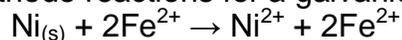


**Type I: Problems based on electrode reactions:**

1) Write the anode and cathode reactions for a galvanic cell that utilizes the reaction:



2) Write the electrode reactions, the overall reactions and the expression for emf for each of the following reversible cells.

1. Pt, H<sub>2(atom)</sub> | HCl<sub>(aq)</sub> | Pt, Cl<sub>2(1 atm)</sub>
2. Hg – Hg<sub>2</sub>Cl<sub>2(s)</sub> | HCl<sub>(aq)</sub> | Pt, H<sub>2(1 atm)</sub>
3. Ag<sub>(s)</sub> – AgCl<sub>(s)</sub> | KCl<sub>(aq)</sub> | Hg<sub>2</sub>Cl<sub>2(s)</sub> – Hg<sub>(s)</sub>
4. Ag – AgCl<sub>(s)</sub> | — | KCl<sub>(s)</sub> | AgCl<sub>(s)</sub> – Ag<sub>(s)</sub>

3) Write the individual electrode reactions and the total cell reaction for the following cells:

- a) Ag<sub>(s)</sub> – AgCl<sub>(s)</sub> | Cl<sup>-</sup> || I<sup>-</sup> | Ag<sub>(s)</sub> = Ag<sub>(s)</sub>
- b) Pt | Fe<sup>2+</sup>, Fe<sup>3+</sup> || MnO<sub>4</sub><sup>-1</sup>, Mn<sup>2+</sup> | Pt
- c) Pt | H<sub>2(g)</sub> | HCl | Cl<sub>2(g)</sub>, Pt
- d) Ag | Ag<sup>+</sup> || Fe<sup>2+</sup> || Fe

**Type II : Problems based on construction of cells**

1) Construct the cells in which the following reactions occur. Which of the electrode cell acts as anode and which one is cathode?

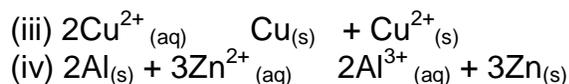
- (i) Zn + CuSO<sub>4</sub> → ZnSO<sub>4</sub> + Cu
- (ii) Fe + SnCl<sub>2</sub> → FeCl<sub>3</sub> + Sn
- (iii) Cu + 2AgNO<sub>3</sub> → Cu(NO<sub>3</sub>)<sub>2</sub> + 2Ag
- (iv) Zn + H<sub>2</sub>SO<sub>4</sub> → ZnSO<sub>4</sub> + H<sub>2</sub>(Pt)

2) Set up the cell corresponding to each of the following cell reactions:

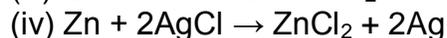
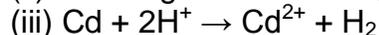
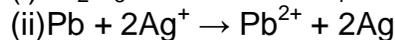
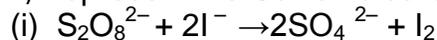
- (i) Sn<sub>(s)</sub> + Sn<sup>4+</sup> → 2Sn<sup>2+</sup>
- (ii) Cd<sub>(s)</sub> + Hg<sub>2</sub><sup>2+</sup> → Cd<sup>2+</sup> + 2Hg<sub>(l)</sub>
- (iii) Zn<sub>(s)</sub> + 2AgCl<sub>(s)</sub> → ZnCl<sub>2</sub> (aq) + 2Ag<sub>(s)</sub>

3) Construct the cell, showing the polarities of the electrodes to produce current from the reaction,

- (i) Zn<sub>(s)</sub> + Cu<sup>2+</sup><sub>(aq)</sub> → Zn<sup>2+</sup><sub>(aq)</sub> + Cu<sub>(s)</sub>
- (ii) Cu<sub>(s)</sub> + 2Ag<sup>+</sup><sub>(aq)</sub> → Cu<sup>2+</sup><sub>(aq)</sub> + 2Ag<sub>(s)</sub>

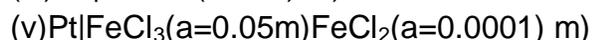
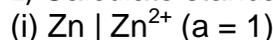


4) Represent the Galvanic cells using line notations for the following cell reactions:



