

Comparative Kinetics of Iron Ore Dissolution in Aqueous HCl-HNO₃ System

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ABSTRACT

The dissolution kinetics of the dissolution of iron ore in aqueous HCl/HNO₃ solution was studied. The elemental composition of the ore was carried out using the inductively coupled plasma-optical emission spectrophotometer (ICP-OES). The result showed that the iron ore contain; Fe (62.1%), O (21.7%), Cu (11.1%), Mg (2.39%), Na (1.51%), Mn (1.47%), K (0.78%), Ca (0.58%) and Zn (0.01%). It was determined that the dissolution rate increased with increased solution concentration, temperature, time and decreased particle size of the ore. The optimum conditions for effective dissolution of 88% of the iron ore were found to be 8 M of the solution, 353 K, 100 min and ore particle size of less than 75 μm. The kinetic evaluation of the dissolution process was studied using three different shrinking core models (SCM); Film diffusion: $k_f t = X_B$; interfacial chemical reaction $k_i t = 1 - (1 - X_B)^{1/3}$ and ash/product layer diffusion: $k_d t = 1 - \frac{2X_B}{3} - (1 - X_B)^{2/3}$ for spherical materials was performed. The results obtained showed that the rate determining step for the dissolution process was the product layer diffusion and therefore, the reaction followed this mechanism. The apparent activation energy (E_a) and the order of reaction were found to be 20.48 kJ/mol and 0.7 respectively.

Keywords: Kinetics; Dissolution; Iron Ore; Shrinkage Core Model

1. Introduction

Dissolution processes have been extensively utilized to separate valuable minerals from their ores. Several researches [1-5] have been carried out on either the dissolution or both the dissolution and kinetic study of iron ore in different reagents such as HCl, H₂SO₄, oxalic acid et cetera. It was observed that the dissolution of iron ore or even the extraction of iron from an ore containing it increases as the concentration, temperature, time and stirring speed increases but decreases as the particle size increases due to its decreasing surface area [3-5]. Baba *et al.* [1,2] observed that iron ore dissolves easily and more efficiently in HCl than in H₂SO₄ or HNO₃ and it was believed to be as a result of ferric-chloride complexes formation. It therefore required less energy for the reaction to occur comparing the activation energies of 13.63 kJ/mol in HCl and 38.29 kJ/mol in H₂SO₄ respectively. The kinetic study of these dissolutions reaction processes

were carried out using the shrinking core models to interpret the processes involved in either the leaching or dissolution [1,3,4,6]. During the leaching process, three major steps occur; diffusion or mass transfer through the liquid film surrounding a solid particle, chemical reaction on the surface of the un-reacted core, and diffusion through the ash/inert solid layer. The slowest between these steps is considered the rate determining step. The model first developed by Yagi and Kunii [6-8] helped to derive the rate determining step from the experimental data using the equations below:

$$X = 3K_f M_s C_{At} / a \rho_s r_0 = k_f t \quad (1)$$

$$1 - \frac{2X_B}{3} - (1 - X_B)^{2/3} = 2M_s D C_{At} / a \rho_s r_0^2 = k_d t \quad (2)$$

$$1 - (1 - X_B)^{1/3} = K_r M_s C_{At} / a \rho_s r_0 = k_r t \quad (3)$$

where K_f , K_d , and K_r are the rate constants for the liquid film diffusion, ash/inert solid layer diffusion, and surface chemical reaction respectively. X_B is the fraction reacted,

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M_S is the molecular weight of the solid, C_A is the concentration of the dissolved lixiviant A in the bulk of the solution, "a" is the stoichiometric coefficient of reagent in the leaching reaction, r_0 is the initial radius of the solid particle, ρ_s is the density of the solid, D is the diffusion coefficient in the porous product layer, K_g is the mass transfer coefficient between fluid and solid particle, "K" is the first-order rate constant for the surface reaction and t is the contact time. This research work is intended to study the dissolution of iron ore in a 3:1 HCl-HNO₃ system (similar to *aqua regia*) which is a well known reagent for dissolving un-reactive metal minerals such as gold, silver, et cetera and also the kinetic evaluation using three different shrinking core models (SCM). So far, there is no data to this effect viz-a-viz the use of Nigerian iron ore is concerned.

