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Is the Free Energy Change of Adsorption Correctly Calculated?

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In the study of adsorption, changes in free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) have been most frequently calculated from the Langmuir equilibrium constant. In a strict theoretical sense, the Langmuir equilibrium constant with units of liters per mole and the thermodynamic equilibrium constant without units are not the same. Moreover, the equilibrium constants for thermodynamic calculation have also been derived in different ways in the literature, for example, Frumkin isotherm, Flory−Huggins isotherm, distribution constants, and so on. As a result, values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ of adsorption reported in the literature are very confusing. This study shows that for a dilute solution of charged adsorbates or for a solution of uncharged adsorbates at any concentration, the thermodynamic equilibrium constant of adsorption would be reasonably approximated by the Langmuir equilibrium constant, and thus the use of the Langmuir equilibrium constant for calculation of $\Delta G°$ and subsequent determination of $\Delta H°$ and $\Delta S°$ of adsorption would be acceptable. However, special attention should be given if the equilibrium constants derived from other adsorption isotherm equations or distribution constants were used for determination of $\Delta G°$.

Introduction

A number of different adsorption isotherm equations have been applied to describe adsorption behavior at equilibrium. In the study of adsorption thermodynamics, the equilibrium constants derived from various isotherms, such as the Langmuir, Frumkin, and Flory−Huggins isotherms as well as from some specially defined formulas, have often been used for calculation of changes in free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) of adsorption.[1−6] It is obvious that determination of the equilibrium constant is a key toward correct estimates of $\Delta G°$, $\Delta H°$, and $\Delta S°$, whereas the equilibrium constant for adsorption is related to the isotherm equation employed. In the sense of reaction thermodynamics, $\Delta G°$ can be determined according to the unitless thermodynamic equilibrium constant, whereas the Langmuir equilibrium constant has units of liters per mole. Therefore, this study attempted to shed light on how $\Delta G°$ of adsorption can be correctly calculated.

Calculation of $\Delta G°$ from Langmuir Equilibrium Constant

The Gibbs energy change ($\Delta G°$) indicates the degree of spontaneity of an adsorption process, and a higher negative value reflects a more energetically favorable adsorption. According to thermodynamic law, $\Delta G°$ of adsorption is calculated as follows

$$\Delta G° = -RT \ln K_a \tag{1}$$

in which K_a is the thermodynamic equilibrium constant without units, T is the absolute temperature in kelvins, and R is the gas constant with a value of 8.314 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. In the study of adsorption, eq 1 is employed for determination of $\Delta G°$. The relationship of $\Delta G°$ to enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) of adsorption is expressed as

$$\Delta G° = \Delta H° - T\Delta S° \tag{2}$$

Substituting eq 1 into eq 2 gives

$$\ln K_a = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{3}$$

The plot of ln K_a against $1/T$ theoretically yields a straight line that allows calculation of $\Delta H°$ and $\Delta S°$ from the respective slope and interception of eq 3. These thermodynamic estimates can offer insight into the type and mechanism of an adsorption process. Basically, the heat evolved during the physical adsorption is of the same order of magnitude as the heat of condensation, that is, (2.1 to 20.9) $\text{kJ}\cdot\text{mol}^{-1}$,[7] whereas the heats of chemisorption generally fall into a range of (80 to 200) $\text{kJ}\cdot\text{mol}^{-1}$.[8,9] The positive value of $\Delta H°$ implies that adsorption would be an endothermic process, whereas a negative $\Delta H°$ indicates an exothermic adsorption process. A low $\Delta S°$ value often signifies no remarkable change in entropy during adsorption, whereas a positive $\Delta S°$ value reflects the increased randomness at the solid−solution interface during adsorption. It should be realized that determination of $\Delta G°$, $\Delta H°$, and $\Delta S°$ indeed is dependent on the estimate of the thermodynamic constant (K_a).

