## SURREY SUPPLEMENT: THERMODYNAMICS

1) For oxygen difluoride, $\mathrm{OF}_{2}(\mathrm{~g})$, the Gibbs free energy of formation is $+40.6 \mathrm{~kJ} / \mathrm{mol}$.
a) Is the preparation of $\mathrm{OF}_{2}(\mathrm{~g})$ from its elements at $25^{\circ} \mathrm{C}$ a spontaneous process? [No]
b) For ozone, $\mathrm{O}_{3}(\mathrm{~g})$, the Gibbs free energy of formation is $+163.43 \mathrm{~kJ} / \mathrm{mol}$. Is it theoretically possible to prepare $\mathrm{OF}_{2}(\mathrm{~g})$ at $25^{\circ} \mathrm{C}$ by the reaction:
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\(3 \mathrm{~F}_{2}(\mathrm{~g})+\mathrm{O}_{3}(\mathrm{~g}) \longrightarrow 3 \mathrm{~F}_{2}(\mathrm{~g})\)
[Yes]
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2) The standard enthalpy of formation of $\mathrm{CS}_{2}(\mathrm{I})$ is $+87.9 \mathrm{~kJ} / \mathrm{mol}$. The absolute molar entropy of C (graphite) is $5.69 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$, of S (rhombic) is $31.9 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$, and of $\mathrm{CS}_{2}(\mathrm{I})$ is $151.0 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$. Calculate the standard Gibbs free energy of formation of $\mathrm{CS}_{2}(\mathrm{I}) .[63.7 \mathrm{~kJ} / \mathrm{mol}]$
3) Look up the necessary data in the appendices of your textbook or online to determine the $K_{p, 298}$ value for the reaction:
$\mathrm{SO}_{2}(\mathrm{~g})+\mathrm{NO}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{SO}_{3}(\mathrm{~g})+\mathrm{NO}(\mathrm{g})$
[1.45 x 10 ${ }^{6}$ ]
4) For the reaction:
$\mathrm{NH}_{4} \mathrm{CO}_{2} \mathrm{NH}_{2}(\mathrm{~s}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})+\mathrm{CO}_{2}(\mathrm{~g})$
$\Delta \mathrm{G}^{\circ}{ }_{298}=+31.00 \mathrm{~kJ}$ and $\Delta \mathrm{H}^{\circ}{ }_{298}=+159.95 \mathrm{~kJ}$
a) Calculate the value of $K_{p}$ at 298 K [3.67 $\times \mathbf{1 0}^{-6}$ ]
b) Calculate the pressure of $\mathrm{NH}_{3}$ and $\mathrm{CO}_{2}$ at equilibrium at $298 \mathrm{~K}\left[\mathbf{P}_{\mathrm{co} 2}=\mathbf{9 . 7} \times \mathbf{1 0}^{-\mathbf{3}}\right.$ bar and $\left.\mathbf{P}_{\mathrm{NH} 3}=1.94 \times 10^{-2} \mathrm{bar}\right]$
c) Calculate the value of $\mathrm{K}_{\mathrm{p}}$ at $500 \mathrm{~K}\left[7.8 \times 10^{-5}\right]$
d) Calculate the absolute molar entropy of $\mathrm{NH}_{3}$ at 298 K given the following absolute molar entropies: $\mathrm{CO}_{2}(\mathrm{~g})=213.60 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$ and $\mathrm{NH}_{4} \mathrm{CO}_{2} \mathrm{NH}_{2}(\mathrm{~s})=166.10 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}[192.6 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$ ]
5) Given the following standard electrode potentials and Gibbs free energies of formation at 298 K :

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\begin{aligned}
& \mathrm{Cu}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightleftharpoons \mathrm{Cu}(\mathrm{~s}) \quad \varepsilon^{\circ}=+0.337 \mathrm{~V} \\
& \mathrm{Cu}^{+}(\mathrm{aq})+\mathrm{e}^{-} \rightleftharpoons \mathrm{Cu}(\mathrm{~s}) \varepsilon^{\circ}=+0.521 \mathrm{~V} \\
& \Delta \mathrm{G}^{\circ} \mathrm{f}, 298\left(\mathrm{Cu}(\mathrm{OH})_{2}(\mathrm{~s})\right)=-356 \mathrm{~kJ} / \mathrm{mol}
\end{aligned}
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a) Calculate $\varepsilon^{\circ}$ for the reaction: $\mathrm{Cu}^{2+}(\mathrm{aq})+\mathrm{e}^{-} \rightleftharpoons \mathrm{Cu}^{+}(\mathrm{aq})$ [0.152 V]
b) Calculate $\Delta \mathrm{G}^{\circ}$ and $\mathrm{K}_{\mathrm{c}}$ at 298 K for the reaction: $2 \mathrm{Cu}^{+}(\mathrm{aq}) \rightleftharpoons \mathrm{Cu}^{2+}(\mathrm{aq})+\mathrm{Cu}(\mathrm{s})$ [0.184 V]
c) Given the $\mathrm{K}_{\mathrm{sp}}$ of $\mathrm{Cu}(\mathrm{OH})_{2}=1.6 \times 10^{-19}$, calculate $\Delta \mathrm{G}^{\circ}{ }_{\mathrm{f}, 298}$ for $\mathrm{OH}^{-}(\mathrm{aq})$. [-156.9 kJ/mol]
d) Using the Gibbs free energies of formation at 298 K for the $\mathrm{OH}^{-}$and $\mathrm{H}^{+}$ions along with the $\Delta \mathrm{G}^{\circ}{ }_{\mathrm{f}, 298}$ for $\mathrm{H}_{2} \mathrm{O}(\mathrm{I})=-237 \mathrm{~kJ} / \mathrm{mol}$, calculate the $\mathrm{K}_{\mathrm{w}}$ for water at $25^{\circ} \mathrm{C}$. [9.1 $\times \mathbf{1 0}^{-15}$ ]
6) For the reaction:
$\mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{I}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{Agl}(\mathrm{s})$
$\varepsilon^{\circ}=+0.951 \mathrm{~V}$ at $25^{\circ} \mathrm{C}$ and $\mathrm{K}_{328}=1.88 \times 10^{14}$
a) Calculate $\Delta \mathrm{G}^{\circ}$ for the above reaction at 298 K [-91.8 kJ]
b) Calculate $\Delta \mathrm{H}^{\circ}$ and $\Delta \mathrm{S}^{\circ}$ for this reaction at 298 K . Assume that $\Delta \mathrm{H}^{\circ}$ and $\Delta \mathrm{S}^{\circ}$ are independent of temperature. [ $\Delta \mathrm{H}^{\circ}=-113.6 \mathrm{~kJ}$ and $\left.\Delta \mathrm{S}^{\circ}=-73.3 \mathrm{~J} / \mathrm{K}\right]$
c) Given that the Gibbs free energy of formation of $\mathrm{Ag}^{+}(\mathrm{aq})$ at 298 K is $+77.11 \mathrm{~kJ} / \mathrm{mol}$, calculate $\varepsilon^{\circ}{ }_{298}$ for the half reaction: $\mathrm{Ag}(\mathrm{s})+\mathrm{l}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{Agl}(\mathrm{s})+\mathrm{e}^{-}[0.152 \mathrm{~V}]$

