	3 x 10^{23}
1	4 x 10^{20}
10^{-3}	4 x 10^{17}

Table 1. Magnitude of bombardment rate of molecule

This shows a massive amount of collision between gaseous molecules and the surface even at a pressure of 10^{-3} Torr. A fraction of gas molecules striking the surface will condense and is held by the surface force until these adsorbed molecules evaporate again (see Figure 10.4.). Langmuir (1918) quoted that there is good experimental evidence that this fraction is unity, but for a real surface which is usually far from ideal this fraction could be much less than unity. Allowing for the sticking coefficient a (which accounts for non perfect sticking), the rate of adsorption in mole adsorbed per unit bare surface area per unit time is:

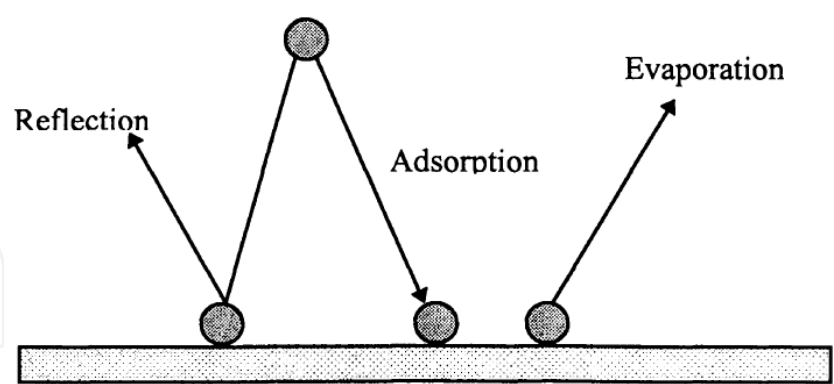$$R_a = \frac{\alpha P}{\sqrt{2\pi M R_g T}} \qquad (54)$$

Fig. 4. Schematic diagram of Langmuir adsorption mechanism on a flat surface

This is the rate of adsorption on a bare surface. On an occupied surface, when a molecule strikes the portion already occupied with adsorbed species, it will evaporate very quickly, just like a reflection from a mirror. Therefore, the rate of adsorption on an occupied surface is equal to the rate given by eq. (54) multiplied by the fraction of empty sites, that is:

$$R_a = \frac{\alpha P}{\sqrt{2\pi M R_g T}}(1-\theta) \qquad (55)$$

where Θ is the fractional coverage. Here R_a is the number of moles adsorbed per unit area (including covered and uncovered areas) per unit time. The rate of desorption from the surface is equal to the rate, which corresponds to fully covered surface (k_d), multiplied by the fractional coverage, that is:

$$R_d = k_d \theta = k_{d\infty} \exp\left(\frac{-E_d}{R_g T}\right)\theta \tag{56}$$

where E_d is the activation energy for desorption, which is equal to the heat of adsorption for physically adsorbed species since there is no energy barrier for physical adsorption. The parameter $k_{d\infty}$ is the rate constant for desorption at infinite temperature. The inverse of this parameter is denoted as

$$\tau_{d\infty} = \frac{1}{k_{d\infty}} \tag{57}$$

The average residence time of adsorption is defined as:

$$\tau_a = \tau_{d\infty} e^{E_d/RT} \tag{58}$$

This means that the deeper is the potential energy well higher E_d the longer is the average residence time for adsorption. For physical adsorption, this surface residence time is typically ranging between 10^{-13} to 10^{-9} sec, while for chemisorption this residence time has a very wide range, ranging from 10^{-6} (for weak chemisorption) to about 10^{9} for systems such as CO chemisorbed on Ni. Due to the Arrhenius dependence on temperature this average surface residence time changes rapidly with temperature, for example a residence time of 10^{9} at 300K is reduced to only 2 sec at 500K for a system having a desorption energy of 120 kJ/mole. Equating the rates of adsorption and desorption (Equations. 55 and 56), we obtain the following famous Langmuir isotherm written in terms of fractional loading:

$$\theta = \frac{bP}{1 + bP} \tag{59}$$

where

$$b = \frac{\alpha \exp(Q / R_g T)}{k_{d\infty}\sqrt{2\pi M R_g T}} = b_\infty \exp(Q / R_g T) \tag{60}$$

Here Q is the heat of adsorption and is equal to the activation energy for desorption, E_d. The parameter b is called the affinity constant or Langmuir constant. It is a measure of how strong an adsorbate molecule is attracted onto a surface. The pre exponential factor b_∞ of the affinity constant is:

$$b_\infty = \frac{\alpha}{k_{d\infty}\sqrt{2\pi M R_g T}} \tag{61}$$

which is inversely proportional to the square root of the molecular weight. When P is in Torr, the magnitude of b_∞ for nitrogen is given by Hobson (1965) as:

$$b_\infty = 5.682 \times 10^{-5} (MT)^{-1/2} Torr^{-1} \tag{62}$$

The isotherm equation (59) reduces to the Henry law isotherm when the pressure is very low (bP << 1), that is the amount adsorbed increases linearly with pressure, a constraint demanded by statistical thermodynamics. When pressure is sufficiently high, the amount adsorbed reaches the saturation capacity, corresponding to a complete coverage of all adsorption sites with adsorbate molecules, this is called monolayer coverage, $\theta \to 1$. The behavior of the Langmuir isotherm (Θ versus P) is shown in Fig. 5.
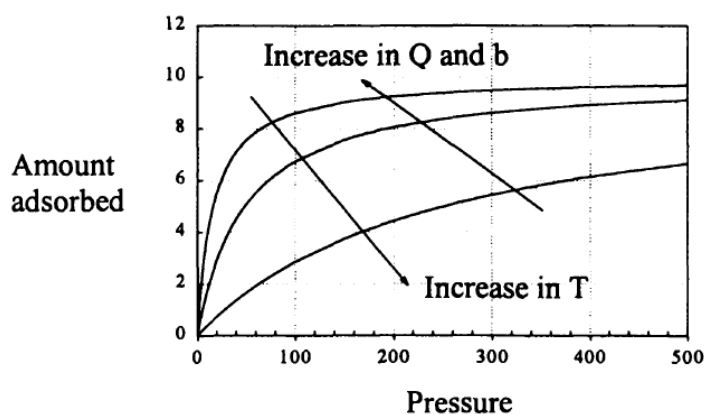
Fig. 5. Behavior of the Langmuir equation

When the affinity constant b is larger, the surface is covered more with adsorbate molecule as a result of the stronger affinity of adsorbate molecule towards the surface. Similarly, when the heat of adsorption Q increases, the adsorbed amount increases due to the higher energy barrier that adsorbed molecules have to overcome to evaporate back to the gas phase. Increase in the temperature will decrease the amount adsorbed at a given pressure. This is due to the greater energy acquired by the adsorbed molecule to evaporate. The isotherm equation (59) written in the form of fractional loading is not useful for the data correlation as isotherm data are usually collated in the form of amount adsorbed versus pressure. We now let C_μ be the amount adsorbed in mole per unit mass or volume[1], and $C_{\mu s}$ be the maximum adsorbed concentration corresponding to complete monolayer coverage, then the Langmuir equation written in terms of the amount adsorbed useful for data correlation is:

$$C_\mu = C_{\mu s} \frac{b(T)P}{1 + b(T)P} \tag{63}$$

where

$$b(T) = b_\infty \exp(Q / R_g T) \tag{64}$$

Here we use the subscript μ to denote the adsorbed phase, and this will be applied throughout this text. For example, C_μ is the concentration of the adsorbed phase, and D_μ is

---

[1] This volume is taken as the particle volume minus the void volume where molecules are present in free form.

the diffusion coefficient of the adsorbed phase, V_μ is the volume of the adsorbed phase, etc. The temperature dependence of the affinity constant (e.g. 60) is $T^{-1/2} \exp(Q/R_g T)$. This affinity constant decreases with temperature because the heat of adsorption is positive, that is adsorption is an exothermic process. Since the free energy must decrease for the adsorption to occur and the entropy change is negative because of the decrease in the degree of freedom, therefore

$$\Delta H = \Delta G + T\Delta S < 0 \tag{65}$$

The negativity of the enthalpy change means that heat is released from the adsorption process. The Langmuir equation can also be derived from the statistical thermodynamics, based on the lattice statistics.

4.2 Isosteric heat of adsorption

One of the basic quantities in adsorption studies is the isosteric heat, which is the ratio of the infinitesimal change in the adsorbate enthalpy to the infinitesimal change in the amount adsorbed. The information of heat released is important in the kinetic studies because when heat is released due to adsorption the released energy is partly absorbed by the solid adsorbent and partly dissipated to the surrounding. The portion absorbed by the solid increases the particle temperature and it is this rise in temperature that slows down the adsorption kinetics because the mass uptake is controlled by the rate of cooling of the particle in the later course of adsorption. Hence the knowledge of this isosteric heat is essential in the study of adsorption kinetics. The isosteric heat may or may not vary with loading. It is calculated from the following thermodynamic van't Hoff equation:

$$\frac{\Delta H}{R_g T^2} = -\left(\frac{\partial \ln P}{\partial T}\right)_{C_\mu} \tag{66}$$

For Langmuir isotherm of the form given in eq. (63), we take the total differentiation of that equation and substitute the result into the above van't Hoff equation to get:

$$\frac{\Delta H}{R_g T^2} = \frac{Q}{R_g T^2} + \delta(1 + bP) \tag{66}$$

in which we have allowed for the maximum adsorbed concentration ($C_{\mu s}$) to vary with temperature and that dependence is assumed to take the form:

$$\frac{1}{C_{\mu s}}\frac{dC_{\mu s}}{dT} = -\delta \tag{67}$$

Since $(1+bP) = 1/(1-\Theta)$, eq. (66) will become:

$$-\Delta H = Q + \frac{\delta R_g T^2}{1 - \theta} \tag{68}$$

The negativity of the enthalpy change indicates that the adsorption process is an exothermic process. If the maximum adsorbed concentration, C^s, is a function of temperature and it decreases with temperature, the isosteric heat will increase with the loading due to the second term in the RHS of eq. (68). For the isosteric heat to take a finite value at high

coverage (that is $\Theta \longrightarrow 1$) the parameter δ (thermal expansion coefficient of the saturation concentration) must be zero. This is to say that the saturation capacity is independent of temperature, and as a result the heat of adsorption is a constant, independent of loading.

4.3 Isotherms based on the gibbs approach

The last section dealt with the basic Langmuir theory, one of the earliest theories in the literature to describe adsorption equilibria. One should note that the Langmuir approach is kinetic by nature. Adsorption equilibria can be described quite readily by the thermodynamic approach. What to follow in this section is the approach due to Gibbs. More details can be found in Yang (1987) and Rudzinski and Everett (1992).

