

EFFECT OF TEMPERATURE ON A FREE ENERGY AND EQUILIBRIUM CONSTANTS DURING DRY FLUE GAS DESULPHURISATION CHEMICAL REACTIONS

by

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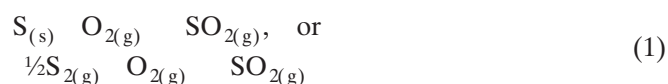
During dry flue gas desulphurisation (FGD) dry particles of reagents are inserted (injected) in the stream of flue gas, where they bond SO_2 . As reagents, the most often are used compounds of calcium ($CaCO_3$, CaO or $Ca(OH)_2$). Knowledge of free energy and equilibrium constants of chemical reactions during dry FGD is necessary for understanding of influence of flue gas temperature to course of these chemical reactions as well as to SO_2 bonding from flue gases.

Key words: sulphur-dioxide, free energy, equilibrium constant, temperature

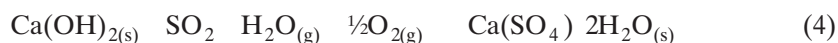
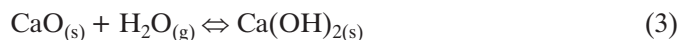
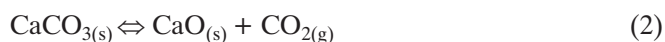
Introduction

According to Moroz *et al.* [1] and Kuburović *et al.* [2], the chemistry of dry flue gas desulphurisation (FGD) can be describe as follows:

– formation of SO_2 :



– SO_2 bonding (ab/adsorption):



Calculations of reaction free energy assuming that is water in a liquid and gaseous phase – reactions (3) and (4).

Calculation

Chemical reaction enthalpy (heat of reaction) is defined according to the following equation 3 :

$$\Delta H = (b_i \Delta h_i)_{\text{products}} - (b_i \Delta h_i)_{\text{reactants}} \quad (5)$$

where b_i is stoichiometric numbers of moles of the i^{th} component of reactants and products, respectively, and Δh_i is bond energy of the i^{th} component.

Dependence of reaction enthalpy on temperature is defined by equation:

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta C_{mp}(T) dT \quad (6)$$

where is:

$$\Delta C_{mp}(T) = (b_i C_{mpi})_{\text{products}} - (b_i C_{mpi})_{\text{reactants}} \quad (7)$$

and represent a sum of specific molar heat capacities.

Another relation defines entropy of reaction:

$$\Delta S = (b_i s_i)_{\text{products}} - (b_i s_i)_{\text{reactants}} \quad (8)$$

where s_i is specific entropies of bonds of the i^{th} component.

Dependence of reaction entropy on temperature, at constant pressure is defined as:

$$\Delta S_{T_2} - \Delta S_{T_1} = \int_{T_1}^{T_2} \frac{\Delta C_{mp}(T)}{T} dT \quad (9)$$

Free energy is defined by following expression:

$$\Delta G = (b_i \Delta g_i)_{\text{products}} - (b_i \Delta g_i)_{\text{reactants}} \quad (10)$$

where Δg_i is Gibbs specific free energy of the i^{th} component.

Another relation gives impact of enthalpy, temperature and entropy on free energy of reaction:

$$\Delta G = \Delta H - T \Delta S \quad (11)$$

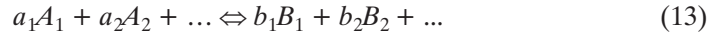
If $\Delta G > 0$ reaction occurs in course of reactants formation, and if $\Delta G < 0$ reaction runs in course of products formation.

During occurrence of the considered chemical reactions, the achieving of equilibrium state in reactor space take place in direction of the lowest value of free energy:

$$G = H - TS \quad (12)$$

where G is free energy, H is enthalpy, S is entropy, and T is absolute temperature at which chemical reaction occurs.

For generalized chemical reaction:



and in states of minimum of free energy (under condition that components react as gases), chemical equilibrium constant may be described by the components concentration :

$$K_c = \frac{C_{B_1}^{b_1} C_{B_2}^{b_2} \dots}{C_{A_1}^{a_1} C_{A_2}^{a_2} \dots} \quad (14)$$

and/or, *via* components partial pressure:

$$K_p = \frac{p_{B_1}^{b_1} p_{B_2}^{b_2} \dots}{p_{A_1}^{a_1} p_{A_2}^{a_2} \dots} \quad (15)$$

At absolute temperature in the system (T) and at change of mole numbers $\Delta n = (b_1 + b_2 + \dots) - (a_1 + a_2 + \dots)$ ratio of K_p and K_c is determined by next expression:

$$K_c = K_p (R_u T)^{-\Delta n} \quad (16)$$

where R_u is universal gas constant.