The Langmuir isotherm with the following form has been commonly used for description of adsorption data at equilibrium

$$q_e = q_{\max}\frac{C_e K_L}{C_e K_L + 1} \tag{4}$$

in which q_e and $q_{\max}$ are the adsorption capacity of adsorbent at equilibrium (milligrams per gram) and its maximum value, C_e, is the equilibrium concentration of adsorbate in solution (moles per liter), whereas K_L is the Langmuir equilibrium constant of adsorption with units of liters per mole. The Langmuir equilibrium constant has been employed very often for calculation of $\Delta G°$ using eq 1 in adsorption studies.[1,3,5,10−15] It should be pointed out that the thermodynamic equilibrium constant in eq 1 is unitless, whereas the Langmuir equilibrium constant has

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units of liters per mole. Therefore, a simple but hardly asked question in adsorption studies is whether use of the Langmuir equilibrium constant for calculation of $\Delta G°$ by eq 1 is reasonable.

According to Langmuir,[16] the adsorption process can be depicted as follows

$$A + B \leftrightarrow AB \tag{5}$$

in which A represents free adsorptive solute molecules, B is vacant sites on the adsorbent, and AB is the occupied sites. For eq 5, the thermodynamic equilibrium constant (K_a) can be written as follows[17]

$$K_a = \frac{\text{activity of occupied sites}}{(\text{activity vaccant sites})(\text{activity of solute in solution})} \tag{6}$$

It is reasonable to consider that the activity coefficients of the occupied and unoccupied sites are the same,[17] and thus eq 6 becomes

$$K_a = \frac{\theta_e}{(1 - \theta_e)a_e} \tag{7}$$

in which θ_e is the fraction of the surface covered at equilibrium and a_e is the activity of the adsorbate in solution at equilibrium. In the sense of chemistry, the activity of a substance is related to its molar concentration (C_e) by the following formula[18]

$$a_e = \gamma_e \frac{C_e}{C_s} \tag{8}$$

In eq 8, γ_e is the activity coefficient at the adsorption equilibrium, and C_s is the molar concentration of the standard reference solution, which is equal to 1 mol·L^{-1},[18] and thus

$$a_e = (\gamma_e \cdot C_e) \cdot (1\ \text{L} \cdot \text{mol}^{-1}) \tag{9}$$

Substituting eq 9 into eq 7 gives

$$K_a = \frac{\theta_e}{(1 - \theta_e)\gamma_e C_e} \cdot (1\ \text{mol} \cdot \text{L}^{-1}) \tag{10}$$

In the study of adsorption, θ_e is defined as

$$\theta_e = \frac{q_e}{q_{\max}} \tag{11}$$

Inserting eq 11 into eq 4 yields

$$K_L = \frac{\theta_e}{(1 - \theta_e)C_e} \tag{12}$$

The comparison of eqs 10 and 12 shows that

$$K_a = \frac{K_L}{\gamma_e} \cdot (1\ \text{mol} \cdot \text{L}^{-1}) \tag{13}$$

Replacing K_a in eq 1 by eq 13 leads to

$$\Delta G° = -RT \ln\left[\frac{K_L}{\gamma_e} \cdot (1\ \text{mol} \cdot \text{L}^{-1})\right] \tag{14}$$

So far, all adsorbates studied in the literature can be roughly divided into two big groups according to their charge characteristics, that is, charged species (e.g., heavy metal ions) and neutral species or species with weak charges (e.g., organic compounds). According to the Debye−Huckel limiting law, γ_e is a function of the ionic strength (I_e) of the solute at adsorption equilibrium and the charge carried by solute (z)

$$\log \gamma_e = -Az^2 I_e^{1/2} \tag{15}$$

According to eq 15, for neutral adsorbates or adsorbates with weak charges, eq 14 turns to

$$\Delta G° \approx -RT \ln[K_L \cdot (1\ \text{mol} \cdot \text{L}^{-1})] = -RT \ln K_L \tag{16}$$