2. Materials and Methods

2.1. Materials

Iron ore from the Toto Muro iron ore deposit in Nasarawa State of Nigeria was used for this study. Chemical analysis of the sample ore was done with Leeman Model of Inductively coupled plasma-optical emission spectrophotometer. Different particle sizes (<75 μm , 75 μm , 125 μm and 150 μm) were obtained with the use of 8 inch diameter size mechanical sieve shaker. Distilled water and analytical grade chemicals (BDH) were used as provided to prepare all the solutions.

2.2. Methods

Particle sizes of less than 75 μm sample of the iron ore was used for the experiment at a constant concentration HCl-HNO₃ solution and a fixed temperature of 331 K but at different contact time. 1.0 g of the given particle size sieve sample was weighed and then transferred into a 250 ml beaker containing 15 ml of 8 M HCl and 5 ml of 8 M HNO₃ and made to 100 ml with distilled water. The mixture was agitated manually with a glass stirrer. The mixture was stirred and heated to 331 K for various contact times of 20, 30, 60 and 100 min. At the end of each period, the solution was cooled and filtered into a 100 ml standard flask and analyzed.

The same procedure was also repeated for different acid (HCl-HNO₃) concentrations of 4 M, 2 M and 1 M at 331 K for 20, 30, 60 and 100 min. This same procedure described above was repeated for 343 K and 353 K for 20, 30, 60 and 100 min with 8 M acid concentration. The following particle size fractions were examined 75 μm , 125 μm and 150 μm at a fixed temperature of 353 K for 30 min with 8 M acid concentration. The kinetics of the ore dissolution was also investigated for the effects of temperature, acid concentration, particle size and contact time.

3. Results and Discussion

3.1. Chemical Analysis

The iron ore was analyzed chemically using the inductively coupled plasma-optical emission spectrophotometer and the results are shown in **Table 1**. The primary elements found in the sample included 62.10% Fe, 21.7% O, 11% Cu. Other elements such as Mn, Mg, K, Ca et cetera make up the 5.2% of the sample. From these analytical results, it is concluded that the ore was an iron ore.

3.2. Effect of Acid Concentration

The effect of 3:1 HCl-HNO₃ solution concentration on the dissolution of the iron ore was studied using the following concentrations; 1 M, 2 M, 4 M, and 8 M. **Figure 1** is the graphical presentation of the result. From the figure, it can be seen that the iron dissolution rate increases as the concentration of the HCl-HNO₃ system increases from 1 M to 8 M at the same contact time. The optimum dissolution of 81% iron was achieved at the system concentration of 8 M.

3.3. Effect of Temperature and Time

The effects of temperature and contact time on iron dissolution were studied at varying temperatures (331 K, 343 K and 353 K) and at varying time (20 min, 30 min, 60 min, and 100 min). The results are shown in **Figure 2**. From **Figure 2** it is observed that as the temperature increases, dissolution of the iron increased with tempera-

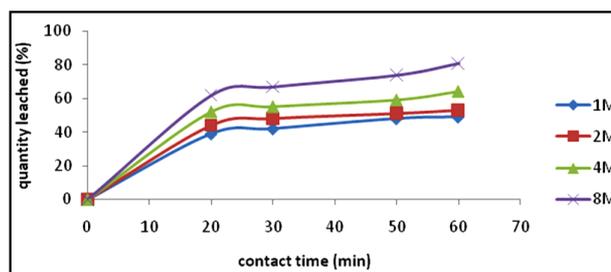


Figure 1. A graph of quantity of iron leached (%) vs contact time (min) with respect to concentration [particle size, <75 μm ; temperature, 351 K; mass of ore, 1 g].

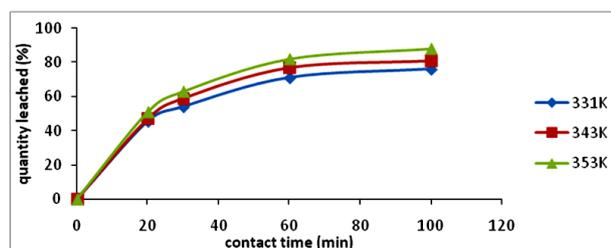


Figure 2. A graph of iron leached (%) vs contact time (min) with respect to temperature [particle size, <75 μm ; conc., 8 M; mass of ore, 1 g].