When the normal state of each component is the pure state at the given p and T ($p_0 = 1.013 \cdot 10^5$ Pa), eq. (16) becomes:

$$K_p = \frac{K_p}{p_0^{\Delta n}} e^{-\frac{\Delta G}{R_u T}} = e^{-\frac{\Delta H - T\Delta S}{R_u T}} = e^{\frac{\Delta S}{R_u}} e^{-\frac{\Delta H}{R_u T}} \quad (17)$$

where $\Delta G = \Delta H - T\Delta S$ is change of the system enthalpy.

The specific molar heat capacities are usually expressed in the following form 4 :

$$C_{mp} = a + b \cdot 10^{-3} T + c \cdot 10^6 T^2 \quad (18)$$

Coefficients a , b , and c for individual components are shown in Table 1 4

Temperature dependence of specific heat capacities of water in a liquid state and gaseous oxygen are summarized in Tables 2 and 3 .

Specific molar heat capacity of solid rhomboid sulphur as a function of temperature and in temperature range between 24.9-95.5 °C is given by the following expression (6):

$$C_{mp} = 14.9887 + 26.1256 \cdot 10^{-3} T \quad (19)$$

Table 1. Value of coefficients

Component	<i>a</i>	<i>b</i>	<i>c</i>	Temperature range K
SO _{2(g)}	43.459	10.634	-5.945	298-1800
CO _{2(g)}	44.171	9.043	-8.541	298-2500
H ₂ O _(g)	30.019	10.718	0.335	298-5000
CaCO _{3(s)}	104.586	21.939	-25.958	298-1200
CaO _(s)	49.655	4.522	-6.950	298-2888
Ca(OH) _{2(s)}	105.365	11.953	-18.979	298-1000
CaSO ₄ ·2H ₂ O _(s)	221.230	98.808	-	298-1000

Table 2. Specific molar capacity of water in a liquid state as a function of temperature

<i>T</i> [K]	20	40	100	200	300	320	340	360	373
<i>C_{mp}</i> [kJ/(kmol K)]	2.05	6.13	15.88	28.22	75.14	75.15	75.30	75.57	75.82

Table 3. Specific heat capacity of gaseous oxygen as a function of temperature

<i>T</i> [K]	298	400	500	600	700	800	900	1000	1500	2000
<i>C_{mp}</i> [kJ/(kmol K)]	29.36	30.10	31.08	32.09	32.99	33.74	34.36	34.87	36.56	37.78

Enthalpies, free energy, and entropies of the chemical bonds of inorganic components at 1.013·10⁵ Pa and 298 K are shown in Table 4 .

Table 4. Enthalpy, free energy, and entropy of the chemical bonds of inorganic components*

Component	Formula	State	Δh [kJ/kmol]	Δf [kJ/kmol]	<i>s</i> [kJ/(kmol·K)]
Calcium carbonate	CaCO ₃	solid	-1207683	-1129515	92.95
Calcium oxide	CaO	solid	-635975	-604574	39.77
Calcium sulphate (gypsum)	CaSO ₄ ·2H ₂ O	solid	-2019960	-	194.27
Calcium hydroxide	Ca(OH) ₂	solid	-986600	-896800	76.1
Oxygen	O ₂	gas	0	0	205.17
Sulphur	S	solid	0	0	31.90
Sulphur dioxide	SO ₂	gas	-297095	-300570	248.70
Carbon dioxide	CO ₂	gas	-393776	-394647	213.78
Water	H ₂ O	gas	-241989	-228750	188.85
		liquid	-286030	-237350	69.99

* - at 1.013 10⁵ Pa and 298 K

Results and discussion

The influence of temperature on enthalpy, entropy, and free energy of the SO₂ formation reaction – reaction (1), are shown in Table 5 [5].

Table 5. Influence of temperature on enthalpy, entropy, and free energy of reaction (1)

T [K]	Δh [kJ/mol]	Δs [kJ/(kmol·K)]	$\Delta f/T$ [kJ/(kmol·K)]
298	361.4	-71.0	1141.1
300	361.5	-71.0	1134.0
400	361.9	-72.5	832.2
500	362.2	-73.0	651.4
600	362.3	-73.2	530.6
700	362.3	-73.3	444.3
800	362.3	-73.3	379.6
900	362.2	-73.2	329.2
1000	362.1	-73.1	289.0
1100	362.0	-72.9	256.2
1200	361.9	-72.8	228.8
1300	361.7	-72.7	205.5
1400	361.5	-72.6	185.6
1500	361.3	-72.5	168.4

Therefore, the influence of temperature on free energy and chemical equilibrium constants of reaction (2-4) are given in Figs. 1-5 [7].

