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Kinetics of uptake of Fe(II) from aqueous solutions by Co/Mo layered double hydroxide (Part 2)

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ABSTRACT

The kinetics of the Fe(II) uptake by Co/Mo layered double hydroxide (Co/Mo-LDH) intercalated with carbonate $(CO_3)^{2-}$ as an interlayer anion was studied. The results revealed that the maximum adsorption capacities were 29.5, 59.1, and 77.9 mg/g when the initial ferrous ion concentration was 25 mg/l at 298, 308, and 318 K, respectively. These results displayed a high efficiency of the Fe(II) uptake from aqueous solution at higher temperature. The adsorption isotherms were seen to be consistent with Langmuir's adsorption isotherm. The equilibrium adsorption contact time was determined for Co/Mo-LDH. This suggested that the pseudo-first-order equation might not be sufficient to depict the kinetics of Fe(II) onto the Co/Mo-LDH, and the kinetics of adsorption of Fe(II) onto Co/Mo-LDH were best described by the pseudo-second-order model. Also, the paper discussed the thermodynamic parameters of the adsorption (Gibbs free energy, entropy, and enthalpy). Our results demonstrated that the adsorption process was spontaneous and endothermic. The synthesized Co/Mo-LDH product could act as a highly-effective nano-adsorbent of Fe(II) removal from the aqueous solutions.

Keywords: Water treatment; Co/Mo layered double hydroxide; Fe(II) adsorption; Kinetics

1. Introduction

It is well known that the heavy metals produced and released during domestic, agricultural, and industries activities create a serious hazard to the environment [1]. The presence of the heavy metals in the environment can be harmful to a variety of living species. Therefore, the removal of these heavy metals from the environment is very important to protect the public health [2]. The term heavy metal refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration [3]. When iron is present as Fe(II) soluble form in the drinking water supplies, there are many objectionable problems related to its presence. The presence of iron has been giving rise to serious problem for regularity

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authorities related to the industrial and main water supplies for a long time [4]. The European Union has recommended the level of 0.2 mg/l for iron [5], while the environmental protection agency has established secondary standards of 0.3 mg/l for iron [6].

The removal of iron in ground and seawater desalination plants is the key step in designing the plants to avoid RO membrane fouling and scaling which are the most serious problems in membrane processes [7,8]. Heavy metals in solution can be removed using several techniques such as precipitation [9], coagulation, chemical precipitation, adsorption [10], ozonation, membrane filtration, and reverse osmosis [11]. Recently, the adsorption technique is widely used due to its simplicity, potential to regeneration, and sludge-free operation [12]. Moreover, it could be an attractive technique if the used adsorbent could be synthesized cheaply and readily. The efficiency of adsorption depends on many factors, including the surface area, pore size distribution, polarity, and functional groups of the adsorbent [13]. Recently, nano-adsorbents are quite efficient for the fast adsorption of heavy-metal ions and organic molecules from aqueous solutions due to their high specific surface areas and absence of internal diffusion resistances [14].

The layered double hydroxide (LDH), also known as hydrotalcite (HT) is a class of anionic clay with high anion exchange capacities and an effective adsorbent for removal of a variety of pollutants. LDH have positively charged layers of metal hydroxides and the anions and water molecules are located between the layers. The positive charges that are produced from the isomorphous substitution of divalent cations and trivalent cations are counter balanced by anions located between the layers [15].

The purification of water by LDH is well understood and mainly progressed to improve their efficiency, specificity, and applications [16]. Different types of LDHs samples have been synthesized with carbonate as an interlayer anion such as MgAl, ZnAl, and MgAlFe LDHs samples following a standard co-precipitation method from the metal chlorides and have been evaluated in the adsorptive removal of Cr (VI) from aqueous solutions [17]. A ferrous ion concentration 170 mg/l has been removed from aqueous solution of 200 mg/l initial concentration using a synthesized zaccagnaite (LDH) as a good adsorbent for the removal of Cu^{2+}, Fe^{2+}, and Mn^{2+} [4].

The goals of this work are synthesis of Co/Mo (CO_3^{2-})-LDH nanoparticles and applying them for the Fe(II) removal from aqueous solutions, and determination of the adsorption rate and capacity. Finally studying the kinetics and thermodynamics parameters of the uptake process.