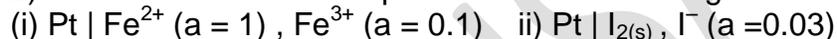
## Type III: Problems based on calculation of single electrode potential

1) Calculate standard potentials of the following electrodes at 298K



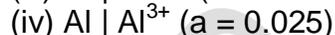
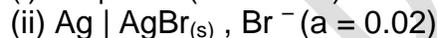
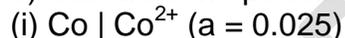
(Ans.: , (i)  $-0.763 \text{ V}$  (ii)  $+0.712 \text{ V}$ , (iii)  $0.09004 \text{ V}$  (iv)  $-0.410 \text{ V}$  (v)  $-0.87 \text{ V}$ )

2) Calculate the electrode potential of the following electrodes at 298K:



(Ans (i)  $0.7118 \text{ V}$  , (ii)  $+0.6257 \text{ V}$ )

3) Calculate the potential of the following electrodes:



(Ans. (i)  $E = -0.3244 \text{ V}$ , (ii)  $E = 0.1716 \text{ V}$ , (iii)  $E = 0.1448 \text{ V}$  , (iv)  $E = 1.6935\text{V}$ )

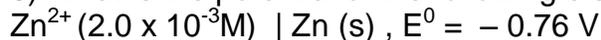
4) Calculate the potential of the electrode,  $\text{Ag} | \text{AgCl}_{(\text{s})} , \text{Cl}^- (a = 0.01)$

(Ans.  $E = 0.3407 \text{ V}$ )

5) For the galvanic cell,  $\text{Zn} | \text{Zn}^{2+}(1\text{M}) || \text{Ag}^+(1\text{M}) | \text{Ag}$ , Calculate the cell potential when the standard reduction electrode potentials of Zn and Ag electrodes are  $-0.763 \text{ V}$  and  $+0.8 \text{ V}$  respectively.

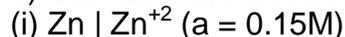
(Ans. Cell potential =  $1.563 \text{ V}$ )

6) What is the potential of the following electrode at 298K:



(Ans.  $E = -0.84 \text{ volts}$ )

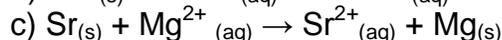
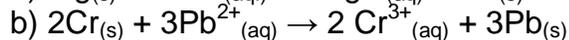
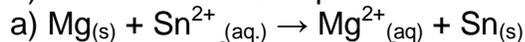
7) Calculate the electrode potential if the following half cells at 298K



$$(\text{Ans : (i)} \quad \quad \quad = -0.7548\text{V} , (\text{ii}) \quad \quad \quad = 0.112\text{V})$$

## Type IV: Problems based on Nernst equation and spontaneity of a process

1) Write the Nernst equation for the following processes at some temperature T.



2) Construct the cell with  $\text{Zn} \mid \text{Zn}^{2+}$  and  $\text{Cd}^{2+} \mid \text{Cd}$  electrode. Write the cell reactions. Also indicate the polarities and determine the standard e.m.f. of the cell. Given that SRP of  $\text{Zn}^{2+} \mid \text{Zn} = -0.763$  volt and of  $\text{Cd}^{2+} \mid \text{Cd} = -0.403\text{V}$ .

$$(\text{Ans.} \quad \quad \quad = +0.360 \text{ volt})$$

3) Construct the cell with  $\text{Zn} \mid \text{Zn}^{2+}$  and  $\text{Ag} \mid \text{Ag}^+$  electrode. Write the cell reactions. Also indicate the polarities and determine the standard e.m.f. of the cell. Given  $\text{Zn}^{2+} \mid \text{Zn} = -0.763$  volt and of  $\text{Ag}^+ \mid \text{Ag} = +0.799\text{V}$ .

$$(\text{Ans.} \quad \quad \quad = 1.562 \text{ volts})$$

4) Construct the cell indicating the polarities of the electrodes to produce current from the reaction:  $\text{Cu}_{(s)} + 2\text{Ag}^+_{(aq)} \rightarrow \text{Cu}^{2+}_{(aq)} + 2\text{Ag}_{(s)}$ . Calculate the std. emf of the cell.