In the bulk α-phase containing N components (Fig. 6), the following variables are specified: the temperature T^α, the volume V^α and the numbers of moles of all species n_i^α (for i = 1, 2, ..., N). The upper script is used to denote the phase. With these variables, the total differential Helmholtz free energy is:

$$dA = -S^\alpha dT^\alpha - P^\alpha dV^\alpha + \sum_{i=1}^{N} \mu_i^\alpha dn_i^\alpha \qquad (69)$$

where S^α is the entropy of the a phase, P^α is the pressure of that phase, n^α is the number of molecule of the species i, and (μ_i^α is its chemical potential.
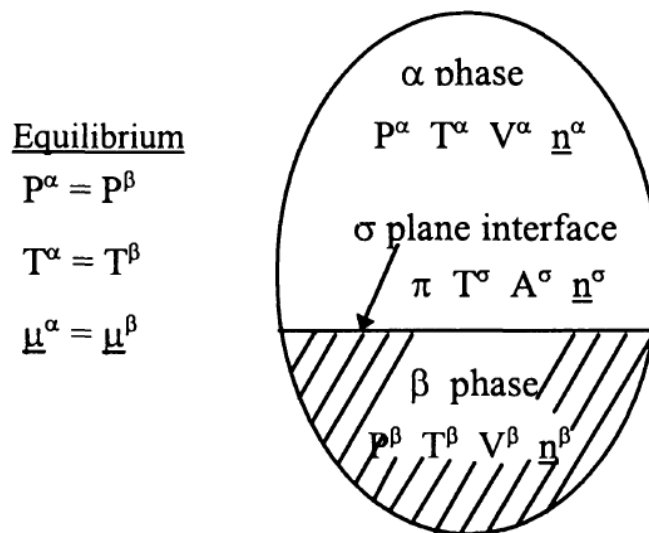

Fig. 6. Equilibrium between the phases α and β separated by a plane interface a δ

Similarly, for the β -phase, we can write a similar equation for the differential Helmholtz free energy:

$$dA = -S^\beta dT^\beta - P^\beta dV^\beta + \sum_{i=1}^{N} \mu_i^\beta dn_i^\beta \qquad (70)$$

If equilibrium exists between the two phases with a plane interface (Fig. 6), we have:

$$T^\alpha = T^\beta ; P^\alpha = P^\beta ; \mu_i^\alpha = \mu_i^\beta \qquad (71)$$

that is equality in temperature, pressure and chemical potential is necessary and sufficient for equilibrium for a plane interface.

$$A^\alpha = -P\,V^\alpha + \sum_{i=1}^{N} \mu_i^\alpha n_i^\alpha \tag{72}$$

Differentiating eq. (72) and subtracting the result from eq. (69) will give the following Gibbs-Duhem equation:

$$-V^\alpha dP - S^\alpha dT + \sum_{i=1}^{N} \mu_i^\alpha n_i^\alpha = 0 \tag{73}$$

for the bulk α phase. As a special case of constant temperature and pressure, the Gibbs-Duhem's relation is reduced to:

$$\sum_{i=1}^{N} \mu_i^\alpha n_i^\alpha = 0 \tag{74}$$

Similarly, the Gibbs-Duhem equation for the (β-phase at constant temperature and pressure is:

$$\sum_{i=1}^{N} \mu_i^\beta n_i^\beta = 0 \tag{75}$$

5. Thermodynamics of the surface phase

We now can develop a similar thermodynamic treatment for the surface phase δ, which is the interface between the phases α and β, and is in equilibrium with these two phases. When the adsorbed phase is treated as a two dimensional surface, fundamental equations in classical thermodynamics can still be applied. Applying the same procedure to surface free energy, we will obtain the Gibbs adsorption equation. This is done as follows. The total differentiation of the surface free energy takes the form similar to eq. (69) with PαdVβ being replaced by πdA :

$$dA^\sigma = -S^\sigma dT - \pi dA + \sum_{i=1}^{N} \mu_i dn_i^\sigma \tag{76}$$

where the surface chemical potentials μ_i have the same values as those of the two joining phases, π is the spreading pressure, playing the same role as pressure in the bulk phase. Integrating eq. (76) with constant T, π and μ_i yields:

$$A^\sigma = -\pi dA + \sum_{i=1}^{N} \mu_i n_i^\sigma \tag{77}$$

which is an analogue of eq. (72). Differentiation of this equation yields:

$$dA^\sigma = -\pi dA - A d\pi + \sum_{i=1}^{N} \mu d_i n_i^\sigma + \sum_{i=1}^{N} n_i^\delta d_i \mu_i \tag{78}$$

Subtracting eq. (72) from eq. (70), we have the Gibbs equation for a planar surface:

$$-S^\sigma dT - Ad\pi + \sum_{i=1}^{N} n_i^\delta d\mu_i = 0 \qquad (79)$$

Adsorption equilibria experiments are usually carried out at constant temperature, therefore the Gibbs adsorption isotherm equation is:

$$-Ad\pi + \sum_{i=1}^{N} n_i^\delta d\mu_i = 0 \qquad (80)$$

For pure component systems (N = 1), we have:

$$-Ad\pi + nd\mu = 0 \qquad (81)$$

where we have dropped the superscript a for clarity. At equilibrium, the chemical potential of the adsorbed phase is equal to that of the gas phase, which is assumed to be ideal, i.e.

$$\mu = \mu_g = \mu_g^0 + R_g T \ln P \qquad (82)$$

Substituting eq.(82) into eq.(81), the following Gibbs isotherm equation is derived:

$$\left(\frac{d\pi}{d\ln P} \right)_T = \frac{n}{A} R_g T \qquad (83)$$

This equation is the fundamental equation relating gas pressure, spreading pressure and amount adsorbed. It is very useful in that if the equation of state relating the spreading pressure and the number of mole on the adsorbed phase is provided, the isotherm expressed as the number of mole adsorbed in terms of pressure can be obtained (Atkins, P.W., 1998).

5.1 Linear isotherm
For an ideal surface at infinite dilution, the equation of state relating the spreading pressure and the number of mole on the surface has the following form:

$$\pi A = n R_g T \qquad (84)$$

an analogue of the ideal gas law (i.e. diluted systems), that is the spreading pressure is linear with the number of molecules on a surface of area A. Substituting this equation of state into the Gibbs equation , we get:

$$\pi = \left(\frac{d\pi}{d\ln P} \right)_T \qquad (85)$$

Integrating this equation at constant T, we obtain n = C(T)P, where C(T) is some function of temperature. This equation means that at equilibrium the spreading pressure in the adsorbed phase is linearly proportional to the pressure in the gas phase. The spreading pressure is not, however, useful in the correlation of adsorption equilibrium data. To relate the amount adsorbed in the adsorbed phase in terms of the gas phase pressure, we use the equation of state to finally get:

$$\frac{n}{A} = K(T)P \qquad (86)$$

where

$$K(T) = \frac{C(T)}{R_g T} \qquad (87)$$

The parameter K(T) is called the Henry constant. The isotherm obtained for the diluted system is a linear isotherm, as one would anticipate from such condition of infinite dilution.

5.2 Volmer isotherm

We have seen in the last section that when the system is dilute (that is the equation of state follows eq. 84), the isotherm is linear because each adsorbed molecule acts independently from other adsorbed molecules. Now let us consider the case where we allow for the finite size of adsorbed molecules. The equation of state for a surface takes the following form:

$$\pi(A - A_0) = nR_g T \qquad (88)$$

where A_0 is the minimum area occupied by n molecules. The Gibbs equation (83) can be written in terms of the area per unit molecule as follows:

$$\left(\frac{\partial \pi}{\partial \ln P}\right)_T = \frac{R_g T}{\delta} \qquad (89)$$

where the variable δ is the area per unit molecule of adsorbate

$$\delta = \frac{A}{n} \qquad (90)$$

Integrating equation (89) at constant temperature, we have:

$$\ln P = \frac{1}{R_g T} \int \delta d\pi \qquad (91)$$

We rewrite the equation of state in terms of the new variable δ and get:

$$\pi(\delta - \delta_0) = R_g T \qquad (92)$$

Substituting the spreading pressure from the equation of state into the integral form of the Gibbs equation (91), we get:

$$\ln P = -\int \frac{\delta d\delta}{(\delta - \delta_0)^2} \qquad (93)$$

But the fractional loading is simply the minimum area occupied by n molecules divided by the area occupied by the same number of molecules, that is

$$\theta = \frac{A_0}{A} = \frac{(A_0 / n)}{(A / n)} = \frac{\delta_0}{\delta} \tag{94}$$

Written in terms of the fractional loading, Θ, eq. (93) becomes:

$$\ln P = \int \frac{d\theta}{\theta(1-\theta)^2} \tag{95}$$

Carrying out the integration, we finally get the following equation:

$$b(T)P = \frac{\theta}{1-\theta} \exp(\frac{\theta}{1-\theta}) \tag{96}$$

where the affinity constant b(T) is a function of temperature, which can take the following form:

$$b(T) = b_\infty \exp(\frac{Q}{R_g T}) \tag{97}$$

Eq. (97) is known as the Volmer equation, a fundamental equation to describe the adsorption on surfaces where the mobility of adsorbed molecules is allowed, but no interaction is allowed among the adsorbed molecules. The factor $\exp(\Theta/(1-\Theta))$ in eq. (96) accounts for the mobility of the adsorbate molecules. If we arrange eq. (96) as follows:

$$\frac{\theta}{1-\theta} = b.\exp(-\frac{\theta}{1-\theta})P \tag{98}$$

the Volmer equation is similar to the Langmuir isotherm equation with the apparent affinity as

$$b_{app} = b.\exp(-\frac{\theta}{1-\theta}) \tag{99}$$

The difference between the Volmer equation and the Langmuir equation is that while the affinity constant remains constant in the case of Langmuir mechanism, the "apparent" affinity constant in the case of Volmer mechanism decreases with loading. This means that the rate of increase in loading with pressure is much lower in the case of Volmer compared to that in the case of Langmuir.

5.3 Hill-deboer isotherm

It is now seen that the Gibbs isotherm equation (83) is very general, and with any proper choice of the equation of state describing the surface phase an isotherm equation relating the amount on the surface and the gas phase pressure can be obtained as we have shown in the last two examples. The next logical choice for the equation of state of the adsorbate is an equation which allows for the co-volume term and the attractive force term. In this theme the following van der Waals equation can be used:

$$\left(\pi + \frac{a}{\delta^2}\right)(\delta - \delta_0) = R_g T \tag{100}$$

With this equation of state, the isotherm equation obtained is:

$$bP = \frac{\theta}{1-\theta}\exp(\frac{\theta}{1-\theta})\exp(-c\theta) \tag{101}$$

where

$$bP = b_\infty\exp(\frac{Q}{R_gT}), c = \frac{2a}{R_gT\delta_0} = \frac{zw}{R_gT} \tag{102}$$

where z is the coordination number (usually taken as 4 or 6 depending on the packing of molecules), and w is the interaction energy between adsorbed molecules. A positive w means attraction between adsorbed species and a negative value means repulsion that is the apparent affinity is increased with loading when there is attraction between adsorbed species, and it is decreased with loading when there is repulsion among the adsorbed species. The equation as given in eq. (101) is known as the Hill-de Boer equation, which describes the case where we have mobile adsorption and lateral interaction among adsorbed molecules. When there is no interaction between adsorbed molecules (that is w = 0), this Hill-de Boer equation will reduce to the Volmer equation obtained. The first exponential term in the RHS of eq. (101) describes the mobility of adsorbed molecules, and when this term is removed we will have the case of localized adsorption with lateral interaction among adsorbed molecules, that is:

$$bP = \frac{\theta}{1-\theta}\exp(-c\theta) \tag{103}$$

This equation is known in the literature as the Fowler-Guggenheim equation, or the quasi approximation isotherm. This equation can also be derived from the statistical thermodynamics. Due to the lateral interaction term $\exp(-c\theta)$, the Fowler-Guggenheim equation and the Hill-de Boer equation exhibit a very interesting behavior. This behavior is the two dimensional condensation when the lateral interaction between adsorbed molecules is sufficiently strong (Adam, N.K., 1968).