2. Materials and methods

2.1. Materials

All chemicals with a purity greater than 99.9% were purchased as follows: ferrous sulfate ($FeSO_4{\cdot}7H_2O$) was purchased from Loba Chemie Co., anhydrous ($MoCl_5$), $CoCl_2{\cdot}6H_2O$, and ammonium carbonate $(NH_4)_2CO_3$ were purchased from Sigma-Aldrich (Germany), and NH_4OH (34%) was purchased from Merck Germany.

2.2. Preparation of Co/Mo-LDH

Adjustable co-precipitation method was performed for the preparation of Co/Mo$(CO_3)^{2-}$-LDH by the same approach used in our previous study [18].

2.3. Adsorption experiments and methodology

From the experimental studies, the ferrous, Fe(II), stock solution concentration of 100 mg/l was prepared by dissolving ferrous sulfate in distilled water. The Fe(II) solution concentrations 8, 10, 15, 20, and 25 mg/l for all experiments was prepared from the stock solution. The standard acid (0.01 M HNO_3) and alkaline solutions (0.125 M NaOH) were used for pH adjustment at pH 5. The pH value of the solution was measured with a pH meter (Mettler-Toledo AG 8603 Schwerzenbach, made by Mettler-Toledo Group). The pH meter was calibrated with buffers of pH 4 and 7 before any measurement.

The removal of ferrous ions from dilute aqueous solutions by adding the adsorbent dosage 0.02 g/l was carried out at different temperatures, 298, 308, and 318 K. After continuous stirring with a magnetic stirrer at 160 rpm for a predetermined time interval (5, 10, 15, 20, 30, 45, and 60 min), the solid and solution were separated by centrifugation at 3,000 rpm for 15 min and then slightly dried at ambient temperature. The Fe(II) concentrations were determined by Spectrophotometer, LaMotte, model SMART Spectro, USA and the solid phase was analyzed. The contact time allows the dispersion of adsorbent and metal ions to reach the equilibrium conditions.

The amount of adsorption capacity q_e (mg/g) was calculated by the following equation [19]:

$$q_e = (C_0 - C_e) \times V/m \tag{1}$$

where C_0 and C_e are the initial Fe(II) concentration and the concentration at equilibrium in mg/l, m is the mass of adsorbent, and V is the volume of solution.

Two adsorption isotherm models have been used to analyze the adsorption data by two equation [20]:

(i) Langmuir

$$C_e/q_e = 1/K_{\mathrm{L}}b + C_e/b \tag{2}$$

where K_{L} (l/mg) and b (mg/g) are the Langmuir constants related to the sorption capacity and the adsorption energy, respectively. While, q_e (mg/g) is the equilibrium adsorption capacity and C_e (mg/l) is the equilibrium concentration.

For a Langmuir type adsorption process, a dimensionless separation factor [21] is defined by:

$$R_L = 1/(1 + k_L C_0) \tag{3}$$

If $R_L > 1$, the isotherm is unfavorable; when $R_L = 1$, the isotherm is linear; in the range $0 < R_L < 1$, the isotherm is favorable, and when $R_L = 0$, the isotherm is irreversible.

(ii) Freundlich

$$\log q_e = \log K_F + 1/n \log C_e \tag{4}$$

while, K_F (l/mg) is the Freundlich constant and n is the heterogeneity factor which represent sorption capacity and sorption intensity, respectively.

The Adsorption kinetics is used to explain the adsorption mechanism and the adsorption characteristics of Co/Mo-LDH. The pseudo-first-order and pseudo-second-order kinetics equations [22,23] in linear forms are expressed as:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \tag{5}$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{6}$$

where q_t and q_e are the amounts of Fe(II) adsorbed at time t and equilibrium e, respectively; k_1 and k_2 are the pseudo-first-order and pseudo-second-order rate constants, respectively, for the adsorption processes.

