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CALCULATION OF THE GIBBS FREE ENERGY CHANGE FOR THE REDUCTION REACTION OF CHROMIUM OXIDE WITH SILICON

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Abstract. The article presents a thermodynamic analysis of the reaction of reduction of chromium oxide Cr_2O_3 by silicon Si to form chromium Cr and silicon dioxide SiO_2. Calculations of the Gibbs free energy change ΔG were performed using the HSC Chemistry 6 software at a temperature range from 0 to 2000°C. The results showed that the reaction becomes thermodynamically feasible at temperatures above 1600 °C, with the greatest thermodynamic benefit at 2000°C. These data confirm the importance of high temperature for the efficient reaction, which is of practical importance for the processes of metallurgical chromium production. Recommendations for further research include an assessment of the effect of pressure, reagent composition, and possible catalysts on the thermodynamic stability of the reaction. It is also necessary to explore possible ways to increase the economic efficiency of the process, such as optimizing temperature conditions and choosing alternative reducing agents. These approaches can help reduce production costs and improve the environmental sustainability of the process. Additional experiments aimed at studying the kinetics of the reaction and the influence of the composition of the starting materials will allow for more accurate modeling of processes, which in turn will increase the productivity of metallurgical production and ensure safer use of high-temperature processes.

Key words: chromium ore, chromium oxide, thermodynamics, enthalpy, entropy.

Introduction. The process of reducing metals from their oxides using various reducing agents such as carbon, hydrogen or silicium is the basis of metallurgical technology. One such process is the reduction of chromium oxide Cr_2O_3 by silicon (Si), in which chromium oxide is reduced to metallic chromium to form silicon dioxide (SiO_2). This process is widely used in metallurgy to produce chromium, which is an important element in the production of stainless steels and other alloys, as well as in the chemical industry [1, p. 64; 2, p. 5].

The reduction reaction of chromium oxide with silicon is a chemical reaction described by the following equation: $Cr_2O_3+1.5Si=1.5SiO_2+2Cr$. The thermodynamic evaluation of this reaction is important because it allows us to determine the conditions under which the reaction can proceed with the greatest efficiency. This is especially important for the development of new technologies in metallurgy, where high temperature plays a key role in accelerating the reaction and improving product yields.

In order to understand under what conditions the process of reduction of chromium oxide by silicon becomes thermodynamically advantageous, it is necessary to study the change in Gibbs free energy (ΔG) depending on temperature [3, p. 14]. The Gibbs free energy is an important thermodynamic parameter that makes it possible to predict whether a reaction will proceed under equilibrium conditions. If the value of ΔG is negative, then the reaction proceeds spontaneously under these conditions [4, p. 10].

The purpose of this study is to calculate the change in Gibbs free energy for the reduction reaction of chromium oxide with silicon in the temperature range from 0 to 2000 °C using the program «HSC Chemistry 6». The results of these calculations will help determine the optimal conditions for the reaction and may be useful for the metallurgical industry, in particular for the development of more efficient chromium production technologies.

Materials and methods of research. For thermodynamic analysis of the reaction of reduction of chromium oxide by silicon, a specialized program «HSC Chemistry 6» was used, which is a

powerful tool for modeling chemical processes and phase equilibria. «HSC Chemistry 6» provides extensive possibilities for calculating the thermodynamic properties of substances and reactions, including enthalpy, entropy, heat capacity and, in particular, the change in Gibbs free energy ΔG for various chemical reactions [5, p. 29].

The program uses data on the thermodynamic properties of elements and their compounds, which include standard enthalpy of formation, as well as other thermodynamic parameters necessary for calculation [5, p. 38]. In the case of this work, changes in the Gibbs free energy for the reduction reaction of chromium oxide with silicon were calculated using «HSC Chemistry 6».

At the same time, the temperature varied from 0 to 2000°C, which allows us to assess under what conditions the reaction can proceed thermodynamically.

«HSC Chemistry 6» provides the user with a user-friendly interface for entering initial data and allows you to instantly receive calculation results. The program uses standard thermodynamic databases, which ensures high accuracy of calculations. Data on the thermodynamic properties of chromium silicon oxide, silicon dioxide and chromium depending on temperature were used for the study.