Table 1. Elemental analysis of the iron ore sample.

Elements	Fe	Cu	Mn	Mg	Ca	Zn	Na	K	O	Others
% composition	62.1	11.1	1.47	2.39	0.38	0.01	1.51	0.78	21.7	2.17

ture and period of contact. When the temperature was increased from 331 K to 343 K at a particular period (20 min) only 2.5% increase in the quantity of iron leached was achieved. At temperature 331 K, there was 8.5% increase in the quantity of iron leached. Optimum temperature and period was found to be 353 K and 100 min respectively in which 88% of the iron was leached.

3.4. Effect of Particle Size

Table 2 shows the experimental data when different particle sizes were investigated at 8 M HCl-HNO₃ solution, temperature of 353 K and contact time of 60 min. Four particle sizes were studied—<75 μm, 75 μm, 125 μm and 150 μm and from the data it was observed that the smallest particle size (<75 μm) gave the highest percentage of iron leached (87%) which is expected due to higher surface area for smaller particle size.

3.5. Kinetic Analysis

The dissolution of the iron ore under study was analyzed using the shrinking core model (SCM) based on the assumption that the material is spherical [3,6,9] and the linearization of a plot of iron dissolved at various temperature and at various contact time was investigated using the three common shrinking core model for spherical material [6]. The Equations (1), (2), and (3) for the models are; $k_f t = X_B$, $k_d t = 1 - 2 \frac{X_B}{3} - (1 - X_B)^{2/3}$,

$k_r t = 1 - (1 - X_B)^{1/3}$ respectively used to test the best fit for the experimental data in which the slowest step is the rate determining step. Where Equations (1)-(3) are film diffusion control mechanism, interfacial chemical reaction control mechanism and ash/product layer diffusion control mechanism respectively with k_f , k_r and k_d as their respective rate constants, t is contact time and X_B is the fraction of iron leached. The activation energy and the order of reaction were also calculated.

3.6. Determination of the Reaction Mechanism

The fraction of iron dissolved (X_B) obtained from the **Figure 2** with respect to the various contact time for various temperature was substituted into Equations (1)-(3) and the results are recorded in **Table 3**. The respective plots of the film diffusion, interfacial chemical reaction and product/ash layer diffusion control mechanisms vs contact time with respect to temperature is given in **Figures 3-5**. **Table 4** give a comparative values of the rate

Table 2. Percentage of iron leached at varying particle sizes. [Temp., 353 K; contact time, 60 min; mass of ore, 1 g].

Particle size (μm)	<75	75	125	150
Percentage iron leached (%)	87	82	62	55

constants k_f , k_r and k_d and their respective regression correlation coefficients (R^2). From the values of the apparent rate constants and their respective R^2 values, it is observed that the experimental data best fit the product/ash layer diffusion control mechanism and therefore is the rate determining step.

3.7. Activation Energy

The relationship between the rate constant k_d and the temperature is given by the Arrhenius equation given by the expression;

$$k_d = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

where A is the frequency factor and E_a is the apparent activation energy.

The rate constants were calculated from **Figure 5** which is the slopes from the graph and are given in **Table 5**. To determine the activation energy for the dissolution of the iron ore in HCl-HNO₃ system, an Arrhenius graph of $\ln k_d$ vs $1/T$ (K^{-1}) was plotted which an Arrhenius plot is obtained and the activation energy also obtained from the slope of the graph (**Figure 6**) using Equation (4) to obtain Equation (5).

$$k_d = \ln A - E_a/RT \quad (5)$$

This is equivalent to $y = mx + c$ and therefore the slope from the graph of $\ln k_d$ vs $1/T$ (K^{-1}) is equivalent to E_a/R , which means $E_a = \text{slope} \times R$.

From **Figure 6** the apparent activation energy was calculated to be 20.46 kJ/mol which is within the range of activation energy for product layer diffusion controlled mechanism.

3.8. Order of Reaction

The results from the effect of acid concentration in **Figure 1**, was applied to Equation (2) which is the product layer diffusion controlled process as was determined to be the mechanism for the reaction and the results are recorded in **Table 6**. They were used in making a plot against time in **Figure 7** to obtain the k_d values.