The thermodynamic parameters provide in-depth information on inherent energetic changes including Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) for the adsorption process which were obtained by the following equations [24,25]:

$$\Delta G^\circ = -RT \ln b \tag{7}$$

$$\ln b = \Delta S^\circ/R - \Delta H^\circ/RT \tag{8}$$

where R is the ideal gas constant (kJ mol^{-1} K^{-1}), T is the temperature (K), and b is a Langmuir constant related to the adsorption energy (from the Langmuir isotherm).

3. Results and discussion

3.1. Effect of initial Fe(II) concentration and adsorption isotherm

The effect of different Fe(II) concentrations was determined after the experimental studies for all metal concentrations. A definite dosage of Co/Mo-LDH adsorbent (0.02 g/l) was added to a series of 100 ml ferrous solutions with different initial concentrations of 8, 10, 15, 20, and 25 mg/l at pH 5. Then these solutions were stirred at 160 rpm for a contact time of 60 min to reach the equilibrium. Fig. 1 indicates that the Co/Mo-LDH apparently removed a considerable amount of ferrous from the aqueous solutions at different temperatures. The adsorption efficiency increased to a certain level and the saturation takes place at a certain concentration. This saturation resulted when no more metal ions could be adsorbed on the surface of Co/Mo-LDH. The experimental studies also showed that the high efficiency for ferrous adsorption could be obtained over a relatively short period of time up to 60 min. However, the higher adsorption capacities of ferrous were observed at the higher initial concentration (25 mg/l). Also the adsorption capacities increased with increasing the temperatures in the order 77.9 mg/g at 318 K >59.1 mg/g at 308 K, and >29.5 mg/g at 298 K.

The adsorption isotherm models are usually used to describe the interaction between the adsorbent and

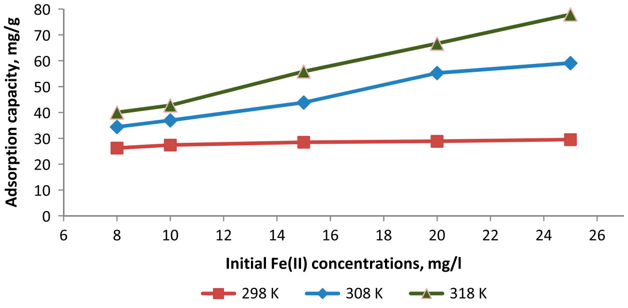

Fig. 1. Effect of Fe(II) initial concentration on adsorption capacity of Co/Mo-LDH at different temperatures (adsorbent dosage [0.02 g/l], pH 5.0, stirring [160 rpm], and contact time [60 min]).

the adsorbate when the adsorption process reaches equilibrium. These models afford the most important parameters for designing a desired adsorption system. The equilibrium data were analyzed using the Langmuir and Freundlich equilibrium models in order to obtain the best fitting isotherm (Eqs. (2) and (4)). The Langmuir model assumes that the adsorption occurs on a homogeneous surface by monolayer coverage with uniform binding sites, equivalent sorption energies, and no interactions between adsorbed species. While, the Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces and adsorption capacity is related to the concentration of the adsorbate at equilibrium.

According to Fig. 2(a), a straight line was obtained and the k_L and b values (sorption capacity and energy of adsorption, respectively) could be obtained by the slope and intercept of the line, Table 1. While from Fig. 2(b), K_F and n are the Freundlich constants, which represent sorption capacity and sorption intensity, respectively. Also they could be evaluated from the intercept and slope of the linear plot of $\log q_e$ vs. $\log C_e$ as given in Table 1. The isotherm study of Fe(II) removal was studied using different initial concentrations ranged from 8.0 to 25.0 mg/l at different temperatures of 298, 308, and 318 K, pH of 5, 0.02 g dosage of Co/Mo-LDH and after 60 min. Table 2 summarizes the Langmuir and Freundlich constants and the calculated correlation coefficients. The results showed that the linear correlation coefficients for Langmuir and Freundlich models were obtained. The higher regression coefficient R^2 for Langmuir model indicated that the Langmuir model fitted the experimental data better than the Freundlich one, which confirms the uniformity of the binding energy on the whole surface of Co/Mo-LDH. In other words, this phenomenon also shows that chemosorption is the principal uptake mechanism in adsorption process [26]. The R_L (Eq. (3)) is equal to the ratio of the unused adsorbent capacity to the maximum adsorbent capacity and thus it can be used as a measurement of the adsorbent capacity and the affinity between the adsorbate and adsorbent. The dimensionless parameter, R_L, which is a measure of adsorption favorability was 0.0013–0.0042 (i.e. $0 < R_L < 1$) suggesting that the adsorption of Fe(II) on Co/Mo-LDH is favorable, as observed experimentally.