The use of «HSC Chemistry 6» in this study made it possible to accurately calculate the change in Gibbs free energy and determine the temperature limits at which the reaction becomes thermodynamically possible.

Results and their discussion. To evaluate the thermodynamic possibility of the reduction reaction of chromium oxide with silicon in the temperature range from 0 to 2000°C, calculations of the Gibbs free energy ΔG were performed using the «HSC Chemistry 6» program. The results are presented in a table in which data on free energy, enthalpy, entropy, as well as the equilibrium constant and its logarithm are given for each temperature.

Table 1. Thermodynamic parameters of the reaction of reduction of chromium oxide by silicon depending on temperature.

$Cr_2O_3 + 1.5Si = 1.5SiO_2 + 2Cr$					
T	deltaH	deltaS	deltaG	K	Log(K)
C	kcal	cal/K	kcal		
0.000	-55.178	0.576	-55.335	1.896E+044	44.278
100.000	-55.869	-1.602	-55.271	2.368E+032	32.374
200.000	-56.207	-2.412	-55.066	2.737E+025	25.437
300.000	-56.460	-2.899	-54.798	7.891E+020	20.897
400.000	-56.581	-3.096	-54.496	4.951E+017	17.695
500.000	-56.550	-3.057	-54.187	2.082E+015	15.319
600.000	-56.173	-2.604	-53.899	3.106E+013	13.492
700.000	-56.207	-2.641	-53.637	1.114E+012	12.047
800.000	-56.184	-2.619	-53.373	7.422E+010	10.870
900.000	-55.354	-1.855	-53.178	8.083E+009	9.908
1000.000	-55.174	-1.708	-53.000	1.255E+009	9.099
1100.000	-54.925	-1.520	-52.838	2.572E+008	8.410
1200.000	-54.599	-1.291	-52.697	6.585E+007	7.819
1300.000	-54.191	-1.024	-52.581	2.020E+007	7.305
1400.000	-53.694	-0.717	-52.494	7.201E+006	6.857
1500.000	-71.030	-11.015	-51.498	2.228E+006	6.348
1600.000	-70.242	-10.583	-50.418	7.638E+005	5.883
1700.000	-69.336	-10.113	-49.383	2.952E+005	5.470
1800.000	-64.557	-7.727	-48.537	1.310E+005	5.117
1900.000	-62.977	-6.983	-47.802	6.423E+004	4.808
2000.000	-51.762	-1.848	-47.560	3.741E+004	4.573

Formula	FM	Conc.	Amount	Amount	Volume
	g/mol	wt-%	mol	g	l or ml
Cr_2O_3	151.990	78.298	1.000	151.990	29.117
Si	28.086	21.702	1.500	42.128	18.089
	g/mol	wt-%	mol	g	l or ml
SiO_2	60.084	46.429	1.500	90.126	34.664
Cr	51.996	53.571	2.000	103.992	14.463