The k_d values were used to plot a graph of $\ln k_d$ vs $\ln[\text{HCl-HNO}_3]$ as shown in **Figure 8** from which the

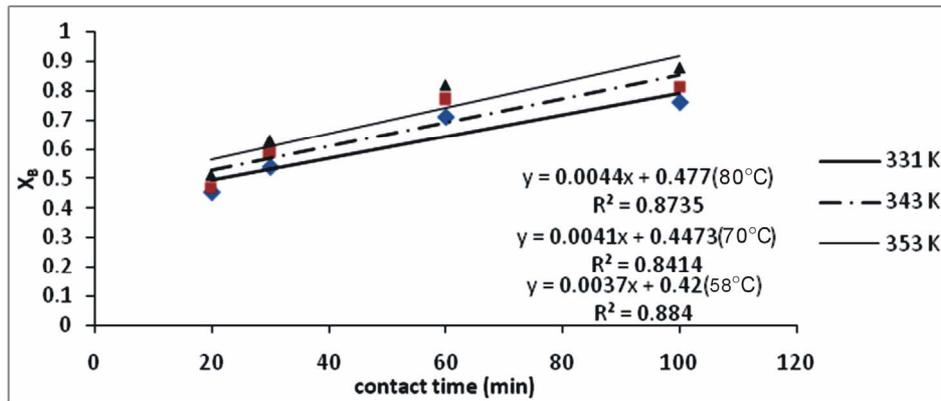


Figure 3. Plot of X_B vs contact time with respect to temperature.

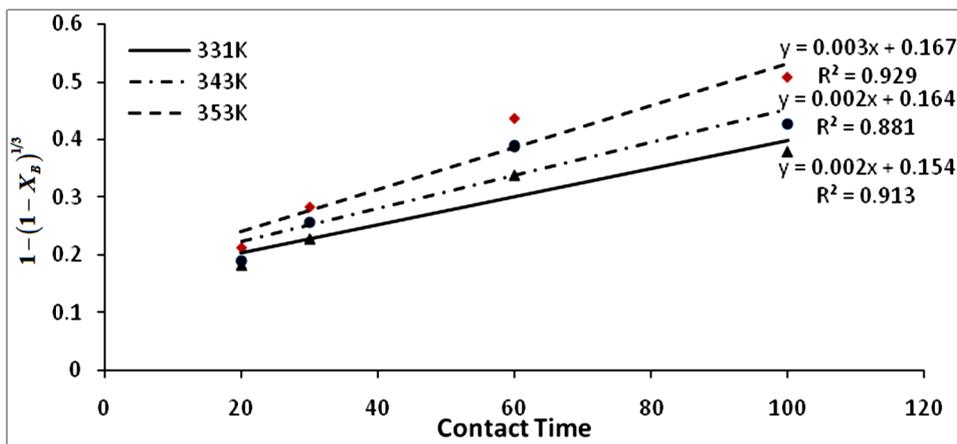


Figure 4. Plot of $1 - (1 - X_B)^{1/3}$ vs contact time (min) with respect to temperature.

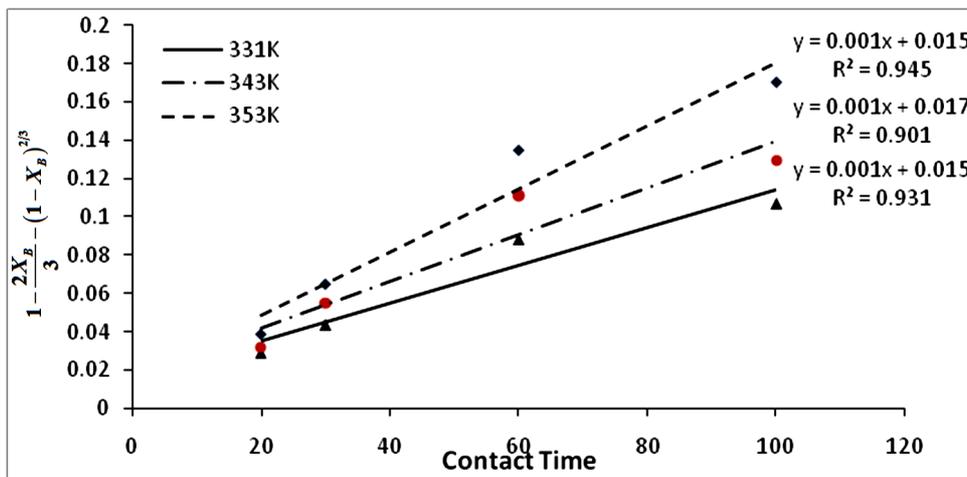


Figure 5. Plot of $1 - \frac{2X_B}{3} - (1 - X_B)^{2/3}$ vs contact time (min) with respect to temperature.