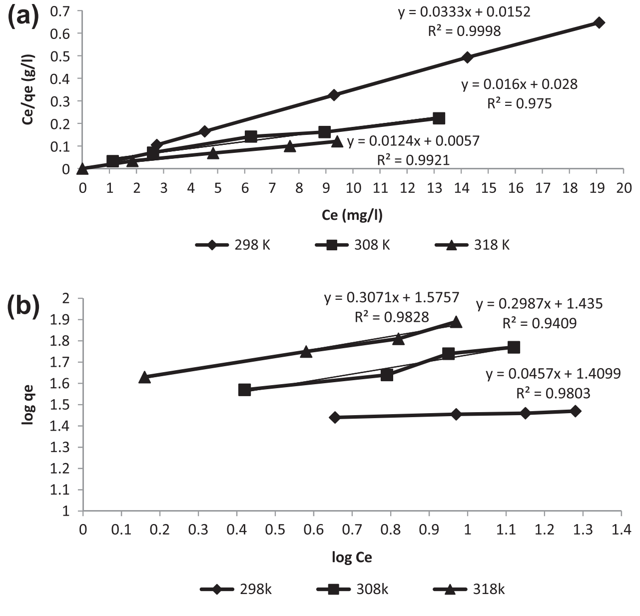

Fig. 2. Adsorption isotherm models: (a) Langmuir and (b) Freundlich for the removal of Fe(II) by Co/Mo-LDH at different temperatures (adsorbent dosage [0.02 g/l], pH 5.0, stirring [160 rpm], and contact time [60 min]).

3.2. Ferrous adsorption kinetics and adsorption mechanism

The better understanding of the mechanism of ferrous adsorption was illustrated by adsorption kinetics. Fig. 3 shows that the effect of contact time on the adsorption capacity of Fe(II) 8.0 mg/l initial concentration onto 0.02 g/l Co/Mo-LDH at pH 5, stirring at 160 rpm and at 298, 308, and 318 K. It can be shown that the adsorption rate was considerably fast within the first 20 min (22.4, 25.4, and 31.2 mg of Fe(II) at 298, 308, and 318 K, respectively, adsorbed per gram of Co/Mo-LDH), then gradually slowed down and thereafter, the adsorption equilibrium reached the maximum values at 60 min (26.25, 34.4, and 40 mg/g. The fast Fe(II) removal rate in the beginning may be attributed to the rapid diffusion of Fe(II) from the solution to the external surfaces of Co/Mo-LDH. On the other hand, the slow adsorption process is attributed to the longer diffusion range of Fe(II) into the inner-sphere of Co/Mo-LDH or the ion-exchange in the inner surface of Co/Mo-LDH. Such slow diffusion will lead to a slow increase in the adsorption curve at later stages [27]. Moreover, the initial rapid adsorption may be because of an increased number of available sites at the initial stage.

To evaluate the adsorption kinetics of Fe(II) ions on Co/Mo-LDH, the pseudo-first-order and pseudo-second-order models (Eqs. (5) and (6)) were applied to analyze the experimental data. In this study, as illustrated in Fig. 4, the slope and intercept of the plot of log $(q_e{-}q_t)$ vs. t were used to determine the first-order rate constant k_1 and equilibrium adsorption density q_e at different initial concentrations of Fe(II). On the other hand, the kinetic parameters for the pseudo-second-order model (rate constant k_2 and

Table 1
Isotherm parameters for ferrous adsorption onto Co/Mo-LDH at different temps (adsorbent dosage [0.02 g/l], pH 5.0, stirring [160 rpm], and contact time [60 min])