5.4 Harkins-jura isotherm

We have addressed the various adsorption isotherm equations derived from the Gibbs fundamental equation. Those equations (Volmer, Fowler-Guggenheim and Hill de Boer) are for monolayer coverage situation. The Gibbs equation, however, can be used to derive equations which are applicable in multilayer adsorption as well. Here we show such application to derive the Harkins-Jura equation for multilayer adsorption. Analogous to monolayer films on liquids, Harkins and Jura (1943) proposed the following equation of state:

$$\pi = b - a\delta \tag{104}$$

where a and b are constants. Substituting this equation of state into the Gibbs equation (67) yields the following adsorption equation:

$$\ln\left(\frac{P}{P_0}\right) = B - \frac{C}{V^2} \tag{105}$$

which involves only measurable quantities. Here P_0 is the vapor pressure. This equation can describe isotherm of type II shown in Figure 10.7. The classification of types of isotherm will be discussed in detail in next section. But for the purpose of discussion of the Harkins-Jura equation, we explain type II briefly here. Type II isotherm is the type which exhibits a similar behavior to Langmuir isotherm when the pressure is low, and when the pressure is further increased the amount adsorbed will increase in an exponential fashion. Rearranging the Harkins-Jura equation (105) into the form of adsorbed amount versus the reduced pressure, we have:

$$V = \frac{\sqrt{C/B}}{\sqrt{1 + \frac{1}{B}\ln(1/x)}} \tag{106}$$

where x is the reduced pressure ($x = P/P_0$), We see that when the pressure approaches the vapor pressure, the adsorbed amount reaches a maximum concentration given below:

$$\lim V = V_{max} = \sqrt{C/B} \tag{107}$$

Thus, the Harkins-Jura isotherm equation can be written as

$$\frac{V}{V_{max}} = \frac{1}{\sqrt{1 + \frac{1}{B}\ln(1/x)}} \tag{108}$$

from which we can see that the only parameter which controls the degree of curvature of the isotherm is the parameter B.

5.5 Characteristics of isotherm

To investigate the degree of curvature of the Harkins-Jura equation (108), we study its second derivative:

$$\frac{d^2}{dx^2}\left(\frac{V}{V_{max}}\right) = \frac{1}{2Bx^2} \frac{\left(\frac{3}{2B} - [1 + \frac{1}{B}\ln(1/x)]\right)}{[1 + 1/B\ln(1/x)]^{5/2}} \tag{109}$$

To find the inflexion point, we set the second derivative to zero and obtain the reduced pressure at which the isotherm curve has an inflexion point

$$x_{inf,} = \exp[-(\frac{3}{2} - B)] \tag{110}$$

For the Harkins-Jura equation to describe the Type II isotherm, it must have an inflexion point occurring at the reduced pressure between 0 and 1, that is the restriction on the parameter B between 3/2>B>0. The restriction of positive B is due to the fact that if B is negative, eq. (105) does not always give a real solution. With the restriction on B as shown in eq. (109), the minimum reduced pressure at which the inflexion point occurs is (by putting B to zero in eq. 110):

$$x_{\text{inf,}} = \exp[-(\frac{3}{2})] \approx 0.22 \qquad (111)$$

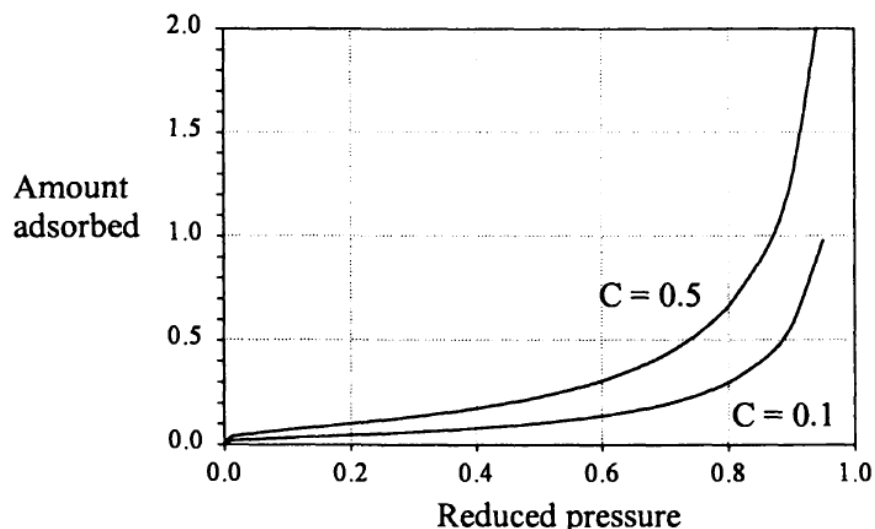Fig. 7 shows typical plots of the Harkins-Jura equation.

Fig. 7. Plots of the Harkins-Jura equation versus the reduced pressure with B = 0.01

Jura and Harkins claimed that this is the simplest equation found so far for describing adsorption from sub-monolayer to multilayer regions, and it is valid over more than twice the pressure range of any two-constant adsorption isotherms. They showed that for TiO_2 in the form of anatase, their isotherm agrees with the data at both lower and higher values of pressure than the commonly used BET equation. Harkins and Jura (1943) have shown that a plot of $\ln(P/P_0)$ versus $1/v^2$ would yield a straight line with a slope of C. The square root of this constant is proportional to the surface area of the solid. They gave the following formula:

$$S_g = 4.06\sqrt{C} \qquad (112)$$

where v is the gas volume at STP adsorbed per unit g, and S has the unit of m^2/g. They also suggested that if the plot of $\ln(P/P_0)$ versus $1/v^2$ exhibits two straight lines, the one at lower pressure range should be chosen for the area calculation as this is the one in which there exists a transition from a monolayer to a polylayer.

5.6 Other isotherms from gibbs equation

We see that many isotherm equations (linear, Volmer, Hill-deBoer, Harkins-Jura) can be derived from the generic Gibbs equation. Other equations of state relating the spreading pressure to the surface concentration can also be used, and thence isotherm equations can be obtained. The following table (Table 2) lists some of the fundamental isotherm equations from a number of equations of state (Ross and Olivier, 1964; Adamson, 1984).

Since there are many fundamental equations which can be derived from various equations of state, we will limit ourselves to a few basic equations such as the Henry law equation, the Volmer, the Fowler-Guggenheim, and the Hill-de Boer equation. Usage of more complex fundamental equations other than those just mentioned needs justification for doing so.

Equation of state	Isotherm	Name
$\pi\delta = R_g T$	$bP = \theta$	Henry law
$\pi\delta = R_g T \ln\left(\dfrac{\delta}{\delta - \delta_0}\right)$	$bP = \dfrac{\theta}{1 - \theta}$	Langmuir
$\pi(\delta - \delta_0) = R_g T$	$bP = \dfrac{\theta}{1 - \theta}\exp(\dfrac{\theta}{1 - \theta})$	Volmer
$\pi\delta = R_g T \dfrac{\delta}{\delta_0}\ln(\dfrac{\delta}{\delta - \delta_0}) - \dfrac{cw}{2}\dfrac{\delta_0}{\delta}$	$bP = \dfrac{\theta}{1 - \theta}\exp(-\dfrac{cw\theta}{RT})$	Fowler-Guggenheim
$\left(\pi + \dfrac{a}{\delta^2}\right)(\delta - \delta_0) = R_g T$	$bP = \dfrac{\theta}{1 - \theta}\exp(\dfrac{\theta}{1 - \theta})\exp(-c\theta)$	Hill-deBoer
$\left(\pi + \dfrac{a}{\delta^3}\right)(\delta - \delta_0) = R_g T$	$bP = \dfrac{\theta}{1 - \theta}\exp(\dfrac{\theta}{1 - \theta})\exp(-\theta^2)$	-
$\left(\pi + \dfrac{a}{\delta^2}\right)\left(\delta - \dfrac{\delta_0}{\delta}\right) = R_g T$	$bP = \sqrt{\dfrac{\theta}{1 - \theta}}\exp(\dfrac{\theta}{1 - \theta})\exp(-c\theta)$	-

Table 2. Isotherm Equations derived from the Gibbs Equation

5.7 Equation 2D of state adsorption isotherm

Numbers of fundamental approaches have been taken to derive the necessary adsorption isotherm. If the adsorbed fluid is assumed to behave like a two dimensional non-ideal fluid, then the Equation of State developed for three dimensional fluids can be applied to two dimensional fluids with a proper change of variables. The 2D- equation of state (2D.EOS) adsorption isotherm equations are not popularly used in the description of data, but they have an advantage of easily extending to multicomponent mixtures by using a proper mixing rule for the adsorption parameters. For 3D fluids, the following 3 parameter EOS equation is popularly used (Dubinin M. M., Radushkevich L.V. 1947)

$$\left(p + \frac{a}{v^2 + \alpha bv + \beta b^2}\right)(v - b) = R_g T \tag{113}$$

where p is the pressure, v is the volume per unit mole, a and b are parameters of the fluid and α and β represent numerical values. Different values obtained of α and β, give different forms of equation of state. For example, when α = β = 0, we recover the famous van der Waals equation. Written in terms of molar density d (mole/volume), the 3D-EOS will become:

$$\left(p + \frac{ad^2}{1 + \alpha bd + \beta b^2 d^2}\right)(1 - bd) = dR_g T \tag{114}$$

Adopting the above form, we can write the following equation for the 2D-EOS as follows:

$$\left(\pi + \frac{a_s \delta^2}{1 + \alpha b_s \delta + \beta b_s^2 \delta^2}\right)(1 - b_s \delta) = \delta R_g T \tag{115}$$

where n is the spreading pressure, a is the surface density (mole/area) and the parameters as and bs are the 2D analogs of a and b of the 3D-EOS. Written in terms of the surface concentration (mole/mass), the above equation becomes:

$$\left(A\pi + \frac{a_s w^2}{1 + \alpha b_s w + \beta b_s^2 w^2} \right)(1 - b_s w) = wR_g T \tag{116}$$

where A is the specific area (m²/g). To provide an EOS to properly fit the experimental data, Zhou et al. (1994) suggested the following form containing one additional parameter

$$\left(A\pi + \frac{a_s w^2}{1 + \alpha b_s w + \beta b_s^2 w^2} \right)(1 - (b_s w)^m) = wR_g T \tag{117}$$

This general equation reduces to special equations when the parameters α, β and m take some specific values. The following table shows various special cases deduced from the above equation.

α	β	m	EOS
0	0	1	van der Waals
0	0	½	Eyring
1	0	1	Soave-Redlich-Kwong
2	-1	1	Peng-Robinson

Table 3. The various special cases deduced from equations

To fit many experimental data, Zhou et al. (1994) have found that m has to be less than 1/2. They suggested a value of 1/3 for m to reduce the number of parameters in the 2D-EOS equation (117). At equilibrium, the chemical potential of the adsorbed phase is the same as that of the gas phase that is

$$\mu_a = \mu_g = \mu_g^0 + R_g T \ln P \tag{118}$$

The chemical potential of the adsorbed phase is related to the spreading pressure according to the Gibbs thermodynamics equation rewritten here for clarity:

$$-Ad\pi + nd\mu = 0 \tag{119}$$

Thus

$$\left(\frac{d\pi}{d\ln P} \right) = \frac{n}{A} R_g T = \delta R_g T \tag{119}$$

But the spreading pressure is a function of a as governed by the equation of state (115). We write

$$d\ln P = \frac{1}{R_g T} \frac{1}{\delta} (\frac{\partial \pi}{\partial \delta})_T d\delta \tag{120}$$

Integrating the above equation, we get

$$\int^P d\ln P = \frac{1}{R_g T}\int^\delta \frac{1}{\delta}(\frac{\partial \pi}{\partial \delta})_T d\delta \qquad (121)$$

Eq. (121) is the adsorption isotherm equation relating the surface density a (mole/m²) in terms of the gas phase pressure. The applicability of this isotherm equation rests on the ability of the 2D-EOS (eq. 121) to describe the state of the adsorbed molecule. Discussions on the usage of the above equation in the fitting of experimental data are discussed in Zhou et al. (1994).

6. Empirical isotherm equations

In this section, we present a number of popularly used isotherm equations. We start first with the earliest empirical equation proposed by Freundlich, and then Sips equation which is an extension of the Freundlich equation, modified such that the amount adsorbed in the Sips equation has a finite limit at sufficiently high pressure (or fluid concentration). We then present the two equations which are commonly used to describe well many data of hydrocarbons, carbon oxides on activated carbon and zeolite: Toth and Unilan equations. A recent proposed equation by Keller et al. (1996), which has a form similar to that of Toth, is also discussed. Next, we describe the Dubinin equation for describing micropore filling, which is popular in fitting data of many microporous solids. Finally we present the relatively less used equations in physical adsorption, Jovanovich and Tempkin, the latter of which is more popular in the description of chemisorption systems (Erbil, H.Y.,1997).