order of reaction was calculated to be the slope of the plot and equal to 0.7. Therefore the order of reaction for the dissolution of the iron ore in HCl-HNO₃ solution is 0.7 indicating a pseudo first order reaction.

4. Conclusion

From the kinetic evaluation for the dissolution of iron ore (obtained from Toto Muro iron ore deposit in Nasarawa

Table 3. Data of three control mechanisms at varying times with respect to temperature.

X_B	$1 - \frac{2X_B}{3} - (1 - X_B)^{2/3}$	$1 - (1 - X_B)^{1/3}$	Time (min)	Temp (K)
0.46	0.03	0.18	20	331
0.47	0.03	0.19	20	343
0.51	0.04	0.21	20	353
0.54	0.04	0.23	30	331
0.59	0.05	0.26	30	343
0.63	0.06	0.28	30	353
0.71	0.09	0.34	60	331
0.77	0.11	0.39	60	343
0.82	0.13	0.44	60	353
0.76	0.11	0.38	100	331
0.81	0.13	0.43	100	343
0.88	0.17	0.51	100	353

Table 4. Apparent rate constants k_f , k_r , and k_d and their respective correlation coefficient, R^2 values at various temperature.

Temperature (K)	Apparent rate constants (min^{-1})			Correlation coefficient (R^2)		
	k_f	k_r	k_d	k_f	k_r	k_d
331	0.0038	0.0024	0.0010	0.8840	0.9131	0.9313
343	0.0041	0.0029	0.0012	0.8414	0.8818	0.9018
353	0.0044	0.0036	0.0016	0.8735	0.9293	0.9450

Table 5. Rates constant values k_d for the dissolution of the iron ore in HCl/HNO₃ at various temperature.

K	$\ln k_d$	T (K)	$1/T (\text{K}^{-1})$
0.001	-6.90776	331	0.003021
0.0012	-6.72543	343	0.002915
0.0016	-6.43775	353	0.002833

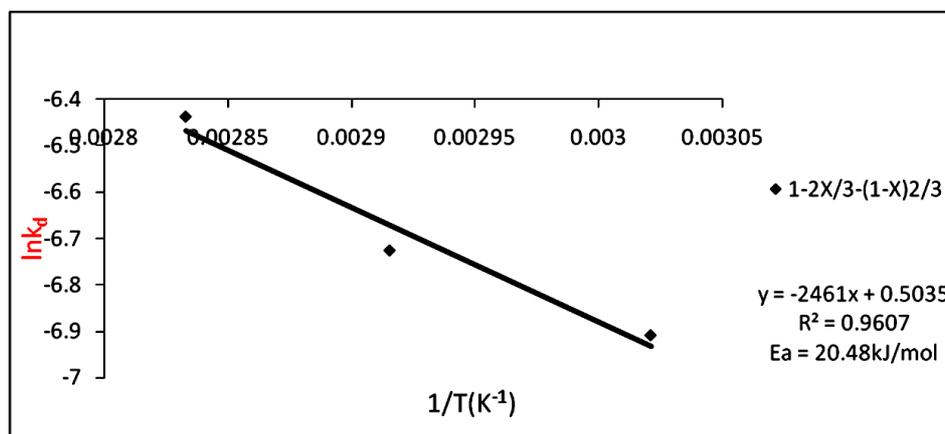
**Figure 6. Arrhenius plot of $\ln k_d$ vs $1/T (\text{K}^{-1})$ for product layer diffusion controlled mechanism.**

Table 6. Product layer diffusion control mechanism at various concentrations.