This implies that for neutral adsorbates or adsorbates with weak charge, the Langmuir equilibrium constant with units of liters per mole can be reasonably used for determination of $\Delta G°$. However, for charged adsorbates (e.g., multivalent ions), the Debye−Huckel limiting law, the extended Debye−Huckel law, the Davies equation, and the specific ion interaction model all show that activity coefficients of charged adsorbates are governed by ionic interactions, and the value of the activity coefficient of a charged adsorbate ranges downward from unity as the concentration of adsorbate is increased. In this case, only for a dilute solution of charged adsorbate, I_e would be negligible, and subsequently, the activity coefficient in eq 14 would be close to unity. Therefore, eq 14 can be reduced to eq 16, indicating that the use of the Langmuir equilibrium constant for determination of $\Delta G°$ is reasonable only for a dilute solution of a charged adsorbate. In fact, such a constraint has often been ignored in adsorption studies of multivalent cations.

Milonjic[19] also questioned the use of the Langmuir equilibrium constant for calculation of $\Delta G°$ of adsorption and thought that if adsorption was investigated in solution, then the Langmuir equilibrium constant could be converted to a dimensionless constant by multiplying it by 55.5 mol water per liter (i.e., 1000 g divided by the molar weight of pure water), and $\Delta G°$ was proposed to be calculated by

$$\Delta G° = RT \ln(55.5K_L) \tag{17}$$

As discussed above, the activity of a substance is the ratio of the concentration of the substance to a reference concentration (1 mol·L^{-1}), and thus the unit of such a ratio always cancels; subsequently, activity has no unit.[18] It seems that eq 17 should result from a misunderstanding of the concept of chemical activity.

Calculation of ΔG° from the Frumkin and Flory−Huggins Equilibrium Constants

Equation 1 shows that $\Delta G°$ is governed by the thermodynamic equilibrium constant. In addition to the Langmuir isotherm equation, some other isotherms have also been employed for calculation of the equilibrium constant of adsorption. For instance, Basar[2] reported the $\Delta G°$ of dye adsorption by activated carbon determined from the Frumkin equilibrium constant, whereas the Flory−Huggins equilibrium constant was also used to compute $\Delta G°$ for adsorption of Ni^{2+} and Pb^{2+}.[4,6]

Calculation of ΔG° from the Frumkin Equilibrium Constant. The Frumkin isotherm equation was developed in taking into account the interaction between adsorbed species. According to Grchev et al.,[20] the Frumkin isotherm can be expressed as follows

$$\frac{\theta_e}{1 - \theta_e} \exp(-f\theta_e) = K_F C_e \tag{18}$$

in which f is the interaction coefficient and K_F is the so-called Frumkin equilibrium constant. In fact, K_F is related to K_L through the following equation

$$K_F = K_L \exp(f\theta_e) \tag{19}$$

At $f = 0$, there is no interaction between adsorbate species, and thus the Frumkin isotherm equation reduces to the Langmuir

Table 1. Comparison of K_F- and K_L-Based $\Delta G°$ for Adsorption of Methylene Blue by Activated Carbon[a]

Langmuir isotherm equation[b]			
	30 °C	40 °C	50 °C
ln K_L	10.10	10.36	10.63
K_L-based $\Delta G°$ (kJ·mol^{-1})	−25.4	−26.9	−28.5
K_L-based $\Delta S°$ (kJ·mol^{-1}·K^{-1})		0.16	
K_L-based $\Delta H°$ (kJ·mol^{-1})		21.5	
Frumkin isotherm equation[c]			
	30 °C	40 °C	50 °C
ln K_F	6.47	6.55	6.45
K_F-based $\Delta G°$ (kJ·mol^{-1})	−16.3	−17.1	−17.4
K_F-based $\Delta S°$ (kJ·mol^{-1}·K^{-1})	Nonlinear relation between K_F and $1/T$ was found		
K_F-based $\Delta H°$ (kJ·mol^{-1})			