6.1 Freundlich equation

The Freundlich equation is one of the earliest empirical equations used to describe equilibria data. The name of this isotherm is due to the fact that it was used extensively by Freundlich (1932) although it was used by many other researchers. This equation takes the following form:

$$C_\mu = KP^{1/n} \qquad (122)$$

where C_μ is the concentration of the adsorbed species, and K and n are generally temperature dependent. The parameter n is usually greater than unity. The larger is this value; the adsorption isotherm becomes more nonlinear as its behavior deviates further away from the linear isotherm. To show the behavior of the amount adsorbed versus pressure (or concentration) we plot $(C_\mu/C_{\mu 0})$ versus (P/P_0) as shown in Figure 10.8, that is

$$\frac{C_\mu}{C_{\mu o}} = \left(\frac{P}{P_0}\right)^{1/n} \qquad (123)$$

where Po is some reference pressure and $C_{\mu 0}$ is the adsorbed concentration at that reference pressure, $C_{\mu 0} = KP_0^{1/n}$

We see from Figure 10.8 that the larger is the value of n, the more nonlinear is the adsorption isotherm, and as n is getting larger than about 10 the adsorption isotherm is approaching a so-called rectangular isotherm (or irreversible isotherm). The term "irreversible isotherm" is normally used because the pressure (or concentration) needs to go

down to an extremely low value before adsorbate molecules would desorb from the surface. The Freundlich equation is very popularly used in the description of adsorption of organics from aqueous streams onto activated carbon. It is also applicable in gas phase systems having heterogeneous surfaces, provided the range of pressure is not too wide as this isotherm equation does not have a proper Henry law behavior at low pressure, and it does not have a finite limit when pressure is sufficiently high. Therefore, it is generally valid in the narrow range of the adsorption data. Parameters of the Freundlich equation can be found by plotting log10 (CM) versus log10 (P)
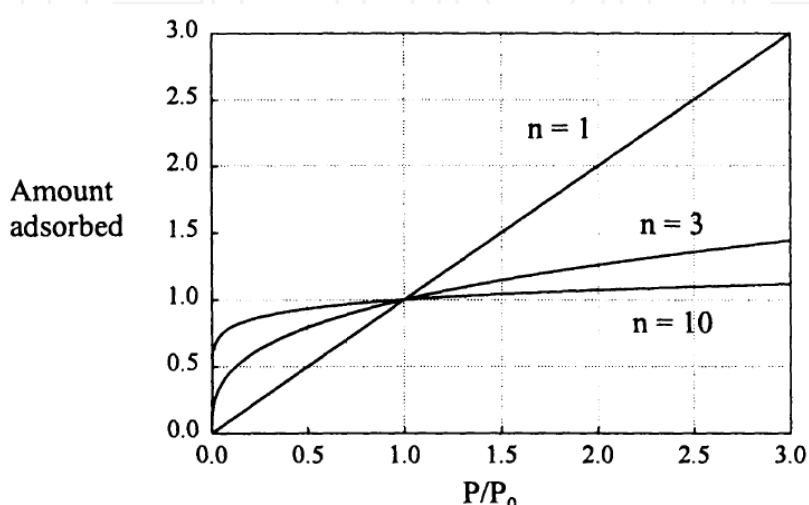
Fig. 8. Plots of the Freundlich isotherm versus P/Po

$$\log_{10}(C_\mu) = \log_{10} K + \frac{1}{n}\log_{10} P \tag{124}$$

which yields a straight line with a slope of (1/n) and an intercept of log10(K).

6.1.1 Temperature dependence of K and n

The parameters K and n of the Freundlich equation (122) are dependent on temperature. Their dependence on temperature is complex, and one should not extrapolate them outside their range of validity. The system of CO adsorption on charcoal has temperature-dependent n such that its inverse is proportional to temperature. This exponent was found to approach unity as the temperature increases. This, however, is taken as a specific trend rather than a general rule. To derive the temperature dependence of K and n, we resort to an approach developed by Urano et al. (1981). They assumed that a solid surface is composed of sites having a distribution in surface adsorption potential, which is defined as:

$$A' = R_g T \ln\left(\frac{P_0}{P}\right) \tag{125}$$

The adsorption potential A' is the work (energy) required to bring molecules in the gas phase of pressure P to a condensed state of vapor pressure Po. This means that sites associated with this potential A will have a potential to condense molecules from the gas phase of pressure P If the adsorption potential of the gas

$$A = R_g T \ln\left(\frac{P_0}{P}\right) \tag{126}$$

is less than the adsorption potential A' of a site, then that site will be occupied by an adsorbate molecule. On the other hand, if the gas phase adsorption potential is greater, then the site will be unoccupied (Fig. 9). Therefore, if the surface has a distribution of surface adsorption potential F(A') with F(A')dA' being the amount adsorbed having adsorption potential between A' and A'+dA', the adsorption isotherm equation is simply:

$$C_\mu = \int_A^\infty F(A')dA' \tag{127}$$
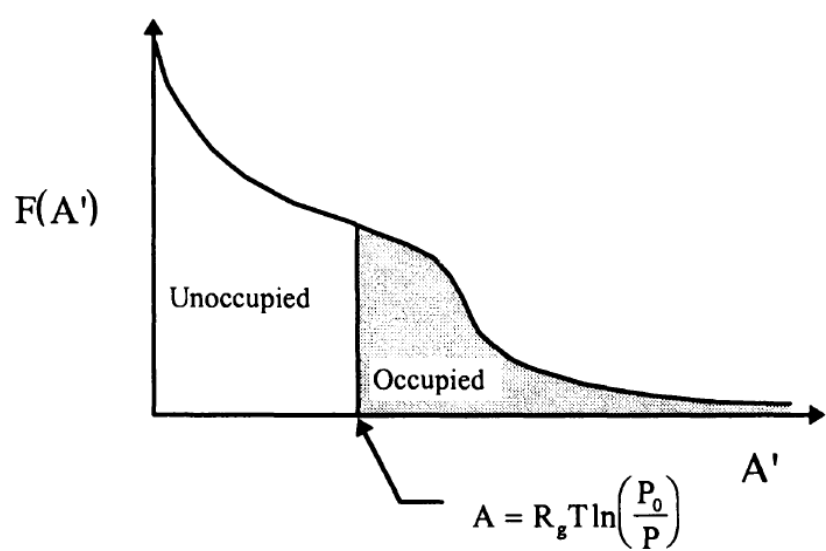
Fig. 9. Distribution of surface adsorption potential

If the density function F(A') takes the form of decaying exponential function

$$F(A) = \delta.\exp(-A / A_0) \tag{128}$$

where Ao is the characteristic adsorption potential, the above integral can be integrated to give the form of the Freundlich equation:

$$C_\mu = KP^{1/n} \tag{129}$$

where the parameter K and the exponent (l/n) are related to the distribution parameters δ, Ao, and the vapor pressure and temperature as follows:

$$K = (\delta A_0)P_0^{-R_g T/A_0} \tag{130}$$

$$\frac{1}{n} = \frac{R_g T}{A_0} \tag{131}$$

The parameter n for most practical systems is greater than unity; thus eq. (131) suggests that the characteristic adsorption energy of surface is greater than the molar thermal energy $R_g T$.

Provided that the parameters 5 and Ao of the distribution function are constant, the parameter l/n is a linear function of temperature, that is nRT is a constant, as experimentally observed for adsorption of CO in charcoal for the high temperature range (Rudzinski and Everett, 1992). To find the temperature dependence of the parameter K, we need to know the temperature dependence of the vapor pressure, which is assumed to follow the Clapeyron equation:

$$\ln P_0 = \alpha - \frac{\beta}{T} \tag{132}$$

Taking the logarithm of K in eq. (131) and using the Clapeyron equation (132), we get the following equation for the temperature dependence of lnK:

$$\ln K = \left[\ln(\delta A_0) + \frac{\beta R_g}{A_0} \right] - \frac{\alpha R_g T}{A_0} \tag{133}$$

This equation states that the logarithm of K is a linear function of temperature, and it decreases with temperature. Thus the functional form to describe the temperature dependence of K is

$$K = K_0 \exp(-\frac{\alpha R_g T}{A_0}) \tag{134}$$

and hence the explicit temperature dependence form of the Freundlich equation is:

$$C_\mu = K_0 \exp\left(-\frac{\alpha R_g T}{A_0} \right) P^{R_g T/A_0} \tag{135}$$

Since $\ln C_\mu$ and $1/n$ are linear in terms of temperature, we can eliminate the temperature and obtain the following relationship between lnK and n:

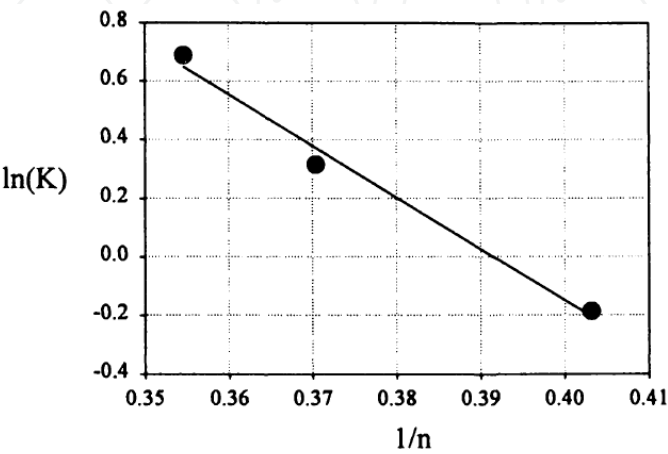$$\ln K = \left[\ln(\delta A_0) + \frac{\beta R_g}{A_0} \right] - \frac{\alpha}{n} \tag{136}$$

Fig. 10. Plot of ln(K) versus 1/n for propane adsorption on activated carbon

suggesting that the two parameters K and n in the Freundlich equation are not independent. Huang and Cho (1989) have collated a number of experimental data and have observed the linear dependence of ln(K) and (1/n) on temperature. We should, however, be careful about using this as a general rule for extrapolation as the temperature is sufficiently high, the isotherm will become linear, that is n = 1, meaning that 1/n no longer follows the linear temperature dependence as suggested by eq. (131). Thus, eq. (136) has its narrow range of validity, and must be used with extreme care. Using the propane data on activated carbon, we show in Figure 10 that lnK and 1/n are linearly related to each other, as suggested by eq.(136).

6.2 Heat of adsorption

Knowing K and n as a function of temperature, we can use the van't Hoff equation

$$\Delta H = -R_g T^2 \left(\frac{\partial \ln P}{\partial T} \right)_{C_\mu} \tag{137}$$

to determine the isosteric heat of adsorption. The result is (Huang and Cho, 1989)

$$\Delta H = -\left[\ln(\sigma A_0) + \frac{R_g \beta}{A_0} \right] A_0 + A_0 \ln C_\mu \tag{138}$$

Thus, the isosteric heat is a linear function of the logarithm of the adsorbed amount.

