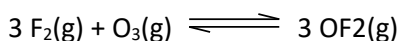


THERMODYNAMICS (no calculator)

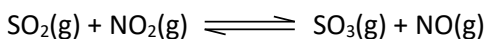
(All questions may be completed without a calculator. Answers given were generated without a calculator.)

- 1) For oxygen difluoride, $\text{OF}_2(\text{g})$, the Gibbs free energy of formation is +40.6 kJ/mol.
- a) Is the preparation of $\text{OF}_2(\text{g})$ from its elements at 25°C a spontaneous reaction? **[No, since $\Delta G^\circ > 0$.]**
- b) For ozone, $\text{O}_3(\text{g})$, the Gibbs free energy of formation is +163.43 kJ/mol. Is it theoretically possible to prepare $\text{OF}_2(\text{g})$ at 25°C by the reaction



[Yes, since $\Delta G^\circ < 0$]

- 2) The standard enthalpy of formation of $\text{CS}_2(\text{l})$ is +88 kJ/mol. The absolute molar entropy (S°) of C(graphite) is 6 J/mol-K, of S(rhombic) is 32 J/mol-K, and of $\text{CS}_2(\text{l})$ is 151 J/mol-K. Calculate the standard Gibbs free energy of formation of $\text{CS}_2(\text{l})$. **[+64 kJ/mol]**
- 3) Determine the approximate K_p value for the following reaction at 298 K:



given the molar Gibbs Free Energies of formation at 298 K:

$\text{SO}_2(\text{g}) = -300 \text{ kJ/mol}$; $\text{NO}_2(\text{g}) = +51 \text{ kJ/mol}$; $\text{SO}_3(\text{g}) = -371 \text{ kJ/mol}$ and $\text{NO}(\text{g}) = +87 \text{ kJ/mol}$
[about 1×10^6]

- 4) For each reaction, predict the sign and find the value of ΔS° :
- a) $3\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{HNO}_3(\text{l}) + \text{NO}(\text{g})$
- b) $\text{N}_2(\text{g}) + 3\text{F}_2(\text{g}) \rightleftharpoons 2\text{NF}_3(\text{g})$
- c) $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightleftharpoons 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

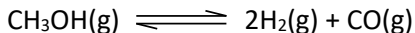
[Answers:

(a) negative, about $-2.7 \times 10^2 \text{ J/K}$

(b) negative, about $-2.8 \times 10^2 \text{ J/K}$

(c) positive, about $+9.7 \times 10^2 \text{ J/K}$]

- 5) One reaction used to produce small quantities of H₂ is:



Given the following data:

Compound	$\Delta H^\circ_{f,298}$ (kJ/mol)	S°_{298} (J/mol-K)
CH ₃ OH(g)	-201	238
H ₂ (g)		131
CO(g)	-110	198

- Determine ΔH°_{298} and ΔS°_{298} for the reaction.
- Assuming that these values are relatively independent of temperature, calculate ΔG° at 38°C, 138°C, and 238°C.
- What is the significance of the different values of ΔG° ?

[Answers:

(a) $\Delta H^\circ \approx +91$ kJ and $\Delta S^\circ \approx +222$ J/K

(b) $\Delta G^\circ_{38^\circ\text{C}} > 0$; $\Delta G^\circ_{138^\circ\text{C}} \approx 0$; $\Delta G^\circ_{238^\circ\text{C}} < 0$

(c) Not spontaneous at 38°C, at equilibrium at 138°C and spontaneous at 238°C.]

- 6) Complete the table below. Use either + (greater than zero), - (less than zero) or 0 for the values of ΔH , ΔS , and ΔG . Use either "spontaneous" or "not spontaneous" for the comment.

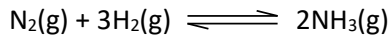
	ΔS_{sys}	ΔH_{sys}	ΔG_{sys}	Comment
(a)	+	-	-	
(b)		0	-	Spontaneous
(c)	-	+		Not spontaneous
(d)	0		-	Spontaneous
(e)		0	+	
(f)	+	+		Spontaneous only when $T\Delta S > \Delta H$

[(a) spontaneous; (b) positive; (c) positive; (d) negative; (e) negative and not spontaneous; (f) negative]

- 7) For the gaseous reaction between N₂O₅ and F₂ to form NF₃ and O₂:
- Write a balanced reaction.
 - Determine $\Delta G^\circ_{\text{rxn},298}$, given that the molar free energies of formation of N₂O₅(g) and NF₃(g) are 118 kJ and -83.3 kJ respectively.

