## THERMODYNAMICS (no calculator)

You can do all of these problems with or without a calculator. Answers given were generated without a calculator.

1) Given the reaction:

$$
2 \mathrm{X}(\mathrm{~g})+2 \mathrm{Y}(\mathrm{~g})+3 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{~W}(\mathrm{~g})+6 \mathrm{Z}(\mathrm{I})
$$

a) Use the enthalpies of formation given to calculate $\Delta H^{\circ}$ for the reaction. (-1250 kJ)

| Compound | $\Delta \mathrm{H}^{\circ} \mathrm{f}(\mathrm{kJ} / \mathrm{mol})$ |
| :---: | :---: |
| $\mathrm{X}(\mathrm{g})$ | -50 |
| $\mathrm{Y}(g)$ | -75 |
| $\mathrm{~W}(g)$ | +150 |
| $\mathrm{Z}(\mathrm{I})$ | -300 |

b) Calculate $\Delta E^{\circ}{ }_{298}$ for the reaction. ( $\mathbf{- 1 2 3 7 . 5} \mathbf{~ k J}$ )
2) Given the thermochemical equation:
$2 \mathrm{NaN}_{3}(s) \longrightarrow 2 \mathrm{Na}(\mathrm{s})+3 \mathrm{~N}_{2}(g) \Delta \mathrm{H}^{\circ}{ }_{298}=+42.7 \mathrm{~kJ}$
Calculate $\Delta H^{\circ}{ }_{f, 298}$ for $\mathrm{NaN}_{3}(s)$. (-21.35 kJ/mol)
3) A 10.00 mmol sample of $A(s)$ was reacted with excess $B(g)$ in a bomb calorimeter. The total heat capacity of the calorimeter was $10.00 \mathrm{~kJ} /{ }^{\circ} \mathrm{C}$. The temperature of the calorimeter and its contents increased from $24.00^{\circ} \mathrm{C}$ to $26.00^{\circ} \mathrm{C}$. Calculate $\Delta H^{\circ}{ }_{298}$ for the reaction:
$\mathrm{A}(\mathrm{s})+6 \mathrm{~B}(\mathrm{~g}) \longrightarrow 2 \mathrm{C}(\mathrm{g})+\mathrm{D}(\mathrm{g})$
(-2007.5 kJ)
4) Determine $\Delta H^{\circ}$ for the reaction
$2 \mathrm{MnO}_{2}(s)+\mathrm{CO}(g) \longrightarrow \mathrm{Mn}_{2} \mathrm{O}_{3}(s)+\mathrm{CO}_{2}(g)$
Given the following data:

| $\mathrm{MnO}_{2}(s)+\mathrm{CO}(g) \longrightarrow \mathrm{MnO}(s)+\mathrm{CO}_{2}(g)$ | $\Delta H^{\circ}=-150 \mathrm{~kJ}$ |
| :--- | :--- |
| $\mathrm{Mn}_{3} \mathrm{O}_{4}(s)+\mathrm{CO}(g) \longrightarrow 3 \mathrm{MnO}(s)+\mathrm{CO}_{2}(g)$ | $\Delta H^{\circ}=-55 \mathrm{~kJ}$ |
| $2 \mathrm{Mn}_{3} \mathrm{O}_{4}(\mathrm{~s})+\mathrm{CO}_{2}(g) \longrightarrow 3 \mathrm{Mn}_{2} \mathrm{O}_{3}(s)+\mathrm{CO}(g)$ | $\Delta H^{\circ}=+140 \mathrm{~kJ}$ |

(about - 217 kJ )
5) Given that $\Delta H^{\circ}{ }_{f}\left(\mathrm{CH}_{4}(g)\right)=-75 \mathrm{~kJ} / \mathrm{mol}$ and
$2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{C}(\mathrm{g}) \longrightarrow \mathrm{CH}_{4}(\mathrm{~g}) \Delta \mathrm{H}^{\circ}=-792 \mathrm{~kJ}$
Calculate $\Delta \mathrm{H}^{\circ}$ sub for C (graphite) in $\mathrm{kJ} / \mathrm{mol}$. ( $+717 \mathrm{~kJ} / \mathrm{mol}$ )
6) For oxygen difluoride, $\mathrm{OF}_{2}(g)$, the Gibbs free energy of formation is $+41 \mathrm{~kJ} / \mathrm{mol}$.
a) Is the preparation of $\mathrm{OF}_{2}(g)$ from its elements at $25^{\circ} \mathrm{C}$ a spontaneous reaction? EXPLAIN. (NO)
b) For ozone, $\mathrm{O}_{3}(\mathrm{~g})$, the Gibbs free energy of formation is $+163 \mathrm{~kJ} / \mathrm{mol}$. Why isn't the Gibbs free energy of formation of ozone $=0$ ? (See your class notes)
c) Is it theoretically possible to prepare $\mathrm{OF}_{2}(g)$ at $25^{\circ} \mathrm{C}$ by the reaction:

$$
3 \mathrm{~F}_{2}(\mathrm{~g})+\mathrm{O}_{3}(\mathrm{~g}) \longrightarrow 3 \mathrm{FF}_{2}(\mathrm{~g})
$$