6.3 Sips equation (langmuir-freundlich)

Recognizing the problem of the continuing increase in the adsorbed amount with an increase in pressure (concentration) in the Freundlich equation, Sips (1948) proposed an equation similar in form to the Freundlich equation, but it has a finite limit when the pressure is sufficiently high.

$$C_\mu = C_{\mu s} \frac{(bP)^{1/n}}{1 + (bP)^{1/n}} \tag{139}$$

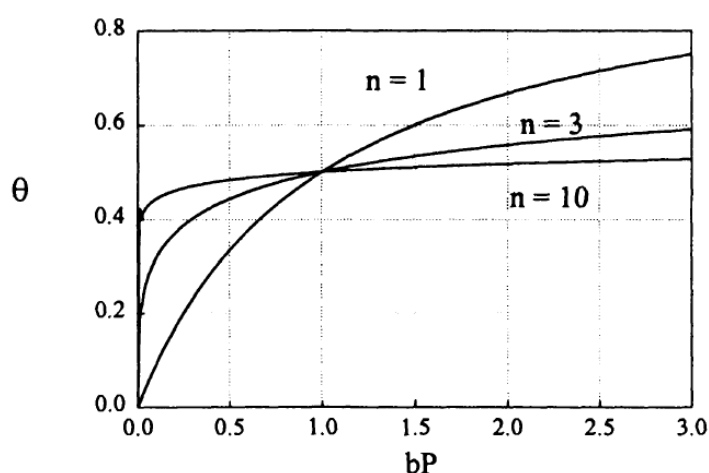Fig. 11. Plots of the Sips equation versus bP

In form this equation resembles that of Langmuir equation. The difference between this equation and the Langmuir equation is the additional parameter "n" in the Sips equation. If this parameter n is unity, we recover the Langmuir equation applicable for ideal surfaces. Hence the parameter n could be regarded as the parameter characterizing the system heterogeneity. The system heterogeneity could stem from the solid or the adsorbate or a combination of both. The parameter n is usually greater than unity, and therefore the larger is this parameter the more heterogeneous is the system. Figure 11 shows the behavior of the Sips equation with n being the varying parameter. Its behavior is the same as that of the Freundlich equation except that the Sips equation possesses a finite saturation limit when the pressure is sufficiently high. However, it still shares the same disadvantage with the Freundlich isotherm in that neither of them have the right behavior at low pressure, that is they don't give the correct Henry law limit. The isotherm equation (139) is sometimes called the Langmuir-Freundlich equation in the literature because it has the combined form of Langmuir and Freundlich equations.

To show the good utility of this empirical equation in fitting data, we take the same adsorption data of propane onto activated carbon used earlier in the testing of the Freundlich equation. The following Figure (Figure 10.12) shows the degree of good fit between the Sips equation and the data. The fit is excellent and it is fairly widely used to describe data of many hydrocarbons on activated carbon with good success. For each temperature, the fitting between the Sips equation and experimental data is carried out with MatLab nonlinear optimization outline, and the optimal parameters from the fit are tabulated in the following table. A code ISOFIT1 provided with this book is used for this optimization, and students are encouraged to use this code to exercise on their own adsorption data.
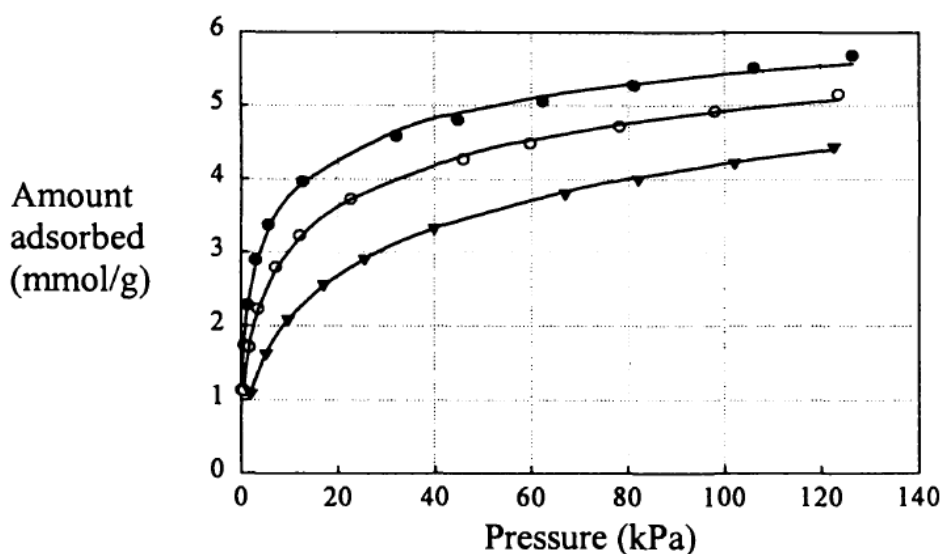

Fig. 12. Fitting of the propane/activated carbon data with the Sips equation (symbol -data; line:fitted equation)

The optimal parameters from the fitting of the Sips equation with the experimental data are tabulated in Table 4.

T (K)	$C_{\mu s}$ (mmole/g)	b (kPa^{-1})	n (-)
283	7.339	0.1107	2.306
303	7.232	0.04986	2.117
333	7.583	0.01545	1.956

Table 4. Optimal parameters for the Sips equation in fitting propane data on activated carbon

The parameter n is greater than unity, suggesting some degree of heterogeneity of this propane/ activated carbon system. The larger is this parameter, the higher is the degree of heterogeneity. However, this information does not point to what is the source of the heterogeneity, whether it be the solid structural property, the solid energetically property or the sorbet property. We note from the above table that the parameter n decreases with temperature, suggesting that the system is "apparently" less heterogeneous as temperature increases.

6.3.1 The temperature dependence of the sips equation

For useful description of adsorption equilibrium data at various temperatures, it is important to have the temperature dependence form of an isotherm equation. The temperature dependence of the Sips equation

$$C_\mu = C_{\mu s} \frac{(bP)^{1/n}}{1 + (bP)^{1/n}} \tag{140}$$

for the affinity constant b and the exponent n may take the following form:

$$b = b_\infty \exp\left(\frac{Q}{R_g T}\right) = b_0 \exp\left[\frac{Q}{R_g T_0}(\frac{T_0}{T}) - 1\right] \tag{141}$$

$$\frac{1}{n} = \frac{1}{n_0} + \alpha\left(1 - \frac{T_0}{T}\right) \tag{142}$$

Here b_∞ is the adsorption affinity constant at infinite temperature, b_0 is that at some reference temperature T_0 is the parameter n at the same reference temperature and a is a constant parameter. The temperature dependence of the affinity constant b is taken from the of the Langmuir equation. Unlike Q in the Langmuir equation, where it is the isosteric heat, invariant with the surface loading, the parameter Q in the Sips equation is only the measure of the adsorption heat. The temperature-dependent form of the exponent n is empirical and such form in eq. (142) is chosen because of its simplicity. The saturation capacity can be either taken as constant or it can take the following temperature dependence:

$$C_{\mu S} = C_{\mu S,0} \exp[x(1 - \frac{T}{T_0})] \tag{143}$$

Here $C_{\mu S,0}$ is the saturation capacity at the reference temperature To, and x is a constant parameter. This choice of this temperature-dependent form is arbitrary. This temperature

dependence form of the Sips equation (142) can be used to fit adsorption equilibrium data of various temperatures simultaneously to yield the parameter b_0, $C_{\mu S,0}$, Q/RT_0, ratio and α.

6.4 Toth equation

The previous two equations have their limitations. The Freundlich equation is not valid at low and high end of the pressure range, and the Sips equation is not valid at the low end as they both do not possess the correct Henry law type behavior. One of the empirical equations that is popularly used and satisfies the two end limits is the Toth equation. This equation describes well many systems with sub-monolayer coverage, and it has the following form:

$$C_{\mu} = C_{\mu s} \frac{bP}{\left[1 + (bP)^t\right]^{1/t}} \tag{144}$$

Here t is a parameter which is usually less than unity. The parameters b and t are specific for adsorbate-adsorbent pairs. When t = 1, the Toth isotherm reduces to the famous Langmuir equation; hence like the Sips equation the parameter t is said to characterize the system heterogeneity. If it is deviated further away from unity, the system is said to be more heterogeneous. The effect of the Toth parameter t is shown in Figure10-13, where we plot the fractional loading ($C_{\mu}/C_{\mu s}$) versus bP with t as the varying parameter. Again we note that the more the parameter t deviates from unity, the more heterogeneous is the system. The Toth equation has correct limits when P approaches either zero or infinity.
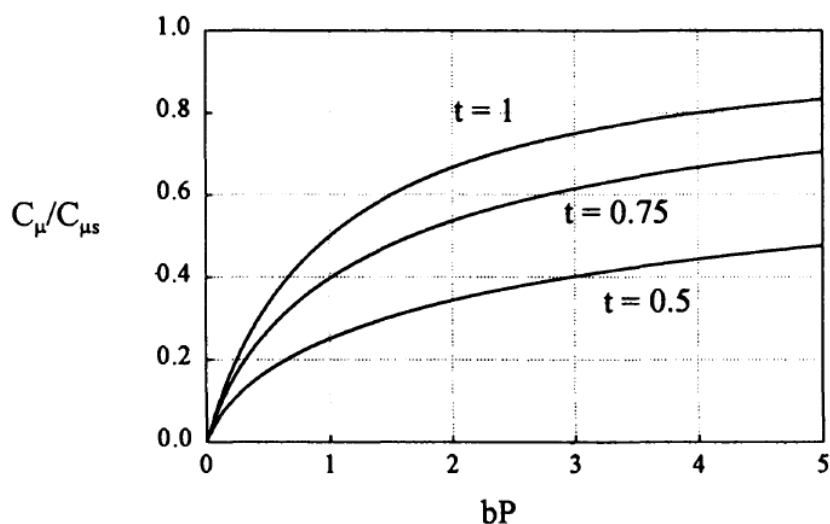

Fig. 13. Plot of the fractional loading versus bP for the Toth equation

Being the three-parameter model, the Toth equation can describe well many adsorption data. We apply this isotherm equation to fit the isotherm data of propane on activated carbon. The extracted optimal parameters are: $C_{\mu s}$=33.56 mmole/g , b=0.069 (kPa)$^{-1}$, t=0.233 The parameter t takes a value of 0.233 (well deviated from unity) indicates a strong degree of heterogeneity of the system. Several hundred sets of data for hydrocarbons on Nuxit-al charcoal obtained by Szepesy and Illes (Valenzuela and Myers, 1989) can be described well by this equation. Because of its simplicity in form and its correct behavior at low and high

pressures, the Toth equation is recommended as the first choice of isotherm equation for fitting data of many adsorbates such as hydrocarbons, carbon oxides, hydrogen sulfide, and alcohols on activated carbon as well as zeolites. Sips equation presented in the last section is also recommended but when the behavior in the Henry law region is needed, the Toth equation is the better choice.

6.4.1 Temperature dependence of the toth equation

Like the other equations described so far, the temperature dependence of equilibrium parameters in the Toth equation is required for the purpose of extrapolation or interpolation of equilibrium at other temperatures as well as the purpose of calculating isosteric heat. The parameters b and t are temperature dependent, with the parameter b taking the usual form of the adsorption affinity that is

$$b = b_\infty \exp\left(\frac{Q}{R_g T}\right) = b_0 \exp\left[\frac{Q}{R_g T_0}(\frac{T_0}{T} - 1)\right] \tag{145}$$

where b_∞ is the affinity at infinite temperature, b_0 is that at some reference temperature To and Q is a measure of the heat of adsorption. The parameter t and the maximum adsorption capacity can take the following empirical functional form of temperature dependence

$$t = t_0 + \alpha\left(1 - \frac{T_0}{T}\right) \tag{146}$$

$$C_{\mu S} = C_{\mu S,0} \exp[x(1 - \frac{T}{T_0})] \tag{147}$$

The temperature dependence of the parameter t does not have any sound theoretical footing; however, we would expect that as the temperature increases this parameter will approach unity.

