



## Research article

# Discussion on the thermodynamic calculation and adsorption spontaneity re Ofudje et al. (2023)

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## ARTICLE INFO

## Keywords:

Thermodynamic parameters  
Partition coefficient  
Standard adsorption equilibrium constant  
Dimension  
Spontaneity

## ABSTRACT

Accurate calculations and precise results are very important for the dissemination of scientific knowledge, whereas the errors of calculation will diminish the academic value of the paper. This discussion focuses on the calculation of thermodynamics and the determination of the spontaneity of adsorption processes in the paper of Ofudje et al. (2023). Ofudje et al. found that the apatite synthesized by chemical method (CHAp) has excellent adsorption properties for cadmium ions, which is an important contribution to the remediation of cadmium pollution. However, the calculation results of standard Gibbs free energy change ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ) and standard entropy change ( $\Delta S^\circ$ ) of the adsorption of  $\text{Cd}^{2+}$  onto CHAp surface need to be corrected due to an incorrect calculation. Firstly, the partition coefficient ( $K_D$ ) with a dimension cannot be used for thermodynamic calculation. Secondly, the adsorbent mass ( $m$ ) described by Ofudje et al. in different Sections is inconsistent, leading to incorrect results of  $K^\circ$  and  $\Delta G^\circ$ . When the appropriate value of the adsorbent mass is selected and the partition coefficient is converted to the standard adsorption equilibrium constant  $K^\circ$ , the calculated  $\Delta G^\circ$  is less than zero, which means that the adsorption is spontaneous. This discussion provides the correct calculation method of standard adsorption equilibrium constants and thermodynamic parameters, which can improve the reader's judgment and understanding of adsorption spontaneity.

## 1. Problems in calculation of adsorption thermodynamics

Ofudje et al. (2023) recently published an article entitled "Adsorption of  $\text{Cd}^{2+}$  onto apatite surface: Equilibrium, kinetics and thermodynamic studies" in Heliyon 9 (2023) e12971 [1]. Their results showed that the apatite synthesized by chemical method (CHAp) has excellent adsorption properties for cadmium ions. There is no doubt that they have made a contribution in the field of adsorption. However, the thermodynamic parameters of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  of the adsorption of  $\text{Cd}^{2+}$  by CHAp need to be corrected due to an incorrect calculation.

In Section 2.12. Thermodynamic studies, the partition coefficient and thermodynamic parameters were determined by Eqs. (1)–(3):

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$$K_D = \frac{Q_e}{C_e} \quad (1)$$

$$\Delta G^\circ = -RT \ln K_D \quad (2)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (3)$$

where  $Q_e$  represents the adsorbed amount of  $\text{Cd}^{2+}$  by CHAp, mg/g;  $C_e$  represents the concentration of  $\text{Cd}^{2+}$  at equilibrium, mg/L;  $K_D$  is the distribution ratio or partition coefficient, L/g [2–4];  $\Delta G^\circ$  represents the standard Gibbs free energy change, J/mol;  $\Delta H^\circ$  represents the standard enthalpy change, J/mol; and  $\Delta S^\circ$  represents the standard entropy change, J/(mol·K);  $R$  represents the gas constant, 8.314 J/(mol·K);  $T$  represents the Kelvin temperature, K; The values of thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ ) were provided in Table 1 (the original Table 4 in Ofudje et al.'s paper).

We found that the calculation results of thermodynamic parameters in Table 1 were incorrect. As an example, the value of  $\Delta G^\circ$  was calculated at 298 K as follows:

$$\Delta G^\circ = -RT \ln K_D = -(8.314 \text{ J/(mol·K)}) \times (298 \text{ K}) \times \ln(1.0028 \text{ L/g}) = -6.928 \text{ (J/mol)}$$