Given  $\text{Cu}^{2+} \mid \text{Cu} = +0.337$  volt and of  $\text{Ag}^+ \mid \text{Ag} = +0.799$  volt

$$(\text{Ans.} \quad \quad \quad = 0.462 \text{ volts})$$

5) The following reaction takes place in a cell:  $\text{Zn}_{(s)} + \text{Co}^{2+} \rightarrow \text{Co}_{(s)} + \text{Zn}^{2+}$  Write down the electrode reactions and calculate the standard e.m.f. of cell.

Given that  $E^0$  of  $\text{Zn} \mid \text{Zn}^{2+} = 0.76$  volt and of  $\text{Co} \mid \text{Co}^{2+} = 0.28\text{V}$ .

$$(\text{Ans.} \quad \quad \quad = 0.48 \text{ volts})$$

6) Calculate the e.m.f. of the cell at 298K :  $\text{Fe} \mid \text{FeSO}_4(0.1\text{M}) \parallel \text{CuSO}_4(0.1\text{M}) \mid \text{Cu}$ .

Given that  $E^0$  of  $\text{Fe} \mid \text{Fe}^{2+} = 0.44$  volt and of  $\text{Cu}^{2+} \mid \text{Cu} = 0.337\text{V}$ .

$$(\text{Ans.} E = 0.75 \text{ volts})$$

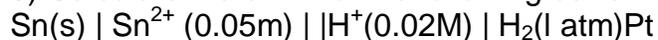
7) Calculate the e.m.f. of the following cell at 298 K



Standard potential of  $\text{Sn}^{2+} \mid \text{Sn} = -0.14 \text{ V}$

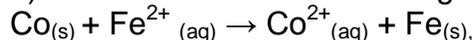
Standard potential of  $\text{Pb}^{2+} \mid \text{Pb} = -0.126\text{V}$

8) Calculate the e.m.f. of the following cell at 298K:



$$(\text{Ans. } 0.08\text{V})$$

9) Predict whether the following reaction would proceed spontaneously at 298 K.



given that  $[\text{Co}^{2+}] = 0.15\text{m}$  and  $[\text{Fe}^{2+}] = 0.68 \text{ m}$

(Ans  $E^0 = -0.14V$  , therefore the reaction is non-spontaneous)

10) Calculate the e.m.f. of the following cells at 298 K.

(i)  $Zn_{(s)}|ZnCl_2(0.0102m),AgCl_{(s)}|Ag$

(ii)  $Pt, H_2(1 atm) | H_2SO_4(0.05m), Hg_2SO_{4(s)} | Hg$

(Ans. (i) 0.717 V, (ii) 0.7353 V)

11) The e.m.f. of the cell :  $Cd | CdI_2(m = ?), AgI_{(s)} | Ag$

is 0.286 V at 298K. Calculate the concentration of  $CdI_2$  solution.

(Ans. Molarity of  $CdI_2 = 0.4002$ )

12) For the reaction  $Fe^{3+} + 3e^- \rightarrow Fe$  ,  $E^0 = -0.04V$  and for reaction  $Fe^{3+} | Fe^{2+}$  ,  $E^0 = +0.77V - 0.04V$ . Calculate  $E^0$  for  $Fe | Fe^{2+}$  reaction.

Is the reaction  $Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$  spontaneous or non-spontaneous.

(Ans.  $E^0 = -0.44 V$ , spontaneous)

13) The e.m.f. of the following cell at 298 K is 0.3991 V

$Ag | AgCl_{(s)}, Cl^-(a = 0.1) || Ag^+(a = 0.01) | Ag$

If the standard potential of silver-silver chloride electrode is + 0.2224. Calculate

The standard potential of  $Ag^+/Ag$  electrode.

(Ans. 0.7991 )

14) Set up the cell in which the following reaction takes place and calculate the e.m.f. of the cell.

$2Al_{(s)} + 3I_2 \rightarrow 2Al^{3+}(0.1m) + 6I^-(0.01m)$

(Ans. 2.20 V)

15) The standard potentials of  $Pb | Pb^{2+}$  and  $Sn | Sn^{2+}$  electrodes are  $-0.126 V$  and  $-0.14 V$  respectively .Construct the galvanic cell, write the cell reaction and

calculate the standard e.m.f. of the cell .