Formation of SO₂ – reaction (1), is an exothermic reaction ($\Delta H < 0$) in temperature range 298-1500 K. Free energy of the considered reactions are negative as well in temperature range 298-1500 K, so the process occurs in direction of SO₂ formation (Table 5 and Fig. 1).

CaSO₃ decomposition reaction – reaction (2), is an endothermic process in temperature range 298-1200 K ($\Delta H > 0$). Free energy of the considered reaction change their sign in temperature range 298-1200 K, hence the reaction carry out in both directions (Fig. 2). At the moment of equilibrium, *e. g.* $\Delta G = 0$, which correspond to CaCO₃ decomposition temperature of app. 1150 K (Fig. 2).

Variation of enthalpy, entropy, and free energy of the Ca(OH)₂ formation reaction – reaction (3), with water in vapor and liquid phase as functions of temperature are shown in Fig. 3. In Fig. 3 is noticeable that enthalpies of the Ca(OH)₂ formation

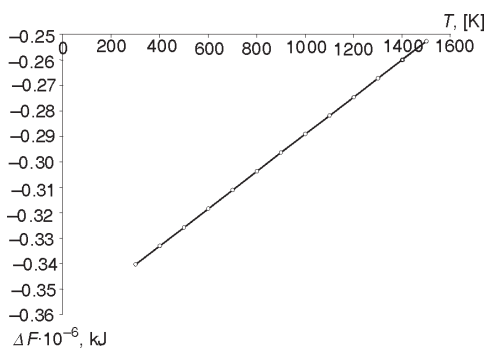


Figure 1. Effect of temperature on free energy (for reaction $\frac{1}{2}S_{2(g)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$)

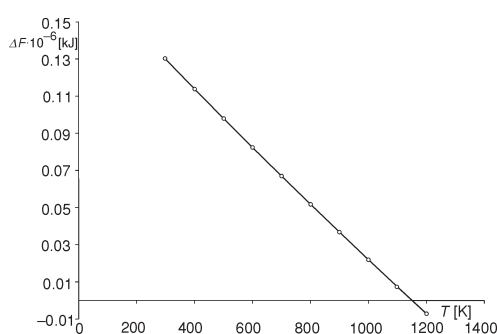


Figure 2. Effect of temperature on free energy (for reaction $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$)

reaction are negative ($\Delta H < 0$), so the process releases heat (exothermic reaction). Free energy of the $Ca(OH)_2$ formation reaction with water in vapor phase change their sign in temperature range 298-1000 K, hence the process occurs in both directions. State of equilibrium is achieved when $\Delta G = 0$ and respective equilibrium temperature is approximately 740 K (Fig. 3).

Free energy of the same reaction with water in a liquid state is negative in temperature range 298-373 K ($\Delta G < 0$), hence the process occurs in direction of $Ca(OH)_2$ formation. Enthalpies of the process with water in a liquid phase is calculated for temperature range 298-373 K, since at temperature $T > 373$ K water evaporated, and at temperature $T < 273$ K water freeze.

Variations of enthalpy, entropy, and free energy of $CaSO_4 \cdot 2H_2O$ formation reaction – reaction (4) with water in vapor phase as functions of temperature are shown in Fig. 4.

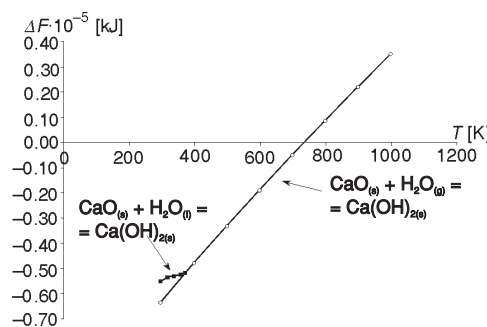


Figure 3. Effect of temperature on free energy of $Ca(OH)_2$ formation reaction

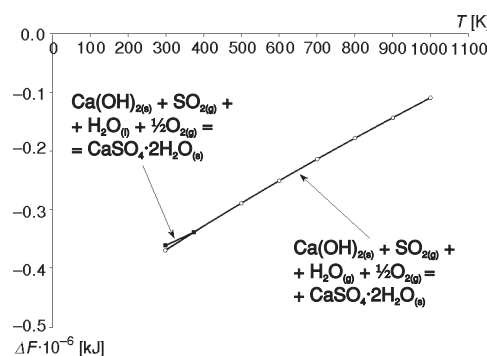


Figure 4. Effect of temperature on free energy of $Ca(SO_4) \cdot 2H_2O$ formation reaction

Enthalpies of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ formation reaction are negative ($\Delta H < 0$) in temperature range 298-1000 K thus the process releases heat (exothermic process) as shown in Fig 4. Free energy of the considered reaction is also negative ($\Delta G < 0$) in the considered temperature interval; therefore the process occurs in direction of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ formation.