6.5 Keller, staudt and toth's equation

Keller and his co-workers (1996) proposed a new isotherm equation, which is very similar in form to the original Toth equation. The differences between their equation and that of Toth are that:
a. the exponent a is a function of pressure instead of constant as in the case of Toth
b. the saturation capacities of different species are different
The form of Keller et al.'s equation is:

$$C_\mu = C_{\mu S} \alpha_m \frac{bP}{\left[1 + (bP)^\alpha\right]^{1/\alpha}} \tag{148}$$

$$\alpha = \frac{1 + \alpha_m \beta P}{1 + \beta P} \tag{149}$$

where the parameter α_m takes the following equation:

$$\frac{\alpha_m}{\alpha_m^*} = \left(\frac{r}{r^*}\right)^{-D}$$ (150)

Here r is the molecular radius, and D is the fractal dimension of sorbent surface. The saturation parameter $C_{\mu S}$, the affinity constant b, and the parameter (3 have the following temperature dependence):

$$C_{\mu S} = C_{\mu S,0} \exp[x(1 - \frac{T}{T_0})]$$ (151)

$$b = b_0 \exp\left[\frac{Q_1}{R_g T_0}(\frac{T_0}{T} - 1)\right]$$ (152)

$$\beta = \beta_0 \exp\left[\frac{Q_2}{R_g T_0}(\frac{T_0}{T} - 1)\right]$$ (153)

Here the subscript 0 denotes for properties at some reference temperature T0. The Keller et al.'s equation contains more parameters than the empirical equations discussed so far. Fitting the Keller et equation with the isotherm data of propane on activated carbon at three temperatures 283, 303 and 333 K, we found the fit is reasonably good, comparable to the good fit observed with Sips and Toth equations. The optimally fitted parameters are:

$C_{\mu s,0}$	16.08 mmole/g
b_0	0.9814 (kPa)$^{-1}$
β_0	3.225 (kPa)$^{-1}$
α_m	0.4438
Q_1/RT_0	10.94
Q_2/RT_0	-0.2863
χ	0.0002476

Table 5. The parameters for Keller, Staudt and Toth's Equation

6.6 Dubinin-radushkevich equation

The empirical equations dealt with so far, Freundlich, Sips, Toth, Unilan and Keller et al., are applicable to supercritical as well as subcritical vapors. In this section we present briefly a semi-empirical equation which was developed originally by Dubinin and his co-workers for sub critical vapors in microporous solids, where the adsorption process follows a pore filling mechanism. Hobson and co-workers and Earnshaw and Hobson (1968) analysed the data of argon on Corning glass in terms of the Polanyi potential theory. They proposed an equation relating the amount adsorbed in equivalent liquid volume (V) to the adsorption potential

$$A = R_g T \ln(\frac{P_o}{P})$$ (154)

where Po is the vapor pressure. The premise of their derivation is the functional form V(A) which is independent of temperature. They chose the following functional form:

$$\ln V = \ln V_0 B A^2 \tag{155}$$

where the logarithm of the amount adsorbed is linearly proportional to the square of the adsorption potential. Eq. (155) is known as the Dubinin-Radushkevich (DR) equation. Writing this equation explicitly in terms of pressure, we have:

$$V = V_0 \exp\left[-\frac{1}{(\beta E_0)^2}\left(R_g T \ln \frac{P}{P_0} \right)^2 \right] \tag{156}$$

where Eo is called the solid characteristic energy towards a reference adsorbate. Benzene has been used widely as the reference adsorbate. The parameter β is a constant which is a function of the adsorptive only. It has been found by Dubinin and Timofeev (1946) that this parameter is proportional to the liquid molar volume. Fig. 14 shows plots of the DR equation versus the reduced pressure with E/RT as the varying parameter (Foo K.Y., Hameed B.H., 2009).
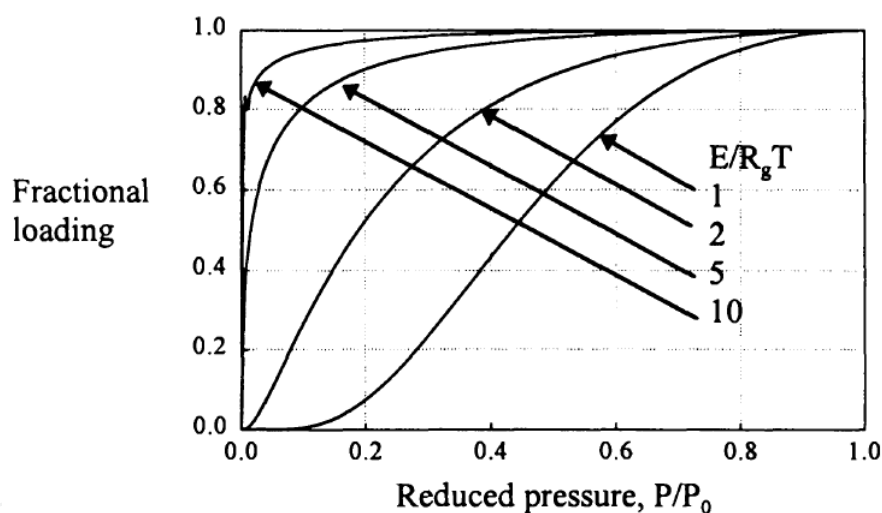
Fig. 14. Plots of the DR equation versus the reduced pressure

We see that as the characteristic energy increases the adsorption is stronger as the solid has stronger energy of interaction with adsorbate. One observation in that equation is that the slope of the adsorption isotherm at zero loading is not finite, a violation of the thermodynamic requirement Eq. (156) when written in terms of amount adsorbed (mole/g) is:

$$C_\mu = C_{\mu S} \exp\left[-\frac{1}{(\beta E_0)^2}\left(R_g T \ln \frac{P}{P_0} \right)^2 \right] \tag{157}$$

Where the maximum adsorption capacity is:

$$C_{\mu S} = \frac{W_0}{V_M(T)} \tag{158}$$

The parameter W_0 is the micropore volume and V_M is the liquid molar volume. Here we have assumed that the state of adsorbed molecule in micropores behaves like liquid. Dubinin-Radushkevich equation (157) is very widely used to describe adsorption isotherm of sub-critical vapors in microporous solids such as activated carbon and zeolite. One debatable point in such equation is the assumption of liquid-like adsorbed phase as one could argue that due to the small confinement of micropore adsorbed molecules experience stronger interaction forces with the micropore walls, the state of adsorbed molecule could be between liquid and solid. The best utility of the Dubinin-Radushkevich equation lies in the fact that the temperature dependence of such equation is manifested in the adsorption potential A, defined as in eq. (154), that is if one plots adsorption data of different temperatures as the logarithm of the amount adsorbed versus the square of adsorption potential, all the data should lie on the same curve, which is known as the characteristic curve. The slope of such curve is the inverse of the square of the characteristic energy E = βE0. To show the utility of the DR equation, we fit eq. (157) to the adsorption data of benzene on activated carbon at three different temperatures, 283, 303 and 333 K. The data are tabulated in Table 10.6 and presented graphically in Figure 10.15.

283 K		303 K		333 K	
P (kPa)	C_μ (mmole/g)	P (kPa)	C_μ (mmole/g)	P (kPa)	C_μ (mmole/g)
0.0133	1.6510	0.0001	0.4231	0.0010	0.4231
0.0933	3.2470	0.0002	0.8462	0.0267	0.8450
0.2932	3.8750	0.0133	1.1110	0.0533	1.1090
0.6798	4.2560	0.0267	1.4060	0.0933	1.4030
1.5590	4.5270	0.0666	1.9540	0.2532	1.9460
2.6520	4.6600	0.0933	2.1660	0.3732	2.1520
4.2920	4.8060	0.1599	2.5090	0.6531	2.4870
6.3580	4.9480	0.3466	2.9730	1.3330	2.9290
8.7440	5.0480	0.6931	3.4310	2.6120	3.3470
10.0200	5.0840	1.2800	3.7610	4.3590	3.6260
		2.8260	4.1490	7.6640	3.9380
		3.9320	4.2770	9.4770	4.0370
		6.6380	4.4410	11.5600	4.2340
		8.5570	4.5370		
		10.410	4.5880		

Table 6. Adsorption data of benzene on activated carbon

The vapor pressure and the liquid molar volume of benzene are given in the following table.

T (K)	P_0 (kPa)	v_M (cc/mmole)
303	16.3	0.0900
333	52.6	0.0935
363	150	0.0970

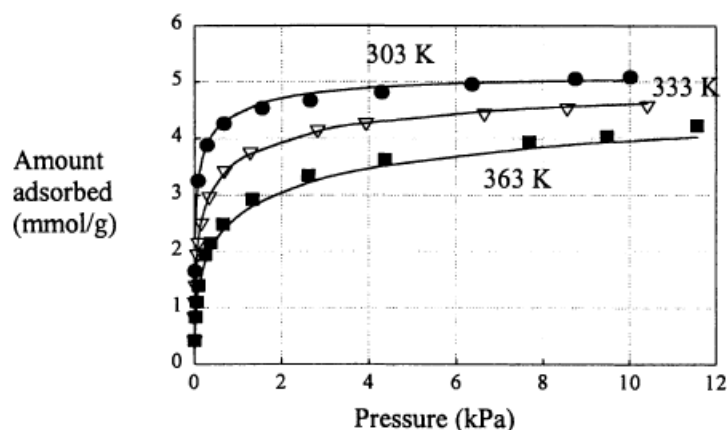Table 7. Vapor pressure and liquid molar volume of benzene

Fig. 15. Fitting the benzene/ activated carbon data with the DR equation

By fitting the equilibria data of all three temperatures simultaneously using the ISOFIT1 program, we obtain the following optimally fitted parameters: W_0 = 0.45 cc/g, E = 20,000 Joule/mole Even though only one value of the characteristic energy was used in the fitting of the three temperature data, the fit is very good as shown in Fig. 15, demonstrating the good utility of this equation in describing data of sub-critical vapors in microporous solids.

6.7 Jovanovich equation

Of lesser use in physical adsorption is the Jovanovich equation. It is applicable to mobile and localized adsorption (Hazlitt et al, 1979). Although it is not as popular as the other empirical equations proposed so far, it is nevertheless a useful empirical equation:

$$1 - \theta = \exp\left[-a\left(\frac{P}{P_0}\right)\right] \tag{159}$$

or written in terms of the amount adsorbed:

$$C_\mu = C_{\mu S}\left[1 - e^{-bP}\right] \tag{160}$$

where

$$b = b_\infty \exp(Q / R_g T) \tag{161}$$

At low loading, the above equation will become $C_\mu \approx (C_{\mu S} b)P = HP$. Thus, this equation reduces to the Henry's law at low pressure. At high pressure, it reaches the saturation limit. The Jovanovich equation has a slower approach toward the saturation than that of the Langmuir equation.

6.8 Temkin equation

Another empirical equation is the Temkin equation proposed originally by Slygin and Frumkin (1935) to describe adsorption of hydrogen on platinum electrodes in acidic solutions (chemisorption systems). The equation is (Rudzinski and Everett, 1992):

$$v(P) = C \ln(c.P) \tag{162}$$

where C and c are constants specific to the adsorbate-adsorbent pairs. Under some conditions, the Temkin isotherm can be shown to be a special case of the Unilan equation (162).