(Ans.  $E^0_{cell} = 0.014V$ )

16) The standard potentials of  $Zn | Zn^{2+}$  and  $Ag | Ag^+$  electrodes are  $-0.763 V$  and  $+0.799 V$  respectively. Construct the galvanic cell , mention the polarities, write the cell reaction and calculate the standard e.m.f. of the cell .

(Ans.  $E^0_{cell} = 1.562V$ )

17) Calculate the emf of the following cell at 298K:

$Pt | I_{2(s)}, I^-(a = 0.03) || Fe^{3+}(a = 0.1), Fe^{2+}(a = 1) | Pt$

(Ans.  $E = 0.0861 V$ )

18) Find the emf of the following cell at 298K:

$Ag | AgCl_{(s)}, Cl^-(a = 0.1) || Ag^+(a = 0.01) | Ag$

(Ans.  $E_{cell} = 0.3991 V$ )

19) The emf of the following cell:

$Pt | Sn^{2+}(a = 0.1), Sn^{4+}(a = 0.1) || Cl^-(a = 0.01), Cl_2(g, 1 atm) | Pt$

(Ans.  $E = 1.3595 V$ )

20) The emf of the cell :  $Ag | AgCl_{(s)}, Cl^-(a = ?) || Fe^{2+}(a = 0.1), Fe^{3+}(a = 0.01) | Pt$  is 0.4303 V. calculate the activity of chloride ions.

(Ans.  $a = 0.1$ )

21) Find the emf of the following cells:

(i)  $Cu^+ | Cu^{2+}(a = 0.1) || Ag^+(a = 0.01) | Ag$

(ii)  $Al | Al^{3+}(a = 0.01) || Cl^-(a = 0.02), Cl_2(g, 1 atm) | Pt$

(iii)  $\text{Ag} | \text{AgBr}_{(s)}, \text{Br}^- (a = 0.01) || \text{Cl}^- (a = 0.02), \text{Cl}_2 (g, 1 \text{ atm}) | \text{Pt}$

(iv)  $\text{Pt} | \text{I}_{2(s)}, \text{I}^- (a = 0.03) || \text{Ag}^+ (a = 0.02) | \text{Ag}$

(Ans. (i)  $E_{\text{cell}} = 0.4325\text{V}$ , (ii)  $E_{\text{cell}} = 3.0335\text{V}$ , (iii)  $E_{\text{cell}} = 1.2707\text{V}$ , (iv)  $E_{\text{cell}} = 0.0729\text{V}$ )

22) What is the standard emf of a galvanic cell made of a Cd electrode dipped in 1.0M  $\text{Cd}(\text{NO}_3)_2$  solution and a Cr electrode dipped in a 1.0M  $\text{Cr}(\text{NO}_3)_3$  solution at  $25^\circ\text{C}$ .

Given

(Ans. = 0.34V)

23) A galvanic cell consists of a Mg electrode in a 1.0M  $\text{Mg}(\text{NO}_3)_2$  solution and a Ag electrode in a 1.0M  $\text{AgNO}_3$  solution. Calculate the standard e.m.f. of the cell at  $25^\circ\text{C}$ .

Given the standard reduction potential of

(Ans. = 3.17V)

24) Predict whether the following reaction will occur spontaneously at 298K:

$\text{Co}_{(s)} + \text{Fe}^{2+} \rightarrow \text{Fe}_{(s)} + \text{Co}^{2+}$ , Given that  $[\text{Co}^{2+}] = 9.15\text{M}$  and  $[\text{Fe}^{2+}] = 0.68\text{M}$

(Ans :  $E_{\text{cell}} = -0.14\text{V}$ , since it is negative the reaction is non-spontaneous)

25) Calculate the emf of the following cell:

$\text{Fe}_{(s)} | \text{Fe}^{2+} (a = 0.1) || \text{Cd}^{2+} (a = 0.05) | \text{Cd}_{(s)}$

Given  $E_{\text{Fe}^{2+}/\text{Fe}} = -0.441\text{V}$ ,  $E_{\text{Cd}^{2+}/\text{Cd}} = -0.403\text{V}$ , will the cell reaction is spontaneous?