The calculated  $\Delta G^\circ$  was different from that in Table 1. The  $\Delta G^\circ$  calculated by Ofudje et al. for  $\text{Cd}^{2+}$  adsorption by CHAp at 298 K was  $-5.937 \text{ kJ mol}^{-1}$ , i.e.,  $-5937 \text{ J/mol}$ , which is 857 times higher than above calculation. Therefore, the thermodynamic parameters in Table 1 were incorrect. In addition, the partition coefficient  $K_D$  with a dimension (L/g) cannot be used for calculation of thermodynamic parameters [5]. According to the regulations of IUPAC (International Union of Pure and Applied Chemistry), only the standard equilibrium constant ( $K^\circ$ ) can be used for thermodynamic calculations. The  $K^\circ$  should be defined as [6–9]:

$$K^\circ = e^{-\frac{\Delta G^\circ}{RT}} \quad (4)$$

Since the exponent ( $-\Delta G^\circ/RT$ ) has no dimension, the  $K^\circ$  is a dimensionless parameter. In Ofudje et al.'s paper, the unit of  $K_D$  is L/g, which is not the standard equilibrium constant  $K^\circ$ . Therefore, their calculations in the original Table 4 are incorrect.

## 2. The calculation of adsorption thermodynamic parameters ( $\Delta S^\circ$ and $\Delta H^\circ$ ) by using nonlinear van't Hoff equation

In Ofudje et al.'s paper, the adsorption thermodynamic parameters ( $\Delta S^\circ$  and  $\Delta H^\circ$ ) were calculated by Eq. (3), which is a linear form of van't Hoff equation. Although the linear form of van't Hoff equation is a commonly used method in literature [10], if  $\Delta H^\circ$  and  $\Delta S^\circ$  vary appreciably with temperature, the van't Hoff plot deviates from linearity [11], therefore, the nonlinear form of van't Hoff equation is more suitable to provide a reliable estimation of the thermodynamic parameters [12]. Lima et al. [13] confirmed that the thermodynamic parameters calculated by the nonlinear equation are statistically higher than those calculated by the linearized equation. Since the statistical bias may result from linear transformations [14], the accurate calculation of the  $\Delta H^\circ$  and  $\Delta S^\circ$  parameters should use the nonlinear form of the van't Hoff equation.

$$K^\circ = \exp \left[ \frac{\Delta S^\circ}{R} - \left( \frac{\Delta H^\circ}{R} \right) \frac{1}{T} \right] \quad (5)$$

In order to calculate the thermodynamic parameters ( $\Delta S^\circ$  and  $\Delta H^\circ$ ), Python software 3.8 was used. The calculation procedure was as follows.

### (1) Loading modules

```
import numpy as np
from scipy.optimize import curve fit
from matplotlib import pyplot as plt.
```

### (2) Calculation of function parameters

```
T = np.array([T1, T2, T3, T4, T5])
```

**Table 1**

Thermodynamic constants for  $\text{Cd}^{2+}$  adsorption by CHAp (the original Table 4 in Ofudje et al.'s paper).

T (K)	$K_D$	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol)	$R^2$
298	1.0028	-5.937	175.591	0.610	0.968
303	1.0035	-8.817			
308	1.0044	-11.261			
313	1.0064	-16.656			
318	1.0072	-20.035			

```
Ko = np.array([Ko1, Ko2, Ko3, Ko4, Ko5])
fun = lambda T, S, H: np.exp(S/8.314-H/(8.314*T))
p,_ = curve_fit(fun, T, ko)
print(p)
```

(3) Calculation of correlation coefficient

```
r2 = 1-np.sum((ko-fun(T,p[0],p [1]))**2)/np.sum(ko**2)
```

Using the above program to solve the nonlinear van't Hoff equation, the nonlinear plot of  $K^\circ$  vs.  $T$  for the adsorption of  $\text{Cd}^{2+}$  at different temperatures were shown in Figs. 1 and 2.