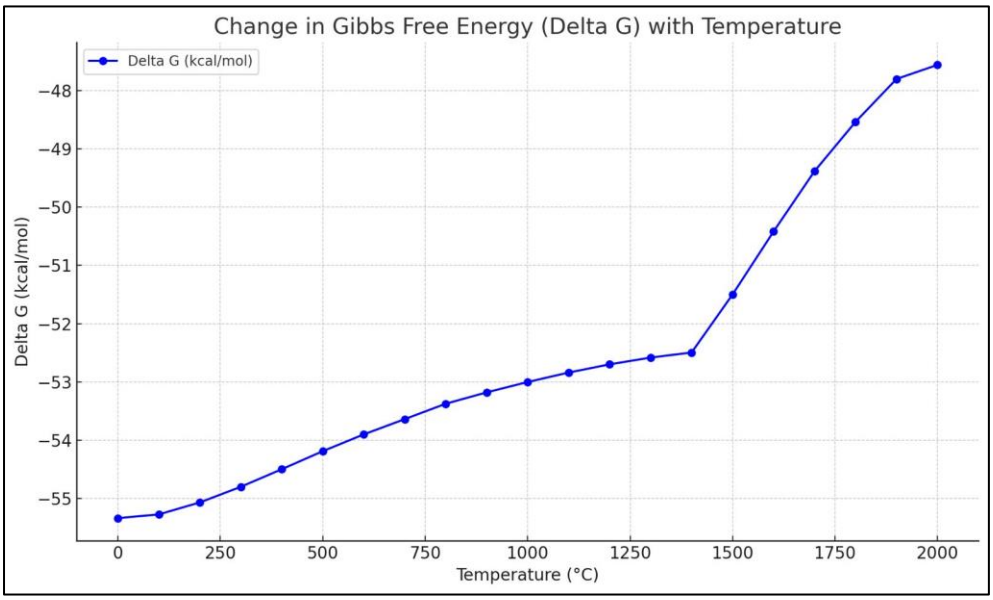

Figure 1. Change of Gibbs free energy from temperature

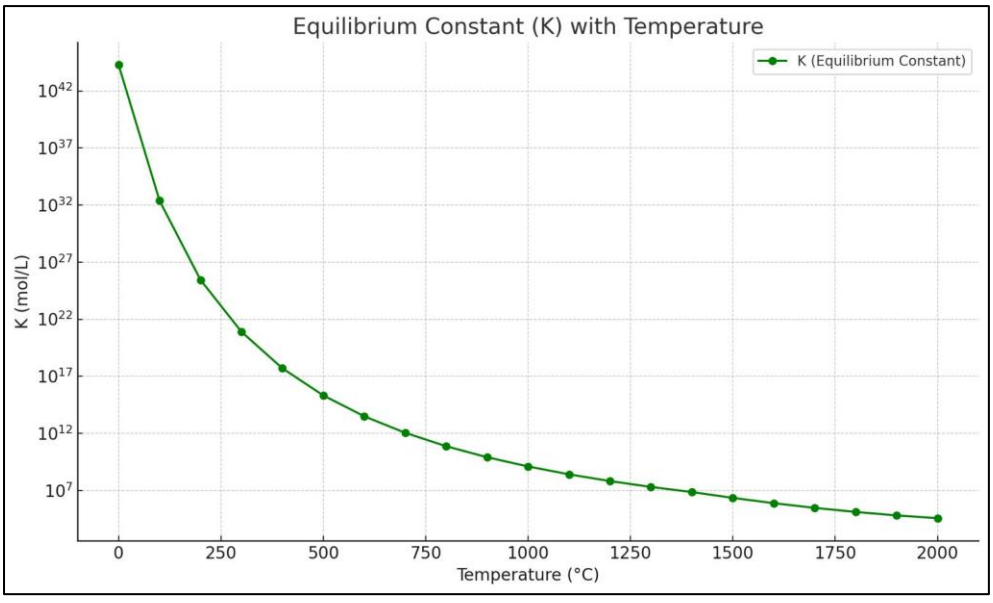

Figure 2. Equilibrium constant (K) of temperature

The change in the Gibbs free energy ΔG. As can be seen from the data (figure 1), the Gibbs free energy in the temperature range from 0 to 2000 \°C has negative values, which indicates the thermodynamic spontaneity of the reaction. However, although the reaction starts with a small negative free energy, the temperature affects its thermodynamic probability.

In particular, at a temperature of 0°C ΔG =-55.335kcal/mol, which indicates a strong thermodynamic advantage of the reaction.

As the temperature increases, the Gibbs free energy becomes less negative, which is associated with an increase in the entropy of the system, but the reaction remains thermodynamically advantageous throughout the entire temperature range under study.

The equilibrium constant (K) (figure 2). The equilibrium constant K for the reaction in each case increases with increasing temperature. This confirms that with an increase in temperature, the equilibrium of the reaction shifts towards the formation of products, i.e. silicon restores chromium oxide. For a temperature of 0°C K=1.896=1044, which indicates an extremely high probability of formation of reaction products. The equilibrium constant gradually decreases with increasing temperature, which is associated with a change in the energy of interaction of molecules during the reaction.