6.9 BET[2] isotherm

All the empirical equations dealt with are for adsorption with "monolayer" coverage, with the exception of the Freundlich isotherm, which does not have a finite saturation capacity and the DR equation, which is applicable for micropore volume filling. In the adsorption of sub-critical adsorbate, molecules first adsorb onto the solid surface as a layering process, and when the pressure is sufficiently high (about 0.1 of the relative pressure) multiple layers are formed. Brunauer, Emmett and Teller are the first to develop a theory to account for this multilayer adsorption, and the range of validity of this theory is approximately between 0.05 and 0.35 times the vapor pressure. In this section we will discuss this important theory and its various versions modified by a number of workers since the publication of the BET theory in 1938. Despite the many versions, the BET equation still remains the most important equation for the characterization of mesoporous solids, mainly due to its simplicity. The BET theory was first developed by Brunauer et al. (1938) for *a flat* surface (no curvature) and there is *no limit* in the number of layers which can be accommodated on the surface. This theory made use of the same assumptions as those used in the Langmuir theory, that is the surface is energetically homogeneous (adsorption energy does not change with the progress of adsorption in the same layer) and there is no interaction among adsorbed molecules. Let S0, S_1, S2 and Sn be the surface areas covered by no layer, one layer, two layers and n layers of adsorbate molecules, respectively (Fig. 16).
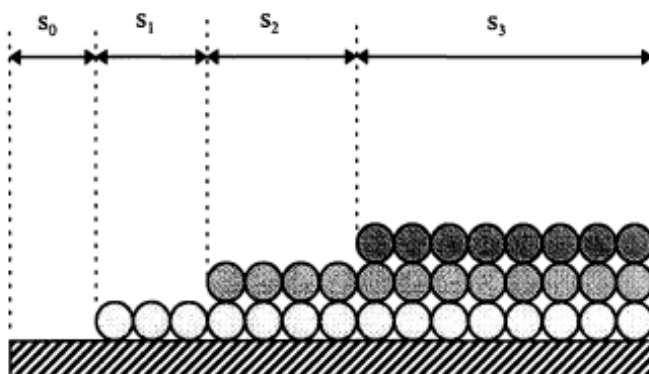

Fig. 16. Multiple layering in BET theory

The concept of kinetics of adsorption and desorption proposed by Langmuir is applied to this multiple layering process, that is the rate of adsorption on any layer is equal to the rate of desorption from that layer. For the first layer, the rates of adsorption onto the free surface and desorption from the first layer are equal to each other:

$$a_1 P s_0 = b_1 s_1 \exp\left(\frac{-E_1}{R_g T}\right) \tag{163}$$

---

[2] Brunauer, Emmett and Teller

where a1, b1 and *E1* are constant, independent of the amount adsorbed. Here E_1 is the interaction energy between the solid and molecule of the first layer, which is expected to be higher than the heat of vaporization. Similarly, the rate of adsorption onto the first layer must be the same as the rate of evaporation from the second layer, that is:

$$a_2 P s_0 = b_2 s_2 \exp\left(\frac{-E_2}{R_g T}\right) \tag{164}$$

The same form of equation then can be applied to the next layer, and in general for the i-th layer, we can write

$$a_i P s_{i-1} = b_i s_i \exp\left(\frac{-E_i}{R_g T}\right) \tag{165}$$

The total area of the solid is the sum of all individual areas, that is

$$S = \sum_{i=0}^{\infty} s_i \tag{166}$$

Therefore, the volume of gas adsorbed on surface covering by one layer of molecules is the fraction occupied by one layer of molecules multiplied by the monolayer coverage V_m:

$$V_1 = V_m \left(\frac{s_1}{S}\right) \tag{166}$$

The volume of gas adsorbed on the section of the surface which has two layers of molecules is:

$$V_2 = V_m \left(\frac{2s_2}{S}\right) \tag{167}$$

The factor of 2 in the above equation is because there are two layers of molecules occupying a surface area of s_2 (Fig. 16). Similarly, the volume of gas adsorbed on the section of the surface having "i" layers is:

$$V_i = V_m \left(\frac{i s_i}{S}\right) \tag{168}$$

Hence, the total volume of gas adsorbed at a given pressure is the sum of all these volumes:

$$V = \frac{V_m}{S} \sum_{i=0}^{\infty} i.s_i = V_m \frac{\sum_{i=0}^{\infty} i.s_i}{\sum_{i=0}^{\infty} s_i} \tag{169}$$

To explicitly obtain the amount of gas adsorbed as a function of pressure, we have to express S_i in terms of the gas pressure. To proceed with this, we need to make a further assumption beside the assumptions made so far about the ideality of layers (so that Langmuir kinetics could be applied). One of the assumptions is that the heat of adsorption of the second and subsequent layers is the same and equal to the heat of liquefaction, EL

$$E_2 = E_3 = ... = E_i = ... = E_L \tag{170}$$

The other assumption is that the ratio of the rate constants of the second and higher layers is equal to each other, that is:

$$\frac{b_2}{a_2} = \frac{b_3}{a_3} = ... = \frac{b_i}{a_i} = g \tag{171}$$

where the ratio g is assumed constant. This ratio is related to the vapor pressure of the adsorbate. With these two additional assumptions, one can solve the surface coverage that contains one layer of molecule (s,) in terms of s_0 and pressure as follows:

$$s_1 = \frac{a_1}{b_1} = Ps_0 \exp(\varepsilon_1) \tag{172}$$

where ε, is the reduced energy of adsorption of the first layer, defined as

$$\varepsilon_1 = \frac{E_1}{R_g T} \tag{173}$$

Similarly the surface coverage of the section containing i layers of molecules is:

$$s_i = \frac{a_1}{b_1} s_0 g . \exp(\varepsilon_1 - \varepsilon_2) \left[\left(\frac{P}{g} \right) \exp \varepsilon_L \right]^i \tag{174}$$

for i = 2, 3, ..., where E_L is the reduced heat of liquefaction

$$\varepsilon_L = \frac{E_L}{R_g T} \tag{173}$$

Substituting these surface coverage into the total amount of gas adsorbed (eq. 169), we obtain:

$$\frac{V}{V_m} = \frac{Cs_0 \sum_{i=0}^{\infty} i.x^i}{s_0 \left(1 + C \sum_{i=1}^{\infty} x^i \right)} \tag{174}$$

where the parameter C and the variable x are defined as follows:

$$y = \frac{a_1}{b_1} P \exp \varepsilon_i \tag{175}$$

$$x = \frac{P}{g} \exp \varepsilon_L \tag{176}$$

$$C = \frac{y}{x} = \frac{a_1 g}{b_1} e^{(\varepsilon_1 - \varepsilon_L)} \tag{177}$$

By using the following formulas (Abramowitz and Stegun, 1962)

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x} ; \sum_{i=1}^{\infty} i x^i = \frac{x}{(1-x)^2} \tag{178}$$

eq. (174) can be simplified to yield the following form written in terms of C and x:

$$\frac{V}{V_m} = \frac{Cx}{(1-x)(1-x+Cx)} \tag{179}$$

Eq. (179) can only be used if we can relate x in terms of pressure and other known quantities. This is done as follows. Since this model allows for infinite layers on top of a flat surface, the amount adsorbed must be infinity when the gas phase pressure is equal to the vapor pressure, that is $P = P_o$ occurs when $x = 1$; thus the variable x is the ratio of the pressure to the vapor pressure at the adsorption temperature:

$$x = \frac{P}{P_0} \tag{180}$$

With this definition, eq. (179) will become what is now known as the famous BET equation containing two fitting parameters, C and V_m:

$$\frac{V}{V_m} = \frac{CP}{(P_0 - P)(1 + (C-1)(P/P_0))} \tag{181}$$

Fig. 17 shows plots of the BET equation (181) versus the reduced pressure with C being the varying parameter. The larger is the value of C, the sooner will the multilayer form and the convexity of the isotherm increases toward the low pressure range.
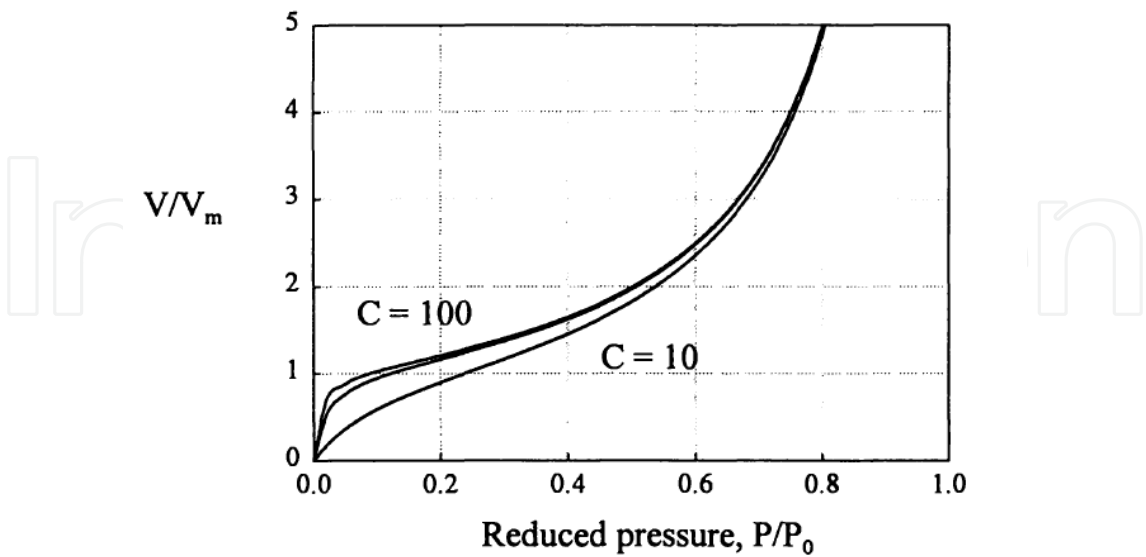
Fig. 17. Plots of the BET equation versus the reduced pressure (C = 10,50, 100)

Equating eqs.(180) and (176), we obtain the following relationship between the vapor pressure, the constant g and the heat of liquefaction:

$$P_0 = g.\exp\left(-\frac{E_L}{R_g T}\right) \tag{182}$$

Within a narrow range of temperature, the vapor pressure follows the Clausius-Clapeyron equation, that is

$$P_0 = \alpha.\exp\left(-\frac{E_L}{R_g T}\right) \tag{183}$$

Comparing this equation with eq.(182), we see that the parameter g is simply the pre-exponential factor in the Clausius-Clapeyron vapor pressure equation. It is reminded that the parameter g is the ratio of the rate constant for desorption to that for adsorption of the second and subsequent layers, suggesting that these layers condense and evaporate similar to the bulk liquid phase. The pre-exponential factor of the constant C (eq.177)

$$\frac{a_1 g}{b_1} = \frac{a_1 b_j}{b_1 a_j} \; ; for j > 1 \tag{184}$$

can be either greater or smaller than unity (Brunauer et al., 1967), and it is often assumed as unity without any theoretical justification. In setting this factor to be unity, we have assumed that the ratio of the rate constants for adsorption to desorption of the first layer is the same as that for the subsequent layers at infinite temperature. Also by assuming this factor to be unity, we can calculate the interaction energy between the first layer and the solid from the knowledge of C (obtained by fitting of the isotherm equation 3.3-18 with experimental data) The interaction energy between solid and adsorbate molecule in the first layer is always greater than the heat of adsorption; thus the constant C is a large number (usually greater than 100).

7. BDDT (Brunauer, Deming, Denting, Teller) classification

The theory of BET was developed to describe the multilayer adsorption. Adsorption in real solids has given rise to isotherms exhibiting many different shapes. However, five isotherm shapes were identified (Brunauer et al., 1940) and are shown in Fig.19. The following five systems typify the five classes of isotherm.