	Langmuir isotherm model			Freundlich isotherm model		
T (k)	k_L (l/mg)	b (mg/g)	R^2	K_F (mg/g)	n	R^2
298	30.3	2.20	0.999	25.64	22.2	0.980
308	62.5	0.57	0.975	27.22	3.36	0.940
318	83.3	2.40	0.992	37.58	3.26	0.982

Table 2
Kinetic parameters of the pseudo-first- and second-order models for the adsorption of Fe(II) on Co/Mo-LDH at 298 K (adsorbent dosage [0.02 g/l], pH 5.0, stirring [160 rpm], and contact time [60 min])

Pseudo first-order kinetic model			Pseudo second-order kinetic model		
k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g mg^{-1} L min^{-1})	q_e (mg/g)	R^2
0.029	7.37	0.971	0.0091	11.36	0.997

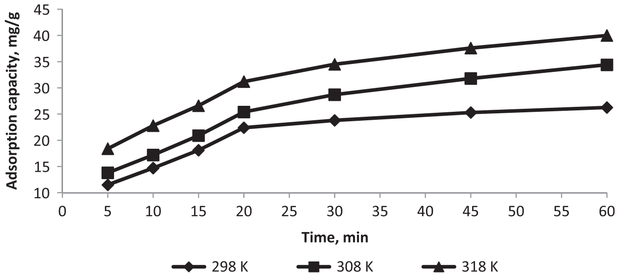

Fig. 3. Effect of contact time on the adsorption capacity of Fe(II) onto Co/Mo-LDH at different temperatures (initial concentration 8.0 mg/l, adsorbent dosage [0.02 g/l], pH 5.0, stirring [160 rpm], and contact time [60 min]).

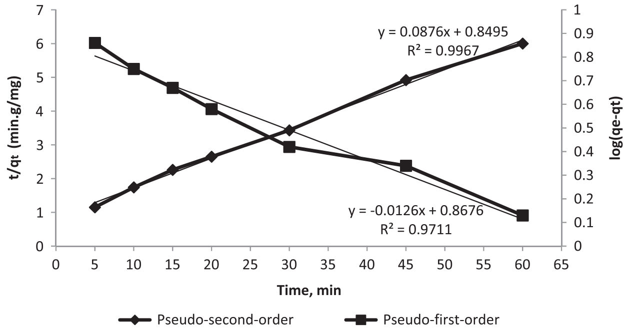

Fig. 4. Adsorption kinetics of the pseudo-first-order and pseudo-second-order models for the adsorption of Fe(II) on Co/Mo–LDH at 298 K (adsorbent dosage [0.02 g/l], pH 5.0, stirring [160 rpm], and contact time [60 min]).

equilibrium adsorption density q_e) were determined from the linear plot of t/q_t against t, Table 2. The correlation coefficients for the pseudo-first- and second-order models were $R^2 = 0.971$ and 0.997, respectively. This suggested that the pseudo-first-order equation might not be sufficient to depict the kinetics of Fe(II) onto the Co/Mo-LDH, and the kinetics of adsorption of Fe(II) onto Co/Mo-LDH were best described by the pseudo-second-order model. When the pseudo-second-order model considers the rate-limiting step by the formation of chemisorptive bond involving sharing or exchange of electrons between adsorbate and the adsorbent [28], the above results obtained consistently suggested that the rate-determining step may be chemical adsorption and the adsorption behavior may involve the valence forces through sharing electrons between the ferrous (II) ions and adsorbents [29,30]. Hence, the higher adsorption capacity of the Co/Mo-LDH was explained by the formation of 4^+ surface

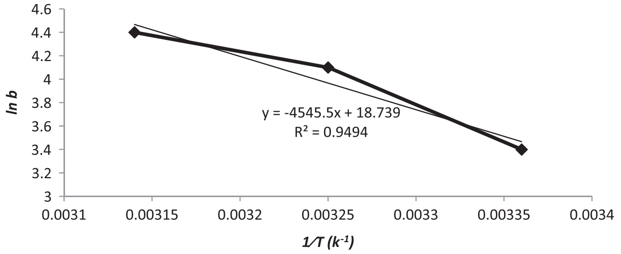

Fig. 5. Plot of the Langmuir isotherm constant (ln b) vs. temperature ($1/T$) (The thermodynamic parameters in Table 3 are determined from this graph).