[Answers: (a) $2\text{N}_2\text{O}_5(\text{g}) + 6\text{F}_2(\text{g}) \rightleftharpoons 4\text{NF}_3(\text{g}) + 5\text{O}_2(\text{g})$; (b) -569 kJ]

8) Consider the formation of ammonia:



- Calculate ΔH° and ΔS° for the reaction, given the molar enthalpy of formation of $\text{NH}_3(\text{g})$ is -45.9 kJ , and the molar entropies of $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$, and $\text{NH}_3(\text{g})$ are 191.5 J/K , 130.6 J/K , and 193 J/K respectively.
- Assuming that ΔH° and ΔS° are independent of temperature, find the temperature at which $K_p = 1.00$.
- Find K_p at 400°C , a typical temperature for NH_3 production.
- Given the lower K_p at the higher temperature, why are these conditions used industrially?

[Answers:

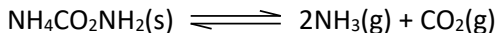
(a) $\Delta H^\circ = -91.8 \text{ kJ}$ and $\Delta S^\circ = -197 \text{ J/K}$,

(b) $K = 1.00$ at about $4.6 \times 10^2 \text{ K}$

(c) about 1×10^{-4}

(d) Because at higher temperatures the rate of the reaction is faster (chemical kinetics) and therefore more ammonia per unit time is produced under these conditions.

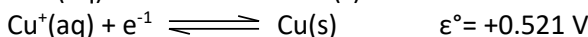
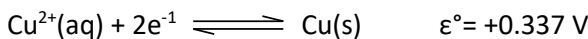
9) For the reaction:



$$\Delta G^\circ_{298} = +31.0 \text{ kJ and } \Delta H^\circ_{298} = +160 \text{ kJ}$$

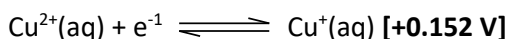
- Calculate the approximate value of K_p at 298 K. [**4×10^{-6}**]
- Calculate the approximate P_{NH_3} and P_{CO_2} at equilibrium at 298 K. [**$P_{\text{CO}_2} \approx 1 \times 10^{-2}$ bar and $P_{\text{NH}_3} \approx 2 \times 10^{-2}$ bar**]
- Calculate the approximate value of K_p at 500 K. [**2×10^5**]
- Calculate the approximate absolute molar entropy of NH_3 at 298 K given the following absolute molar entropies: $\text{CO}_2(\text{g}) = 214 \text{ J/mol-K}$ and $\text{NH}_4\text{CO}_2\text{NH}_2(\text{s}) = 166 \text{ J/mol-K}$. [**about $1.9 \times 10^2 \text{ J/mol-K}$**]

10) Given the following standard electrode potentials and Gibbs free energies of formation at 298 K answer the questions given below.

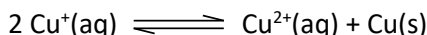


$$\Delta G^\circ_{f,298}(\text{Cu}(\text{OH})_2(\text{s})) = -356 \text{ kJ/mol}$$

a) Calculate ϵ° for the reaction



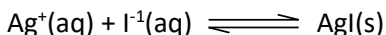
b) Calculate ΔG° and K_c at 298 K for the reaction:



$$\text{[-35 kJ and about } 10^6\text{]}$$

- Given the K_{sp} of $\text{Cu}(\text{OH})_2$ is 1.6×10^{-19} calculate the $\Delta G^\circ_{f,298}$ for $\text{OH}^{-1}(\text{aq})$. [**about -155 kJ/mol**]
- Using the Gibbs free energies of formation at 298 K for the $\text{OH}^{-1}(\text{aq})$ and $\text{H}^+(\text{aq})$ ions along with the $\Delta G^\circ_{f,298}$ for $\text{H}_2\text{O}(\text{l})$ (-237 kJ/mol), calculate the K_w for water at 25°C. [**about 1×10^{-14}**]

11) For the reaction



$$\epsilon^\circ_{298} = +0.95 \text{ V and } \Delta S^\circ_{298} = -73 \text{ J/K}$$

- Calculate ΔG° for the above reaction at 298 K. [**about $-9 \times 10^1 \text{ kJ}$**]
- Calculate ΔH° this reaction at 298 K. [**about $-1.1 \times 10^2 \text{ kJ}$**]
- Given that the Gibbs free energy of formation of $\text{Ag}^+(\text{aq})$ at 298 K is +77 kJ/mol, calculate ϵ°_{298} for the half-reaction