[a] Data from Basar.[2] [b] Recalculated according to the data by Basar.[2] [c] Values reported by Basar.[2]

isotherm equation and $K_F = K_L$. Table 1 shows a comparison of the K_F-based and K_L-based $\Delta G°$ for adsorption of methylene blue by activated carbon. It is obvious that the values of the K_F-based and K_L-based $\Delta G°$ indeed are significantly different. More importantly, a perfect straight line was found between ln K_L and $1/T$, indicated by a very high correlation coefficient of 0.999, and this allows determination of $\Delta H°$ and $\Delta S°$ by using eq 3 (Table 1). However, no linear relationship between ln K_F and $1/T$ was observed, and this eventually leads to a failure in calculating $\Delta H°$ and $\Delta S°$, which in turn is against the theoretical prediction by thermodynamic law (eq 2). Consequently, special attention should be given when the Frumkin equilibrium constant is used for determining $\Delta G°$ of adsorption.

It should be pointed out that all of the isotherm equations are developed according to some specific assumptions, which are unfortunately often ignored when one chooses and applies the isotherms in the studies of adsorption. In the literature, the selection of an isotherm is often based on some statistical analysis (e.g., R^2). Nevertheless, goodness of the curve fitting may not offer any insight into possible adsorption mechanisms. Because of the extremely complex adsorption mechanisms, how to select an isotherm for an adsorption study adequately still remains a big challenge.

Calculation of $\Delta G°$ from the Flory−Huggins Equilibrium Constant. The original Flory−Huggins isotherm accounts for the effect of the surface coverage on adsorption[21]

$$\frac{\theta_e}{(1-\theta_e)^{n_{FH}}}\exp(-2n_{FH}\alpha_{FH}\theta_e) = K_{FH}C_e \tag{20}$$

in which K_{FH} is the so-called Flory−Huggins equilibrium constant, n_{FH} is constant, and α_{FH} is an effective coefficient indicating the interaction between adsorbed molecules. It can be seen that eq 20 turns into a Frumkin-type isotherm (eq 18) at $n_{FH} = 1$.

In some adsorption studies,[4,6] the linearized Flory−Huggins isotherm was expressed as

$$\log\frac{\theta_e}{C_0} = \log K_{FH} + n_{FH}\log(1-\theta_e) \tag{21}$$

in which C_0 is the initial adsorbate concentration and θ_e was calculated according to the following formula[4,6]

$$\theta_e = 1 - \frac{C_e}{C_0} = \frac{C_0 - C_e}{C_0} \tag{22}$$

Different from other adsorption isotherms describing the relationship between θ_e and C_e, eq 21 shows the dependence of θ_e on C_0. However, it is apparent that eq 22 is the definition expression of adsorption efficiency. In the study of adsorption equilibrium, the fraction of surface coverage (θ_e) indeed is defined by eq 11, and at a given dose (X) of adsorbent, eq 11 becomes

$$\theta_e = \frac{q_e}{q_{max}} = \frac{C_0 - C_e}{Xq_{max}} \tag{23}$$

The theoretical origin of eq 22 is still not clear for use in determination of the fraction of surface coverage.

In fact, according to Chritodoulou et al.,[21] the Flory−Huggins isotherm (eq 20) can be rearranged to

$$\ln\frac{\theta_e}{C_e} = \ln K_{FH} + 2n_{FH}\alpha_{FH}\theta_e + n_{FH}\ln(1-\theta_e) \tag{24}$$

As pointed out earlier, α_{FH} in the Flory−Huggins isotherm represents the degree of the interaction between adsorbed molecules. If there is no such interaction between the molecules, then α_{FH} becomes zero, and thus eq 24 reduces to

$$\ln\frac{\theta_e}{C_e} = \ln K_{FH} + n_{FH}\ln(1-\theta_e) \tag{25}$$

It should be realized that eq 25 is a special case of the Flory−Huggins isotherm (eq 20) only when the interaction between the molecules is negligible. Compared with eq 25, the use of eq 21 as the Flory−Huggins isotherm would be debatable, and the resultant K_{FH} and the K_{FH}-based $\Delta G°$ values as reported in the literature[4,6] should need re-examination.