### 3. Modification of thermodynamic calculations

The root reason for errors in Ofudje et al.'s paper is the confusion of the units of equilibrium constant. The partition coefficients can only be used in thermodynamic calculations after being converted to standard equilibrium constants ( $K^\circ$ , dimensionless). As far as a solid-liquid adsorption system in dilute solution was concerned,  $K^\circ$  is represented by the following formula [15,16]:

$$\lim_{C_s \rightarrow 0} \frac{C_s}{C_e} = K^\circ \tag{6}$$

where  $C_s$  represents the amount of solute adsorbed on the adsorbent surface, mg/L;  $C_e$  represents the concentration of solute at equilibrium, mg/L.  $C_s$  is independent of the mass of adsorbent, and only related to the solute concentration before and after adsorption, i.e.,

$$C_s = C_0 - C_e \tag{7}$$

where  $C_0$  represents the liquid-phase initial concentration of adsorbate, mg/L.

Unlike Eq. (1), the adsorption amount of solute ( $C_s$ , mg/L) in Eq. (6) is the same as the unit of solute concentration ( $C_e$ , mg/L) [17, 18]. Substituting  $C_s = C_0 - C_e$  into Eq. (6), an approximate equation for the solute adsorption in dilute solution is obtained [19–21]:

$$K^\circ = \frac{C_0 - C_e}{C_e} \tag{8}$$

The adsorption amount of solute at equilibrium ( $Q_e$ ) is calculated by Eq. (9):

$$Q_e = \frac{(C_0 - C_e)V}{m} \tag{9}$$

where  $V$  represents the volume of adsorbate solution, L;  $m$  represents the mass of adsorbent (CHAp), g.

Combining Eqs. (8) and (9), gives

$$K^\circ = \frac{Q_e}{C_e} \times \frac{m}{V} = K_D \frac{m}{V} \tag{10}$$

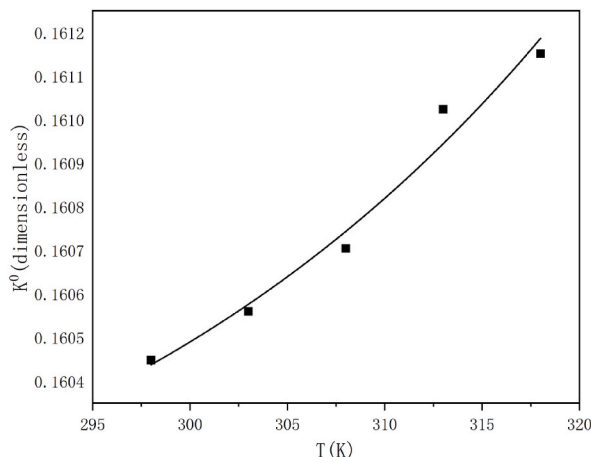
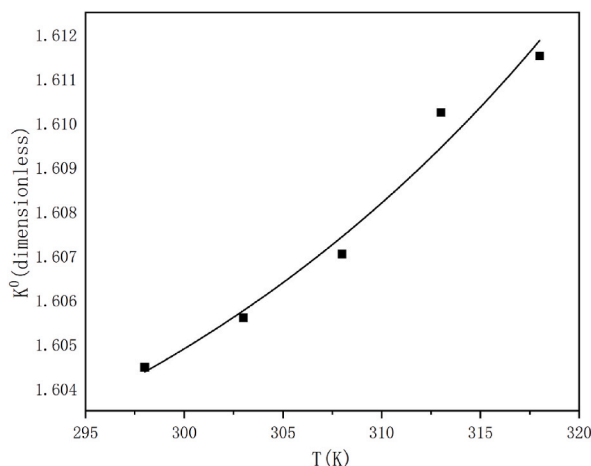


Fig. 1. Nonlinear plot of  $K^\circ$  vs.  $T$  for the adsorption of  $\text{Cd}^{2+}$  at different temperatures (the first correction,  $m = 0.004$  g).



**Fig. 2.** Nonlinear plot of  $\ln K^\circ$  vs.  $T$  for the adsorption of  $\text{Cd}^{2+}$  at different temperatures (the second correction,  $m = 0.04$  g).