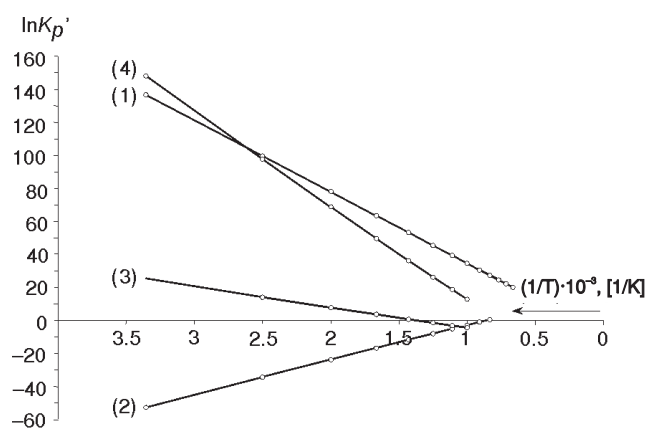


Figure 5. Equilibrium constant K_p' vs. temperature for the reactions (1-4)

Reaction of CaCO_3 decomposition – reaction (2), is endothermic process, therefore, as temperature increases, value of equilibrium constant of that reaction increasing in direction of products formation (Fig. 5). On the other hand, for exothermic reactions (1), (3), and (4), values of equilibrium constants decreases with increasing temperature as result of reaction carry out to the reactants formation (Fig. 5).

Summary and conclusions

In this study is shown that for the considered reactions thermodynamic functions ΔH and ΔS have the same sign, and the sign of ΔG is determined by ratio of enthalpy, and entropy components in Gibbs–Helmholtz equation (11). In other words, temperature of considered reactions becomes decisive factor for thermodynamic conditions. For exothermic reactions (1), (3), and (4), with negative variation of entropy, condition that $\Delta G < 0$ will be satisfied at lower temperatures. However, for endothermic reaction (2), with positive change of entropy, condition $\Delta G < 0$ will be satisfied at higher temperatures, where entropy (*e. g.* $T\Delta S$) becomes dominant. It is shown that increase of temperature causes increase of equilibrium constant of the CaCO_3 formation reaction, according as result of equilibrium state proceeding in direction of products formation. For the SO_2 , $\text{Ca}(\text{OH})_2$, and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ formation reactions it is shown that increase in

temperature corresponding in decrease of equilibrium constant values as result of proceeding of reactions in direction of the reactants formation.

Nomenclature

b_i	– stoichiometric mole number of the i^{th} chemical component, [kmol]
C	– concentration of the chemical component
C_{mp}	– specific molar heat capacity, [kJ/kmol·K]
ΔC_{mp}	– sum of specific molar heat capacities, [kJ/kmol·K]
F	– free energy, [kJ]
ΔF	– reaction free energy, [kJ]
Δf	– specific free energy of component, [kJ/kmol]
G	– Gibbs free energy, [kJ]
ΔG	– reaction Gibbs free energy, [kJ]
Δg_i	– Gibbs specific free energy of the i^{th} component, [kJ/kmol]
H	– enthalpy, [kJ]
ΔH	– reaction enthalpy, [kJ]
Δh	– enthalpy of chemical bond, [kJ/kmol]
K_c	– chemical equilibrium constant expressed by volumetric molar concentrations
K_p	– chemical equilibrium constant expressed by partial pressures of the components
K_p	– chemical equilibrium constant expressed by partial pressures reduced to pressure, $p_0 = 1.013 \cdot 10^5$ Pa
Δn	– change of mole number, [kmol]
p	– partial pressure, [Pa]
p_0	– referent pressure, [Pa]
R_u	– gas constant, [kJ/kmol·K]
S	– entropy, [kJ/K]
ΔS	– reaction entropy, [kJ/K]
s	– specific entropy, [kJ/kmol·K]
Δs	– reaction specific entropy [kJ/kmol·K]
T	– absolute temperature, [K]

Super- and subscripts

i	– chemical component
(g)	– gas
(s)	– solid

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