Calculation of $\Delta G°$ from Distribution Constant

Calculation of $\Delta G°$ from $K_c = C_{ad}/C_e$. In many studies of adsorption thermodynamics,[22−29] the distribution constant (K_c) was used for calculation of $\Delta G°$ of adsorption

$$K_c = \frac{C_{ad}}{C_e} \tag{26}$$

in which C_e and C_{ad} are the solute concentration in solution at equilibrium and the concentration of solute adsorbed at equilibrium, respectively. According to the IUPAC,[30] the distribution constant is defined as the ratio of the concentration of a substance in a single definite form in the extract to its concentration in the same form in the other phase at equilibrium. As eq 5 shows, an adsorption process could not be attributed to a simple distribution of solute in the liquid and adsorbent phases. In fact, it represents a reaction between solute molecules (A) and adsorption sites (B) of the adsorbent. In this sense, no evidence shows that the distribution constant (K_c) has the general feature of the equilibrium constant of adsorption (Table 2).

To look further into the rationality of using K_c for calculation of $\Delta G°$, the equilibrium law is directly applied to eq 5, and the thermodynamic equilibrium constant (K_a) is written as follows

$$K_a = \frac{a_{AB}}{a_A a_B} \tag{27}$$

in which a_A, a_B, and a_{AB} are the respective activities of species A, B, and AB adsorbed at equilibrium. In an extreme case where the adsorption capacity of the adsorbent is much higher than the amount of adsorbate to be removed, the adsorbent B in eq 5 would be regarded as a pure solid; that is, θ_e is very small. Therefore, the activity of pure adsorbent B would be close to unity,[18] and eq 27 reduces to

$$K_a \approx \frac{a_{AB}}{a_A} \tag{28}$$

It should be emphasized that eq 28 is valid only for a dilute solution for which θ_e should be very small. As discussed earlier, for a dilute solution, the activity coefficient is very close to unity, and thus substituting eq 9 into eq 28 gives

$$K_a \approx \frac{C_{AB}}{C_A} = \frac{C_{ad}}{C_e} = K_c \tag{29}$$

Equation 29 suggests that only at very low adsorbate concentrations is K_c equal to the thermodynamic equilibrium constant, and only in this case can it be used for calculation of $\Delta G°$. According to eq 26, K_c can be estimated from the slope of a linear plot of C_{ad} versus C_e. However, it should be realized that the linear relationship between C_{ad} versus C_e holds only for dilute solutions, as discussed above and shown in Figure 1. In fact, such a constraint for eq 26 has often been ignored in the literature.

Calculation $\Delta G°$ from $K_d = q_e/C_e$. In some studies of adsorption,[31−33] the distribution constant (K_d) was defined in a way such that

$$K_d = \frac{q_e}{C_e} \tag{30}$$

and the change in free energy was calculated by $\Delta G° = -RT \ln K_d$. Sawalha et al.[33] proposed that K_d in eq 30 could be calculated from the slope of the plot of q_e versus C_e. It is worth noting that K_d has a units of liters of solution per moles of adsorbent, which is completely different from the Langmuir equilibrium constant. In most studies of adsorption, q_e may not be linearly related to C_e, and it indeed increases with C_e until its equilibrium value is described by a number of isotherm equations. It seems difficult to understand the theoretical origin of K_d as the distribution constant or equilibrium constant for calculation of $\Delta G°$.