Eq (10) reveals the relationship between  $K^\circ$  and  $K_D$ , and the standard equilibrium constant  $K^\circ$  can be obtained by using it. According to Section 2.3.1. Equilibrium study of Ofudje et al.'s paper, the values of  $m$  and  $V$  were 0.004 g and 0.025 L, respectively, therefore,  $K^\circ$  can be calculated by Eq. (10). The revised results for thermodynamic parameters were shown in Fig. 1 and Table 2.

As shown in Table 2, the correlation coefficient ( $R^2$ ) of nonlinear van't Hoff equation was higher than that of linear van't Hoff equation, indicating that the former had a higher certainty for estimating the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  [11–14]. The values of  $\Delta G^\circ$  were positive, indicating that the adsorption of  $\text{Cd}^{2+}$  onto apatite surface was nonspontaneous under the standard conditions. The cause of this phenomenon is most likely due to the inconsistent of the adsorbent mass, leading to an incorrect result of  $K^\circ$  and  $\Delta G^\circ$ . The inconsistent description of the adsorbent mass in the paper of Ofudje et al. was shown in Table 3.

As can be seen from Table 3 that the values of  $m$  in Section 2.3.1. and Section 3.2. are significantly different. Therefore, an error has occurred. According to the description by Ofudje et al. in Section 3.2. Equilibrium studies, the adsorption of  $\text{Cd}^{2+}$  increased with increase of the amount of the adsorbent (CHAp) until it reached saturation at amount of adsorbent 0.04 g. Therefore, 0.04 g is a suitable adsorbent dosage. If the thermodynamic parameters were recalculated by the suitable adsorbent dosage ( $m = 0.04$ ), the results were shown in Fig. 2 and Table 4.

As shown in Table 4, the values of  $\Delta G^\circ$  were negative, indicating that the adsorption of  $\text{Cd}^{2+}$  onto apatite surface was spontaneous. In addition, the value of  $\Delta S^\circ$  increased after correction compared with Table 1, indicating that the degree of freedom of  $\text{Cd}^{2+}$  at the liquid-solid interface increases during adsorption, and the entropy is the driving forces for adsorption [22]. The nonlinear van't Hoff equation provides thermodynamic parameters of  $\Delta H^\circ$  and  $\Delta S^\circ$  statistically more reliable than those from the linear format.

## 4. Discussion

### 4.1. How to judge the spontaneity of adsorption reaction

For a spontaneous adsorption process, the free Gibbs energy of adsorption products is less than that of the adsorption reactants [23], i.e.,

$$\Delta G = \sum \Delta G_{\text{product}} - \sum \Delta G_{\text{reactants}} < 0 \quad (11)$$

However, the calculation of free Gibbs energy using Eq. (2) must be restricted to standard conditions, therefore, the result is  $\Delta G^\circ$  instead of  $\Delta G$ . The  $\Delta G^\circ$  sign is positive or negative depending on the equilibrium state under standard conditions, but not the initial state before adsorption [12,24]. The spontaneity of adsorption is related to the adsorption state. Salvestrini et al. [12] thought that any adsorption is spontaneous when started with a clean adsorbent. The relationship between  $\Delta G$  and  $\Delta G^\circ$  can be expressed as van't Hoff equation:

**Table 2**

Thermodynamic parameters for  $\text{Cd}^{2+}$  adsorption by CHAp (the first correction,  $m = 0.004$  g).

T (K)	$K_D$ (L/g)	$K^\circ$	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (J/mol)	$\Delta S^\circ$ (J/(mol K))	$R^2$	
						Nonlinear	Linear
298	1.0028	0.1604	4.533	183.13	-14.60	0.9999	0.9635
303	1.0035	0.1606	4.608				
308	1.0044	0.1607	4.681				
313	1.0064	0.1610	4.752				

**Table 3**

Values of the adsorbent mass (m) in different sections described by Ofudje et al.

Description source	m (g)
Section 2.3.1. Equilibrium study	0.004
Section 3.2. Equilibrium studies	0.01–0.06

**Table 4**

Thermodynamic parameters for Cd<sup>2+</sup> adsorption by CHAp (the second correction, m = 0.04 g).