Type 1: Adsorption of oxygen on charcoal at -183 °C
Type 2: Adsorption of nitrogen on iron catalysts at -195°C (many solids fall into this type).
Type 3: Adsorption of bromine on silica gel at 79°C, water on glass
Type 4: Adsorption of benzene on ferric oxide gel at 50°C
Type 5: Adsorption of water on charcoal at 100°C

Type I isotherm is the Langmuir isotherm type (monolayer coverage), typical of adsorption in microporous solids, such as adsorption of oxygen in charcoal. Type II typifies the BET adsorption mechanism. Type III is the type typical of water adsorption on charcoal where the adsorption is not favorable at low pressure because of the nonpolar (hydrophobic) nature of the charcoal surface. At sufficiently high pressures, the adsorption is due to the capillary condensation in mesopores. Type IV and type V are the same as types II and III with the exception that they have finite limit as $P \to P_0$ due to the finite pore volume of porous solids.
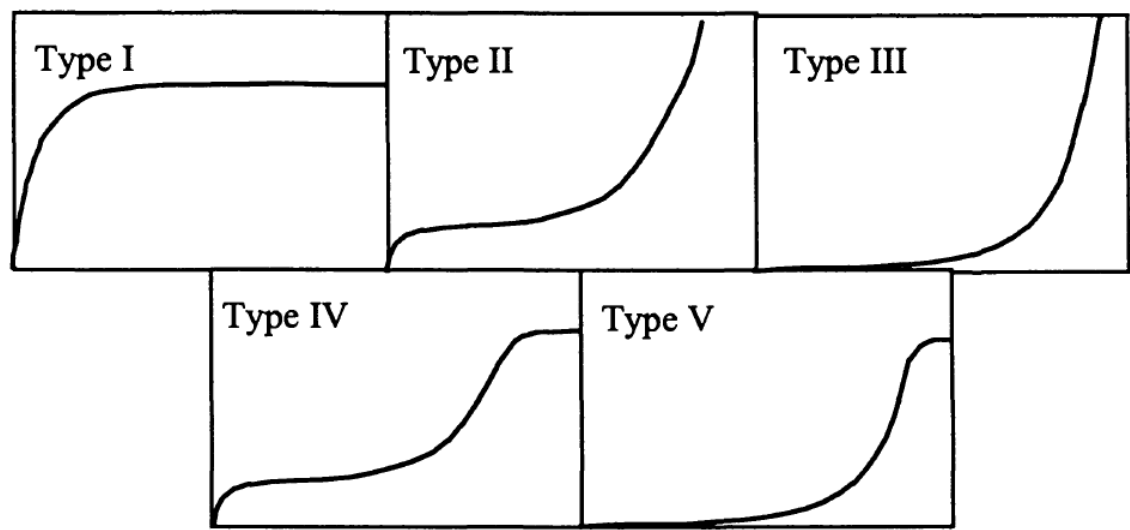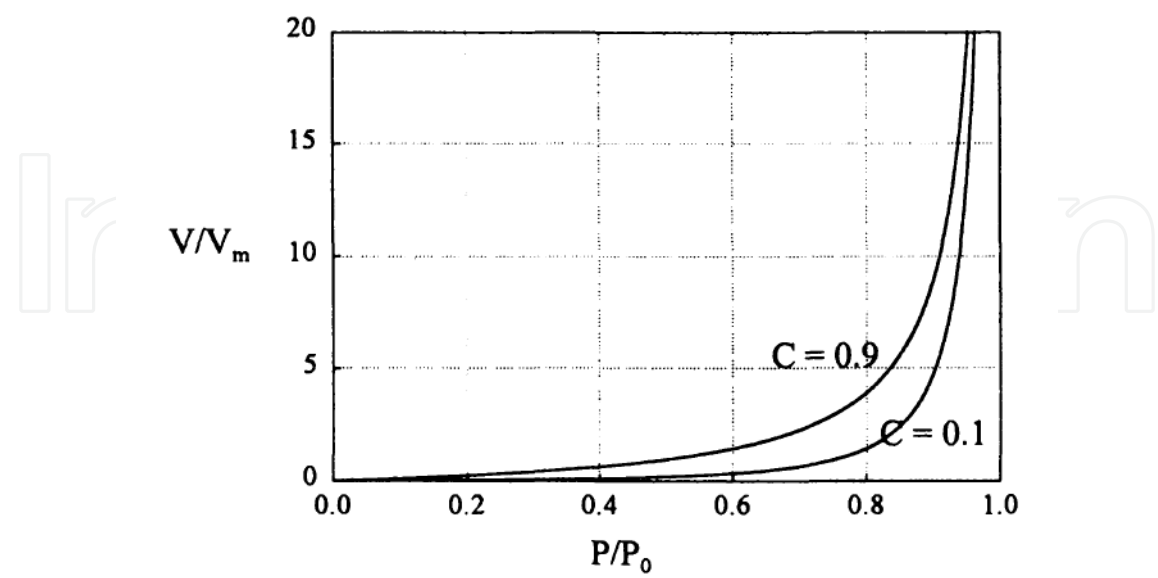
Fig. 19. BDDT classification of five isotherm shapes

Fig. 20. Plots of the BET equation when C < 1

The BET equation developed originally by Brunauer et al. (1938) is able to describe type I to type III. The type III isotherm can be produced from the BET equation when the forces between adsorbate and adsorbent are smaller than that between adsorbate molecules in the liquid state (i.e. E, < EL). Fig. 20 shows such plots for the cases of C = 0.1 and 0.9 to illustrate type III isotherm.

The BET equation does not cover the last two types (IV and V) because one of the assumptions of the BET theory is the allowance for infinite layers of molecules to build up on top of the surface. To consider the last two types, we have to limit the number of layers which can be formed above a solid surface. (Foo K.Y., Hameed B.H., 2009), (Moradi O. , et al. 2003). (Hirschfelder, and et al. 1954).

8. Conclusion

In following chapter thermodynamics of interface is frequently applied to derive relations between macroscopic parameters. Nevertheless, this chapter is included as a reminder. It presents a consist summary of thermodynamics principles that are relevant to interfaces in view of the topics discussed such as thermodynamics for open and close systems, Equilibrium between phases, Physical description of a real liquid interface, Surface free energy and surface tension of liquids, Surface equation of state, Relation of van der Waals constants with molecular pair potentials and etc in forthcoming and special attention is paid to heterogeneous systems that contain phase boundaries.

9. References

Adamson, A.W. and Gast, A.P. (1997) *Physical Chemistry of Surfaces* (6th edn).Wiley, New York, USA.

Abdullah M.A., Chiang L., Nadeem M., Comparative evaluation of adsorption kinetics and isotherms of a natural product removal by Amberlite polymeric adsorbents, Chem. Eng. J. 146 (3) (2009) 370–376.

Ahmaruzzaman M. d., Adsorption of phenolic compounds on low-cost adsorbents: a review, Adv. Colloid Interface Sci. 143 (1–2) (2008) 48–67.

Adam, N.K. (1968) *The Physics and Chemistry of Surfaces*. Dover, New York.

Atkins, P.W. (1998) *Physical Chemistry* (6th edn). Oxford University Press, Oxford.

Aveyard, R. and Haydon, D.A. (1973) *An Introduction to the Principles of Surface Chemistry*. Cambridge University Press, Cambridge.

Dabrowski A., Adsorption—from theory to practice, Adv. Colloid Interface Sci. 93 (2001) 135–224.

Dubinin M. M., Radushkevich L.V., The equation of the characteristic curve of the activated charcoal, Proc. Acad. Sci. USSR Phys. Chem. Sect. 55 (1947) 331–337.

Erbil, H.Y. (1997) Interfacial Interactions of Liquids. In Birdi, K.S. (ed.). *Handbook of Surface and Colloid Chemistry*. CRC Press, Boca Raton.

Foo K.Y., Hameed B.H., Recent developments in the preparation and regeneration of activated carbons by microwaves, Adv. Colloid Interface Sci. 149 (2009) 19–27.

Foo K.Y., Hameed B.H., A short review of activated carbon assisted electrosorption process: An overview, current stage and future prospects, J. Hazard. Mater. 171 (2009) 54–60.

Hirschfelder, J.O.,Curtiss, C.F. and Bird, R.B. (1954) *Molecular Theory of Gases and Liquids*. Wiley, New York.

Israelachvili, J. (1991) *Intermolecular & Surface Forces* (2nd edn). Academic Press, London.

Levine, I.N. (1990) *Physical Chemistry* (3rd edn). McGraw-Hill, New York.

Lyklema, J. (2005) *Fundamentals of interface and colloid science,* Elsevier Ltd.

Lyklema, L. (1991) *Fundamentals of Interface and Colloid Science* (vols. I and II). Academic Press, London.

Keller J.U., (2005) *Gas adsorption equilibria, Experimental Methods and Adsorptive Isotherms*, Springer Science, USA.

Koopal L.K., Van Riemsdijk W. H., Wit J.C.M., Benedetti M.F., Analytical isotherm equation for multicomponent adsorption to heterogeneous surfaces, J. Colloid Interface Sci. 166 (1994) 51–60.

Miladinovic N., Weatherley L.R., Intensification of ammonia removal in a combined ion-exchange and nitrification column, Chem. Eng. J. 135 (2008) 15–24.

Moradi, O, Modarress, H.; Norouzi, M.; Effect of Lysozyme Concentration, pH and Ionic Strength and It Adsorption on HEMA and AA Contact Lenses, "Iranian Polymer Journal", Vol.12, No.6, 477-484, 2003.

Moradi, O, Modarress, H.; Norouzi, M.;Experimental Study of Albumin and Lysozyme Adsorption onto Acrylic Acid (AA) and 2-hydroxyethyl methacrylate (HEMA) surfaces, Journal of colloid and interface science, Vol. 261, No. 1, 16-19, 2004.

Moradi, O. Heavy metal [Cr(VI), Cd(II) and Pb(II)] ions removal by modified jute: Characterization and Modeling, J. Theoretical and Physical Chemistry, Vol. 4, No. 3, 163-168, 2007.

Moradi O., Aghaie M., Zare K., Monajjemi M., Aghaie, H., The Study of Adsorption Characteristics Cu^{2+} and Pb^{2+} Ions onto PHEMA and P(MMA-HEMA) Surfaces from Aqueous Single Solution, journal of Hazardous Materials, 673-679, 170, 2009.

Moradi O., Aghaie M., Zare K., Monajjemi M., Aghaie, H., The Studies of Equilibrium and Thermodynamic Adsorption of Pb(II), Cd(II) and Cu(II) Ions From Aqueous Solution onto SWCNTs and SWCNT –COOH Surfaces, Fullerenes, Nanotubes and Carbon Nanostructures,18,285-302, 2010.

Mohan D., Pittman Jr C.U., Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, J. Hazard. Mater. 137 (2006) 762–811.

Murrell, J.N. and Jenkins, A.D. (1994) *Properties of Liquids and Solutions* (2nd edn). Wiley.

Ng J.C.Y., Cheung W.H., McKay G., Equilibrium studies of the sorption of Cu(II) ions onto chitosan, J. Colloid Interface Sci. 255 (2002) 64–74.

Norde, W., (2003) *colloids and interfaces in life science,* Marcel Dekker, Inc., New York, USA.

Pitzer, K.S. and Brewer L. (1961) *Thermodynamics* (2nd edn). McGraw-Hill, New York.

Prausnitz, J.M., Lichtenthaler, R.N. and Azevedo E.G. (1999) *Molecular Thermodynamics of Fluid-Phase Equilibria* (3rd edn). Prentice Hall, Englewood Cliffs.

Tempkin M. I., Pyzhev V., Kinetics of ammonia synthesis on promoted iron catalyst, Acta Phys. Chim. USSR 12 (1940) 327–356.
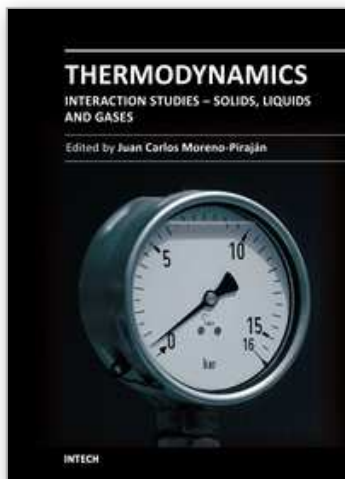
Scatchard, G. (1976) *Equilibrium in Solutions & Surface and Colloid Chemistry*. Harvard University Press, Cambridge.

Zeldowitsch J., Adsorption site energy distribution, Acta Phys. Chim. URSS 1 (1934) 961–973.

Thermodynamics - Interaction Studies - Solids, Liquids and Gases

Edited by Dr. Juan Carlos Moreno Pirajãn

ISBN 978-953-307-563-1

Hard cover, 918 pages

Publisher InTech

Published online 02, November, 2011

Published in print edition November, 2011

Thermodynamics is one of the most exciting branches of physical chemistry which has greatly contributed to the modern science. Being concentrated on a wide range of applications of thermodynamics, this book gathers a series of contributions by the finest scientists in the world, gathered in an orderly manner. It can be used in post-graduate courses for students and as a reference book, as it is written in a language pleasing to the reader. It can also serve as a reference material for researchers to whom the thermodynamics is one of the area of interest.

INTECH
open science | open minds