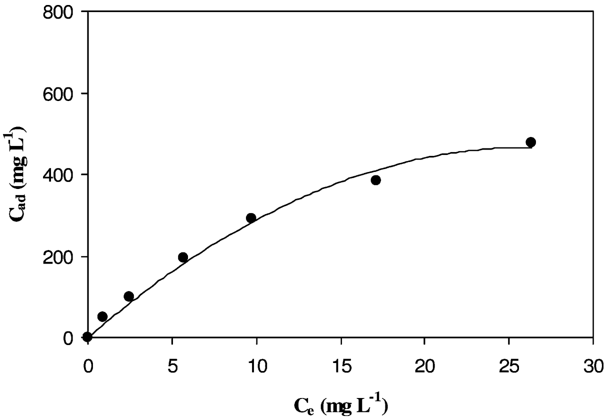

Figure 1. Plot of C_e versus C_{ad} for adsorption of pyridine by fly ash at 10 °C. Data from Lataye et al.[34]

Table 2. Comparison of K_L and K_c Determined by Equations *4* and *26* As Well As the Corresponding $\Delta G°$ Values for Adsorption of Cr^{6+} by Various Adsorbents[a]

		K_c-based $\Delta G°$	K_L	K_L-based $\Delta G°$
adsorbents	K_c	kJ·mol^{-1}	L·mol^{-1}	kJ·mol^{-1}
clarified sludge	52.50	−9.98	6916	−22.3
rice husk ash	49.92	−9.85	4836	−21.3
activated alumina	48.52	−9.78	5928	−21.9
Fuller's earth	13.22	−6.50	1924	−19.1
fly ash	18.05	−7.28	2236	−19.4
saw dust	10.77	−5.98	2028	−19.2
neem bark	10.48	−5.76	1820	−18.9

[a] Values of K_c and K_c-based $\Delta G°$ were taken from Bhattacharya et al.,[29] and K_L and K_L-based $\Delta G°$ were recalculated.

The Freundlich isotherm equation can be expressed as

$$q_e = k_F C_e^n \tag{31}$$

in which K_F and n are the Freundlich empirical constants. Now it becomes clear that at $n = 1$, the Freundlich isotherm equation turns to eq 30, a linear isotherm, and $K_d = K_F$. This in turn suggests that eq 30 would be a special case of the well-known Freundlich isotherm equation. However, at $C_e \ll 1/K_L$, eq 4 is simplified to

$$q_e = q_{max} K_L C_e \tag{32}$$

A comparison of eqs 30 and 32 shows that $K_d = q_{max}K_L$, indicating that K_d may not have any feature of the equilibrium constant in this case. In an adsorption study, q_e is defined as

$$q_e = \frac{C_0 - C_e}{X} = \frac{C_{ad}}{X} \tag{33}$$

Replacing q_e in eq 30 by eq 33 leads to

$$K_d = \frac{C_{ad}}{XC_e} = \frac{K_c}{X} \tag{34}$$

It appears from eq 34 that K_d has no feature of the distribution constant (K_c) as well.

Conclusions

(1) For neutral adsorbates or adsorbates with very weak charge, the Langmuir equilibrium constant with units of liters per mole is numerically equal to the thermodynamic equilibrium constant of adsorption. Therefore, use of the Langmuir equilibrium constant for calculation of $\Delta G°$ and subsequent determination of $\Delta H°$ and $\Delta S°$ is numerically correct. (2) For a dilute solution of charged adsorbate, the thermodynamic equilibrium constant of adsorption can be reasonably approximated by the Langmuir equilibrium constant. In this case, the Langmuir equilibrium constant can be applied for determination of $\Delta G°$. (3) For a charged adsorbate solution at high concentration, the effect of the activity coefficient of solution on the calculation of $\Delta G°$ from the Langmuir equilibrium constant needs to be seriously taken into account. (4) Because determination of the equilibrium constant of adsorption closely depends on the isotherm equation employed, for a given set of adsorption data, values of the equilibrium constant determined by different ways would vary significantly, and such a variation in the equilibrium constant would lead to inadequate estimates of $\Delta G°$, $\Delta H°$, and $\Delta S°$.

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