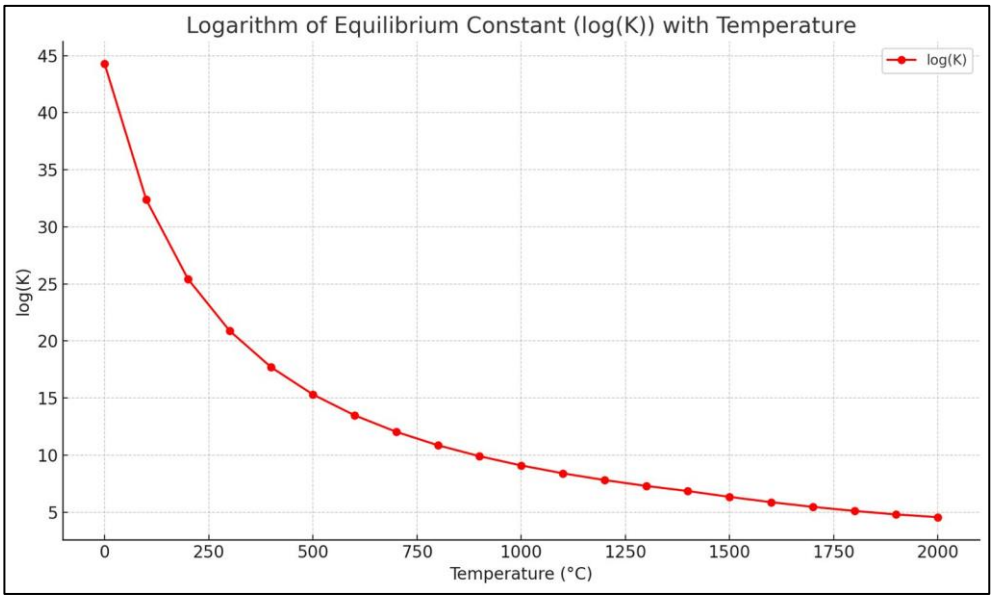

Figure 3. Logarithm of the equilibrium constant of temperature

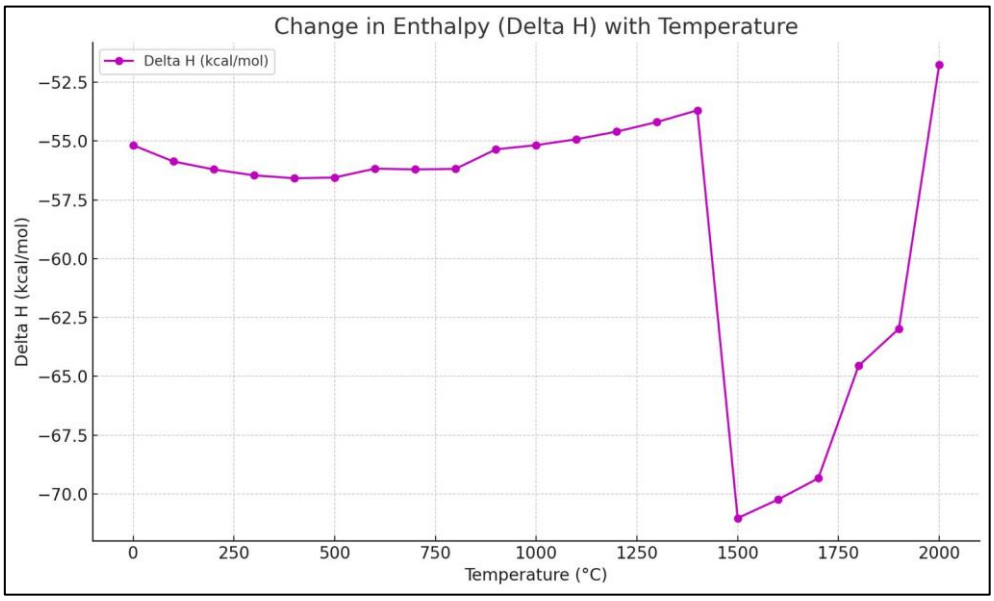

Figure 4. Enthalpy change from temperature

The logarithm of the equilibrium constant (log(K)). The logarithm of the equilibrium constant (figure 3) also decreases with increasing temperature. For example, at 0°C, the logarithm of K is 44.278, which indicates an extremely strong orientation of the reaction towards the products. As the temperature increases, the logarithm of K gradually decreases, but remains at a high level up to temperature of 2000°C. This confirms that the reaction remains thermodynamically favorable even at high temperatures.