T (K)	K <sub>D</sub> (L/g)	K <sup>o</sup>	ΔG <sup>o</sup> (kJ/mol)	ΔH <sup>o</sup> (J/mol)	ΔS <sup>o</sup> (J/(mol K))	R <sup>2</sup>	
						Nonlinear	Linear
298	1.0028	1.604	−1.171	183.13	4.543	0.9999	0.9635
303	1.0035	1.606	−1.193				
308	1.0044	1.607	−1.215				
313	1.0064	1.610	−1.240				
318	1.0072	1.611	−1.262				

$$\Delta G = \Delta G^o + RT \ln Q \quad (12)$$

where  $Q$  is the adsorption quotient, standing for the ratio of [Adsorbed solute]<sub>s</sub> to [Free solute]<sub>aq</sub> at any time. It is no doubt that  $\Delta G$  can be used to judge the adsorption direction. When the adsorption reaches equilibrium,  $\Delta G$  is zero. In this case,  $Q$  (the adsorption quotient) is calculated by the data at equilibrium, then Eq. (12) becomes

$$\Delta G^o = -RT \ln K^o \quad (13)$$

Substituting Eq. (13) into Eq. (12), we have

$$\Delta G = RT \ln \frac{Q}{K^o} \quad (14)$$

If the initial state of an adsorption process is represented by  $Q$ , and the equilibrium state is represented by  $K^o$ , the adsorption direction can be determined by the ratio between them [24]:

$Q/K^o < 1$ ,  $\Delta G < 0$ , the adsorption is spontaneous;

$Q/K^o = 1$ ,  $\Delta G = 0$ , the adsorption is at equilibrium;

$Q/K^o > 1$ ,  $\Delta G > 0$ , the adsorption is non-spontaneous.

Although  $\Delta G$  can accurately predict the direction of adsorption reaction, it is difficult to be obtained at any state during adsorption, resulting in the lack of practicality of this method. Conversely,  $\Delta G^o$  is easily calculated by using  $K^o$ . However, the problem is whether  $\Delta G^o$  can be used to determine the spontaneity of adsorption. Salvestrini and Bollinger [11] pointed out that  $\Delta G^o$  can be less than zero or greater than zero for a spontaneous process ( $\Delta G < 0$ ). The previous experience is that if the absolute value of  $\Delta G^o$  is very large, the sign of  $\Delta G$  is basically determined by  $\Delta G^o$ . Masterton et al. [25] pointed out that if  $\Delta G^o$  is a large negative number, such as  $-40 \text{ kJ mol}^{-1}$ ,  $K^o$  will be much greater than one and the forward reaction will go virtually to completion under universal conditions. Conversely, if  $\Delta G^o$  is a large positive number, such as  $+40 \text{ kJ mol}^{-1}$ ,  $K^o$  will be a small fraction and the reverse reaction will go nearly to completion. In the range  $-40$  and  $+40 \text{ kJ mol}^{-1}$ , the value of  $K^o$  will be such that there will be appreciable amounts of both products and reactants at equilibrium. The above analysis shows that  $\Delta G^o > 0$  does not mean that the adsorption reaction is non-spontaneous.

## 4.2. Factors affecting the sign of $\Delta G^o$

### 4.2.1. The ratio of solute to adsorbent

For a liquid-solid adsorption process (Eq. (15)), if the solution is very dilute, the standard equilibrium constant can be expressed as Eq. (16) [26]:

$$\text{Solute}_{(aq)} + \text{Adsorbent}_{(s)} \xrightleftharpoons[\text{desorption}]{\text{adsorption}} \text{Solute-Adsorbent}_{(s)} \quad (15)$$

$$K^o = \frac{[\text{Adsorbed solute}]_s}{[\text{Free solute}]_{aq}} \quad (16)$$

where [Adsorbed solute]<sub>s</sub> is adsorption amount of solute on the surface of adsorbent (mol/L, it is equivalent  $C_s$  in Eq. (6)), [Free solute]<sub>aq</sub> is the solute concentration at equilibrium (mol/L, it is equivalent  $C_e$  in Eq. (6)).