(Ans :  $E_{\text{cell}} = 0.0291$ , since it is positive the cell reaction is spontaneous)

26) Calculate the emf of the following cells at 298K:

(a)  $\text{Hg}_{(l)} - \text{Hg}_2\text{Cl}_{2(s)} | \text{KCl}_{(\text{sat})} || \text{Co}^{+2}, \text{Co}^{+3} | \text{Pt}$

$E_{\text{Hg}_2\text{Cl}_2/\text{Hg}} = 0.242\text{V}$ ,  $E_{\text{Co}^{3+}/\text{Co}^{2+}} = 1.82\text{V}$

The ratio of  $[\text{Co}^{+3}]/[\text{Co}^{+2}] = 3$

(Ans :  $E_{\text{cell}} = 1.606\text{V}$ )

(b)  $\text{Pt} | \text{Sn}^{+2}, \text{Sn}^{+4} || \text{KCl}_{(\text{sat})} | \text{Hg}_2\text{Cl}_{2(s)} - \text{Hg}_{(l)}$

$E_{\text{Sn}^{4+}/\text{Sn}^{2+}} = 0.140\text{V}$ ,  $E_{\text{Hg}_2\text{Cl}_2/\text{Hg}} = 0.242\text{V}$

(Ans :  $E_{\text{cell}} = 0.3909\text{V}$ )

27) Calculate the emf of the following concentration of cell:

$\text{Mg}_{(s)} | \text{Mg}^{2+} (a = 0.01) || \text{Mg}^{2+} (a = 0.02) | \text{Mg}_{(s)}$

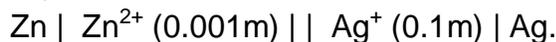
(Ans :  $E_{\text{cell}} = 0.3909\text{V}$ )

28) Calculate the standard emf of a cell that uses  $\text{Mg}/\text{Mg}^{2+}$  and  $\text{Cu}/\text{Cu}^{2+}$  half cell at  $25^\circ\text{C}$ . Write the cell representation Write the equations for the cell reaction that occurs under standard state conditions.

29) Calculate the standard emf of a cell that uses  $\text{Ag}/\text{Ag}^+$  and  $\text{Al}/\text{Al}^{3+}$  half cell reactions. Represent the cell using line notations and write the overall cell reaction under standard

state conditions.

30) Calculate the em.f. of the cell:

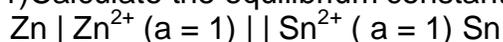


The standard potentials of  $\text{Ag} | \text{Ag}^+$  and  $\text{Zn} | \text{Zn}^{2+}$  electrodes are  $+0.799\text{V}$  and  $-0.763\text{V}$  respectively.

(Ans.  $E_{\text{cell}} = 1.5916\text{V}$ )

## Type V: Problems based on calculation of equilibrium constant

1) Calculate the equilibrium constant for the reaction taking place in the cell:



(Ans.  $K = 1.122 \times 10^{21}$ )

2) An excess of metallic zinc is added to  $0.1\text{M}$  solution of  $\text{AgNO}_3$ . Calculate the (i) equilibrium constant and (ii) concentration of  $\text{Ag}^+$  ions at equilibrium.

(Ans. (i)  $K = 5.888 \times 10^{52}$ , (ii)  $= 9.215 \times 10^{-28}$ )

3) At  $298\text{K}$ , an excess of finely divided aluminium is added to a solution  $0.3\text{M}$  in cupric ions. Calculate the concentration of  $\text{Cu}^{2+}$  when equilibrium is reached. Assume activity and concentration to be equal. Experimentally it has been found that the reaction goes practically to completion.

(Ans.  $= 1.175 \times 10^{-68}$ )

4) The equilibrium constant for the reaction:  $\frac{1}{2} \text{H}_2 (\text{g}, 1 \text{ atm}) + \text{AgI}_{(\text{s})} = \text{H}^+ + \text{I}^- + \text{Ag}_{(\text{s})}$  is  $2.68 \times 10^{-3}$  at  $298\text{K}$ . Devise a cell in which this reaction takes place and calculate the standard potential of the  $\text{Ag} | \text{AgI}_{(\text{s})}, \text{I}^-$  electrode.

(Ans.  $= -0.1523\text{V}$ )

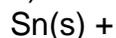
5) For the following cell,  $\text{Pt} | \text{H}_2 (\text{g}, 1 \text{ atm}) | \text{HI solution} (a = 1) | \text{I}_{2(\text{s})} | \text{Pt}$  calculate (i) the emf, (ii)  $\Delta G^0$  and (iii) equilibrium constant for the cell reaction at  $298\text{K}$ .