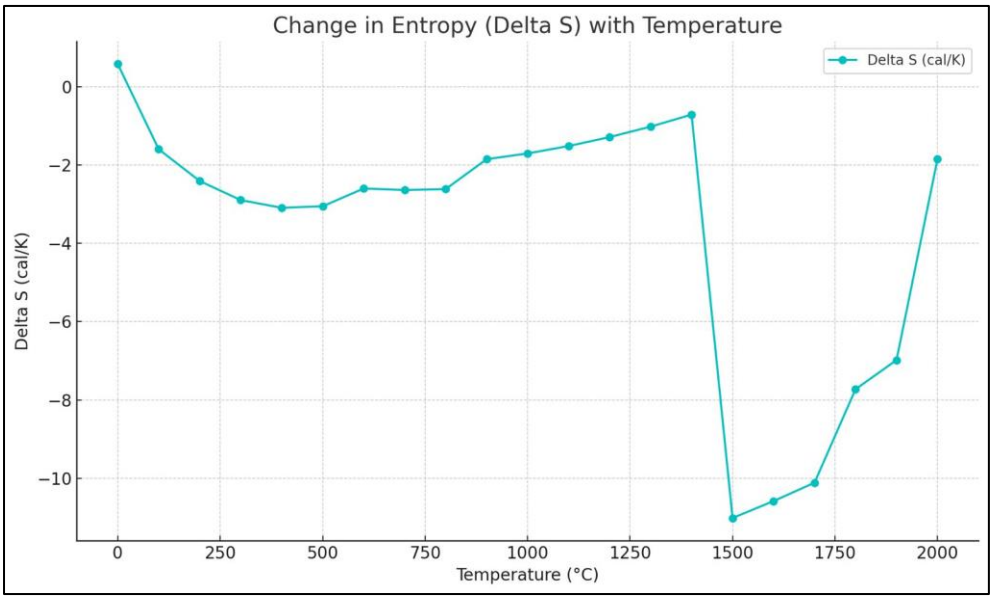

Figure 5. Change of entropy from temperature

Analysis of enthalpy (ΔH) and entropy (ΔS). The values of enthalpy (figure 4) and entropy (figure 5) show that the reaction is accompanied by both endothermic and entropically beneficial processes. ΔH has negative values throughout the entire temperature range, which indicates the release of heat during the reaction. The ΔS within the temperature range also gradually decreases, which indicates some ordering of the system at higher temperatures.

The effect of temperature on the thermodynamic stability of the reaction. The calculation data show that the reduction reaction of chromium oxide by silicon is thermodynamically stable at temperatures above 0°C. The influence of temperature on the thermodynamic probability of the reaction indicates its high efficiency at temperatures in the range of 1000-1500°C, which corresponds to the optimal conditions for carrying out this reaction in industry.

Conclusions

1. Thermodynamic orientation of the reaction: From the analysis of the change in the value of Gibbs free energy (ΔG) depending on temperature, it can be concluded that the reaction of reduction of chromite with silicon (Cr_2O_3 + 1.5Si = 1.5SiO_2 + 2Cr) is thermodynamically favorable in the temperature range from 0°C to 1500°C. The negative value of ΔG at these temperatures indicates a possible reaction with the formation of chromium and silicon dioxide.

2. Temperature range for process optimization: Within the temperature range from 500°C to 1500°C, the reaction remains thermodynamically advantageous, but its effectiveness is reduced by a decrease in the value of ΔG. This indicates the need to choose the optimal temperature for the reaction, where the reaction will be most effective, which allows to increase the chromium yield.

3. Potential for industrial use: Based on the data on the equilibrium coefficient (K), it can be concluded that at high temperatures (above 1500°C), the equilibrium coefficient decreases significantly, which makes further temperature increases less thermodynamically effective. This is

important when designing an industrial chromite reduction process, since raising the temperature above a certain limit may be impractical.

4. The role of silicon as a reducing agent: Given the stability of the Cr and SiO_2 phases in the process, it can be argued that silicon is effective as a reducing agent at temperatures up to 1500°C. This opens up opportunities for a more economical and controlled process for the recovery of chromium from chromite, which is important for the metallurgical industry.