Time (min)	Concentration (M)	Quantity leached (%)	X_B	$1 - \frac{2X_B}{3} - (1 - X_B)^{2/3}$
20	1	39	0.39	0.020739
30	1	42	0.42	0.024519
50	1	48	0.48	0.033351
60	1	49	0.49	0.035001
20	2	44	0.44	0.027267
30	2	48	0.48	0.033351
50	2	51	0.51	0.038467
60	2	53	0.53	0.042164
20	4	52	0.52	0.040286
30	4	55	0.55	0.046103
50	4	59	0.59	0.054772
60	4	64	0.64	0.067274
20	8	62	0.62	0.062034
30	8	67	0.67	0.075794
50	8	74	0.74	0.099303
60	8	81	0.81	0.129502

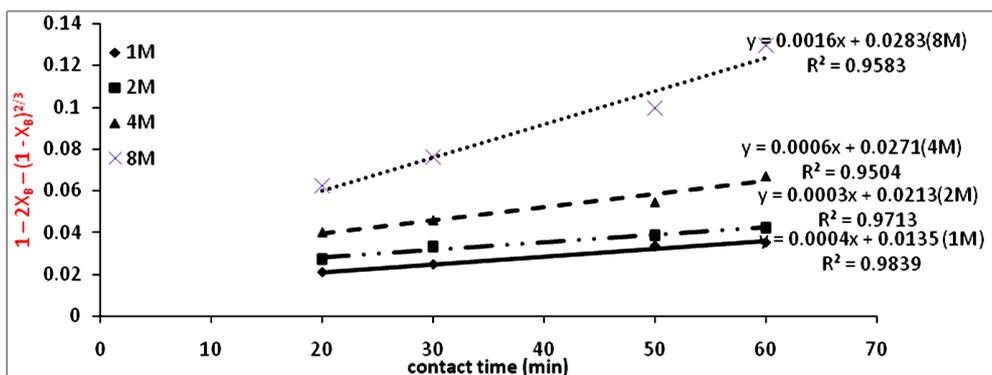


Figure 7. Plot of $1 - 2X_B - (1 - X_B)^{2/3}$ vs contact time (min) at various aqua-regia concentration.

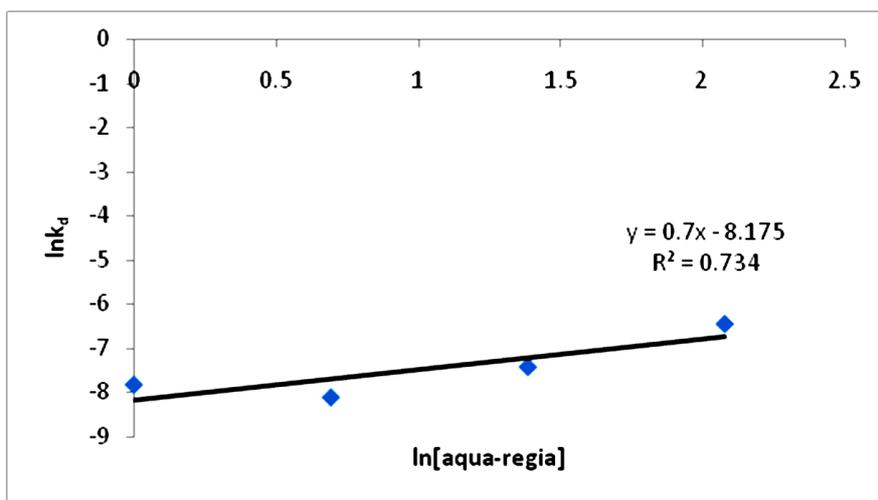


Figure 8. Plot of $\ln k_d$ vs $\ln[\text{HCl-HNO}_3]$.

State) in HCl-HNO₃ solution, it was observed that the rate of dissolution increases with increasing system concentration, temperature, and time but with decreasing particle size. The optimum conditions for the effective dissolution of 88% of the iron ore in HCl-HNO₃ solution were obtained at concentration of 8 M, temperature of 353 K, and contact time of 100 min and particle size of less than 75 μm. Also the reaction was found to be controlled by the product layer diffusion controlled process and this conformed to the shrinking core model equation:

$$k_f t = 1 - \frac{2X_B}{3} - (1 - X_B)^{2/3}$$

The apparent Activation energy (E_a) and the order of reaction for the dissolution of 1 g of the iron ore in HCl-HNO₃ system were found to be 20.48 kJ/mol and 1 respectively.

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