(Ans. (i)  $= 0.5355\text{V}$ ,  $\Delta G^0 = -51.68\text{kJ}$ , (iii)  $K = 1.111 \times 10^9$ )

6) Calculate the standard free energy change for the following reaction at  $298\text{K}$ :  $2\text{Au}_{(\text{s})} + \dots \rightarrow 2\text{Au}^{3+} + 3\text{Ca}_{(\text{s})}$ , state whether this reaction is spontaneous or not.

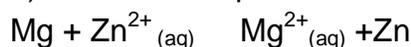
(Ans.  $\Delta G^0 = 2.53 \times 10^3\text{kJ/mol}$ , spontaneous)

7) Calculate the equilibrium constant for the following reaction at  $298\text{K}$ :



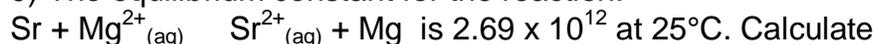
(Ans :  $K = 6.367 \times 10^9$ )

8) What is the equilibrium constant for the following reactions at  $25^\circ\text{C}$ .



(Ans.  $K = 1.536 \times 10^{51}$ )

9) The equilibrium constant for the reaction:



(Ans.  $= 0.368\text{V}$ )

## Type VI: Problems based on calculation of $\Delta G$ , $\Delta H$ and $\Delta S$

1) The emf of the cell,  $\text{Pb} | \text{PbCl}_{2(s)} , \text{KCl(soln)} , \text{Hg}_2\text{Cl}_{2(s)} | \text{Hg}$  is 0.5356 V at 298K. The temperature coefficient is  $1.45 \times 10^{-4} \text{VK}^{-1}$ . Calculate the  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the cell reaction at 298K.

$$(\text{Ans. } \Delta G = -103.4 \text{ kJ} , \Delta H = -95.03 \text{ kJ} , \Delta S = 27.99 \text{ JK}^{-1} )$$

2) For the cell,  $\text{Zn} | \text{ZnCl}_{2(aq)} | \text{AgCl}_{(s)} \text{Ag}$  the emf is 1.02 V at 273K and 1.0196 at 274K. Write the cell reaction and calculate  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for the cell reaction at 273K.

$$(\text{Ans. } \Delta H = -217.9 \text{ kJ} , \Delta S = -77.2 \text{ J} , \Delta G = -196.9 \text{ kJ} )$$

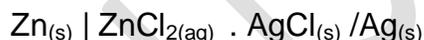
3) The emf of the cadmium – calomel cell in which the reaction  $\text{Cd} + \text{Hg}_2\text{Cl}_{2(s)} = \text{Cd}^{2+} + 2\text{Hg}$ , takes place is, represented by  $E = 0.6705 - 1.02 \times 10^{-4}(T - 298) - 2.40 \times 10^{-6}(T - 298)^2$  volt. Set up the cell and calculate  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for the cell reaction at 298K.

$$(\text{Ans. } \Delta H = -135.27 \text{ kJ} , \Delta S = -19.69 \text{ J} , \Delta G = -129.41 \text{ kJ} )$$

4) The emf of a Clark cell is 1.4209 V at 298 K and 1.391 V at 318 K. The cell reaction is  $\text{Zn} + \text{Hg}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + 2\text{Hg}$ , Calculate  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  at 298 K.

$$(\text{Ans. } : \Delta G = -274233 \text{ J} , \Delta S = -288.53 \text{ J.K}^{-1} \text{ and } \Delta H = -360215.6 \text{ J} )$$

5) The emf of the cell



is 0.20 at 275 K and 1.011 V at 285K.

Write the cell reaction, calculate temperature coefficient of cell emf and  $\Delta S$ ,  $\Delta G$ , and  $\Delta H$  at 285 K for the cell reaction.

$$(\text{Ans. } = - = 0.811 \text{ V K}^{-1} . \Delta S = 156523 \text{ J K}^{-1} , \Delta H = \Delta G_{285\text{K}} = 195123 \text{ J. mol}^{-1} \\ \Delta H = 4.449 \times 10^7 \text{ J mol}^{-1})$$

-----X-----