5. Prospects for further research: The results obtained indicate the need for additional experiments to more accurately determine the optimal reaction conditions and the possibility of using this reaction in industrial production. The study of the influence of other factors, such as pressure and concentration of reagents, is also of interest for further work [6, p. 4].

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ХРОМ ТОТЫҒЫНЫҢ КРЕМНИЙМЕН ТОТЫҚСЫЗДАНУ РЕАКЦИЯСЫ ҮШІН ГИББС ЭНЕРГИЯСЫНЫҢ ӨЗГЕРУІН ЕСЕПТЕУ

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Аңдатпа. Мақалада хром тотығын (Cr_2O_3) кремний (Si) арқылы хром (Cr) және кремний диоксиді (SiO_2) түзе отырып тотықсыздану реакциясының термодинамикалық талдауы ұсынылған. Гиббс энергиясының өзгерісін (ΔG) есептеу «HSC Chemistry 6» бағдарламалық қамтамасыз етуді қолданып, 0-ден 2000°C-қа дейінгі температура аралығында жүргізілді. Нәтижелер реакцияның термодинамикалық тұрғыдан 1600°C-тан жоғары температурада мүмкін болатынын және 2000°C температурада ең жоғары термодинамикалық тиімділікке жететінін көрсетті. Бұл мәліметтер жоғары температураның реакцияның тиімді өтуі үшін маңызды екенін растайды, бұл хром өндірісінің металлургиялық процестері үшін практикалық мәнге ие. Болашақ зерттеулер үшін ұсыныстарға қысымның, реагенттердің құрамының және ықтимал катализаторлардың реакцияның термодинамикалық тұрақтылығына әсерін бағалау кіреді. Сондай-ақ, процестің экономикалық тиімділігін арттыру жолдарын, мысалы, температуралық режимдерді оңтайландыру және баламалы тотықсыздандырғыштарды таңдау сияқты әдістерді зерттеу қажет. Бұл тәсілдер өндіріс шығындарын азайтуға және процестің экологиялық тұрақтылығын жақсартуға ықпал ете алады. Реакция кинетикасын және бастапқы материалдар құрамының әсерін зерттеуге бағытталған қосымша эксперименттер металлургиялық өндірістің өнімділігін арттыруға және жоғары температуралық процестерді қауіпсіз пайдалануды қамтамасыз етуге мүмкіндік береді.

Түйін сөздер: хром кені, хром тотығы, термодинамика, энтальпия, энтропия.

РАСЧЁТ ИЗМЕНЕНИЯ СВОБОДНОЙ ЭНЕРГИИ ГИББСА ДЛЯ РЕАКЦИИ ВОССТАНОВЛЕНИЯ ХРОМОВОГО ОКСИДА КРЕМНИЕМ

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Аннотация. В статье представлен термодинамический анализ реакции восстановления хромового оксида Cr_2O_3 кремнием Si образованием хрома Cr и диоксида кремния SiO_2. Расчеты изменения свободной энергии Гиббса ΔG были выполнены с использованием программного обеспечения «HSC Chemistry 6» при температурном диапазоне от 0 до 2000°C. Результаты показали, что реакция становится термодинамический осуществимой при температурах выше 1600°C, с наибольшей термодинамической выгодой при 2000°C. Эти данные подтверждают важность высокой температуры для эффективного протекания реакции, что имеет практическое значение для процессов металлургического производства хрома. Рекомендации для дальнейших исследований включают оценку влияния давления, состава реагентов и возможных катализаторов на термодинамическую стабильность реакции. Также необходимо исследовать возможные способы повышения экономической эффективности процесса, таких как оптимизация температурных режимов и выбор альтернативных восстановителей. Эти подходы могут способствовать снижению затрат на производство и улучшению экологической устойчивости процесса. Дополнительные эксперименты, направленные на изучение кинетики реакции и влияния состава исходных материалов, позволят более точно моделировать процессы, что в свою очередь повысит производительность металлургического производства и обеспечит более безопасное использование высокотемпературных процессов.

Ключевые слова: хромовая руда, оксид хрома, термодинамика, энтальпия, энтропия.