Table 3
Thermodynamic constants for the adsorption of Fe(II) onto Co/Mo-LDH at various temps (adsorbent dosage [0.02 g/l], pH 5.0, stirring [160 rpm], and contact time [60 min])

T (k)	ln b	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	R (kJ mol^{-1} K^{-1})	R^2
298	3.4	−8.424	37.79	0.156	8.3×10^{-3}	0.949
308	4.1	−10.499				
318	4.4	−11.624				

charges between the bivalent and hexavalent cations (Co^{2+} and Mo^{6+}) which means formation of a highly energetic surface layers as detected by XPS [18].

3.3. Effect of temperature and adsorption thermodynamics

It is well known that the temperature is an important factor in the adsorption process which determines the nature of the adsorption with the calculation of the thermodynamic parameters. The adsorption capacity of Fe(II) onto Co/Mo-LDH as a function of initial Fe(II) concentration and contact time at different temperatures are shown in Figs. 1 and 3. The experiments were carried out at 298, 308, and 318 K. The adsorption capacity of ferrous for Co/Mo-LDH increased with the increase in the temperature, which indicated that the interaction between adsorbent and adsorbate is endothermic process. The negative values for the Gibbs free energy (Eq. 7) for Fe(II) showed that the adsorption process is spontaneous and the degree of spontaneity of the reaction increased with the increase in the temperature and the value of ΔG° became more negative indicating that higher temperature facilitated the adsorption of Fe (II) on Co/Mo-LDH due to a greater driving force of adsorption. Eq. 8 represented the enthalpy (ΔH°) and the entropy (ΔS°) changes that were calculated from a plot of ln b (from the Langmuir isotherm) vs. $1/T$, Fig. 5. The results of these thermodynamic calculations are shown in Table 3. The positive value of ΔH° suggested that the interaction of Fe(II) adsorbed by Co/Mo-LDH was endothermic process. Table 3 also shows that the ΔS° value was positive which revealed the increased randomness at the solid–solution interface during the process of adsorption [31–33].

4. Conclusions

This paper presented the detailed results of the adsorption process for Fe(II) removal from aqueous solution using Co/Mo-LDH. The experimental data well fitted to Langmuir equation confirming the monolayer coverage of ferrous solution onto LDH adsorbent. The main mechanism controlling the adsorption of Fe(II) onto $Co/Mo(CO_3)^{2-}$-LDH could be occurred by the ion exchange with carbonate. Kinetically, the adsorption process followed the pseudo-second-order mechanism that considered the rate-limiting step by the formation of chemisorptive bond involving sharing or exchange of electrons between the ferrous (II) ions and Co/Mo-LDH. The thermodynamic parameters of this paper discussed the Gibbs free energy, entropy, and enthalpy, which demonstrated that the adsorption process was spontaneous and endothermic. The synthesized Co/Mo-LDH product could act as a highly-effective nano-adsorbent in Fe(II) removal from aqueous solutions by the formation of 4^+ surface charges between Co^{2+} and Mo^{6+} which means the formation of a highly energetic surface layers.

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Symbols

q_t — amount of adsorption capacity q_t, mg/g
C_0 — initial concentration, mg/l
C_t — concentration at time t, mg/l
m — mass of the adsorbent, g
v — volume of solution, l
C_e — equilibrium adsorption concentration, mg/l
q_e — equilibrium adsorption capacity, mg/g
K_L — Langmuir constant related to the sorption capacity, l/mg
b — Langmuir constant related to the energy of adsorption, mg/g
K_F — Freundlich constant related to sorption capacity, l/mg
n — heterogeneity factor related to sorption intensity
k_1 — pseudo-first-order rate constant for the adsorption process
k_2 — pseudo-second-order rate constant for the adsorption process

ΔG° — Gibbs free energy for the adsorption process, kJ mol^{-1}
ΔH° — enthalpy change for the adsorption process, kJ mol^{-1}
ΔS° — entropy change for the adsorption process, kJ mol^{-1} K^{-1}
R — ideal gas constant, kJ mol^{-1} K^{-1}
T — temperature, K

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