The normal ratio of solute to adsorbent is that most of solute can be adsorbed by adsorbent, thus the adsorption goes smoothly and  $K^o$  will be greater than 1, resulting a negative value of  $\Delta G^o$ . However, if the adsorption ratio is set improperly, for example, the initial concentration of solute is much higher than the concentration of adsorbed solute,  $K^o$  is much less than 1, resulting a positive value of

$\Delta G^\circ$ . In addition, a very small difference in  $K^\circ$  can have a large influence on the estimation of  $\Delta G^\circ$  due to the logarithmic function, especially  $K^\circ$  is around 1, so the approximation of the quantities used by the Ofudje et al. (2023) might be a root for the observed differences as well.

#### 4.2.2. The changes of $\Delta H^\circ$ during adsorption process

The effects of changes of enthalpy and entropy on  $\Delta G^\circ$  is described by the Gibbs-Helmholtz equation Eq.(17).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (17)$$

It can be seen from Eq. (17) that exothermic adsorptions ( $\Delta H^\circ < 0$ ) tend to be spontaneous inasmuch as they contribute to a negative value of  $\Delta G^\circ$ . On molecular level, this means that there will be a tendency to form strong bonds at the expense of weak ones. If the entropy change is positive ( $\Delta S^\circ > 0$ ), the term  $-T\Delta S^\circ$  will make a negative contribution to  $\Delta G^\circ$ . Hence there will be a tendency for an adsorption to be spontaneous if the products are less ordered than the reactants.

For an enthalpy-driven adsorption ( $\Delta H^\circ < 0$ ,  $\Delta S^\circ < 0$ ), the sign of  $\Delta G^\circ$  may change during the adsorption process. Previous studies have reported that the heat of adsorption as indication of the value of entropy ( $\Delta H^\circ$ ) decreases at high loadings or loadings close to the saturation, the change of entropy ( $\Delta S^\circ$ ) is small, so it is not expected that the term  $-T\Delta S^\circ$  varies significantly or has a large influence. Therefore,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  can become positive due to the decrease of  $\Delta H^\circ$  value. Nevertheless, the negative value of enthalpy still makes things easier for the molecules to be adsorbed instead of the effect of outer stimuli (catalysis, electric/magnetic field, etc.). This means that adsorption can also be spontaneous in the case of positive  $\Delta G^\circ$ , which agrees with views of Masternton et al. [25].

## 5. Conclusions

Ofudje et al. found that the apatite synthesized by chemical method (CHAp) has excellent adsorption properties for cadmium ions, which is an important contribution to the remediation of cadmium pollution. However, the method of thermodynamic calculation needs to be modified. Accurate calculations and precise results are very important for the dissemination of scientific knowledge. Once an error is made, subsequent references will accelerate the negative impact. The present discussion has two contributions, one is to provide a correct method for calculating thermodynamics from the partition coefficient, and the other is to discuss the feasibility of using standard free energy to determine the spontaneity of adsorption, which can improve reader's judgment and understanding of adsorption spontaneity.

## Funding statement

The research is funded by the National Natural Science Foundation of China (No. 31971551), the project for Local Science and Technology Development Guided by the Central Government in Shanxi Province, China (YDZJSX2022A055), the Graduate Education Innovation Project of Shanxi Normal University, Shanxi Province, China (2022XSY006) and the Graduate Education Innovation Project of Shanxi Province, China (2022Y485).

## Data availability statement

Data are contained within the article.

## CRediT authorship contribution statement

**Xueyong Zhou:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Xin Yu:** Validation, Methodology, Investigation, Formal analysis, Data curation. **Rehanguli Maimaitiniyazi:** Validation, Methodology, Investigation, Formal analysis, Data curation. **Xiaoying Zhang:** Validation, Software, Methodology, Formal analysis, Data curation. **Qianwen Qu:** Visualization, Validation, Investigation, Data curation.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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