(YES)
7) The standard enthalpy of formation of $\mathrm{CS}_{2}(\mathrm{I})$ at 298 K is $+90 \mathrm{~kJ} / \mathrm{mol}$. The absolute molar entropy ( $S^{\circ}$ ) of C (graphite) at 298 K is $6 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$, of $\mathrm{S}\left(\right.$ rhombic) is $32 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$, and of $\mathrm{CS}_{2}(\mathrm{I})$ is $151 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$. Calculate the standard Gibbs free energy of formation of $\mathrm{CS}_{2}(\mathrm{I})$ at 298 K .
( $\Delta \boldsymbol{G}^{\circ}{ }_{f, 298} \cong \mathbf{~ + ~} \mathbf{6 6} \mathrm{~kJ} / \mathrm{mol}$ )
8) When 100 mL of 0.1250 M HCl at $24.00^{\circ} \mathrm{C}$ was mixed with 250 mL of $0.1000 \mathrm{M} \mathrm{Ba}(\mathrm{OH})_{2}$ at $24.00^{\circ} \mathrm{C}$ (assume the calorimeter constant $=0 \mathrm{~J} /{ }^{\circ} \mathrm{C}$ ), the temperature rose to $24.50^{\circ} \mathrm{C}$.
Calculate $\Delta H^{\circ}$ for the reaction
$2 \mathrm{HCl}(a q)+\mathrm{Ba}(\mathrm{OH})_{2}(a q) \longrightarrow \mathrm{BaCl}_{2}(a q)+2 \mathrm{H}_{2} \mathrm{O}(/)$
Assume the specific heat for the solution is $4.184 \mathrm{~J} / \mathrm{g}-{ }^{\circ} \mathrm{C}$. In calculating heat flow assume no heat is lost to the surroundings and ignore the small amount of water formed in the reaction.
(-117 kJ)
9) For the reaction
$\mathrm{A}(\mathrm{s}) \rightleftharpoons 2 \mathrm{~B}(\mathrm{~g})+\mathrm{C}(\mathrm{g})$
$\Delta \mathrm{G}^{\circ}{ }_{298}=+23.0 \mathrm{~kJ}$ and $\Delta \mathrm{H}^{\circ}{ }_{298}=+150 \mathrm{~kJ}$
a) Calculate the approximate value of $K_{p}$ at $298 \mathrm{~K} .\left(1 \times \mathbf{1 0}^{-4}\right)$
b) Calculate $\mathrm{P}_{\mathrm{B}}$ and $\mathrm{P}_{\mathrm{C}}$ at equilibrium at 298 K . ( $\mathrm{P}_{\mathrm{B}} \approx \mathbf{6 \times 1 0 ^ { - 2 }}$ bar and $\mathrm{P}_{\mathrm{C}} \approx \mathbf{3 \times 1 0 ^ { - \mathbf { 2 } }}$ bar)
c) Calculate the approximate value of $K_{p}$ at $500 \mathrm{~K} .\left(\mathbf{1} \times \mathbf{1 0}^{6}\right)$
d) Calculate the absolute molar entropy of B at 298 K given that the absolute molar entropies of $\mathrm{C}(\mathrm{g})$ and $\mathrm{A}(\mathrm{s})$ are $200 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$ and $150 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$ respectively. ( $185 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$ )
10) Given the following standard electrode potentials and Gibbs free energies of formation at 298 K :
$\mathrm{M}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \longrightarrow \mathrm{M}(\mathrm{s}) \quad \varepsilon^{\circ}=+0.3 \mathrm{~V}$
$\mathrm{M}^{+}(\mathrm{aq})+\mathrm{e}^{-} \longrightarrow \mathrm{M}(\mathrm{s}) \varepsilon^{\circ}=+0.5 \mathrm{~V}$
(You may use the value for the Faraday as $1 \times 10^{5}$ Coulombs for these calculations.)
a) Calculate $\varepsilon^{\circ}$ for the reaction

$$
\begin{aligned}
& \mathrm{M}^{2+}(\mathrm{aq})+\mathrm{e}^{-} \longrightarrow \mathrm{M}^{+}(\mathrm{aq}) \\
& \left(\varepsilon^{\circ}=+0.1 \mathrm{~V}\right)
\end{aligned}
$$

b) Calculate $\Delta G^{\circ}$ and $K_{c}$ at 298 K for the reaction

$$
2 \mathrm{M}^{+}(\mathrm{aq}) \rightleftharpoons \mathrm{M}^{2+}(\mathrm{aq})+\mathrm{M}(\mathrm{~s})
$$

$$
\left(\Delta \mathrm{G}^{\circ} \approx-40 \mathrm{~kJ} \text { and } \mathrm{K}_{\mathrm{c}} \approx 1 \times 10^{7}\right)
$$

11) For the reaction
$\mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{r}^{-}(\mathrm{aq}) \longrightarrow \mathrm{AgI}(\mathrm{s})$
$\varepsilon^{\circ}{ }_{298}=+0.95 \mathrm{~V}$ and $\Delta \mathrm{G}^{\circ}{ }_{328}=-90 \mathrm{~kJ}$
(You may use the value for the Faraday as $1 \times 10^{5}$ Coulombs for these calculations.)
a) Calculate $\Delta \mathrm{G}^{\circ}$ for the above reaction at $298 \mathrm{~K} .(-95 \mathrm{~kJ})$
b) Calculate $\Delta \mathrm{S}^{\circ}$ and $\Delta \mathrm{H}^{\circ}$ for this reaction at 298 K . Assume that $\Delta \mathrm{S}^{\circ}$ and $\Delta \mathrm{H}^{\circ}$ are independent of temperature. ( $\Delta \mathrm{S}^{\circ} \approx \mathbf{- 1 7 0 ~ J} / \mathrm{K}$ and $\Delta \mathrm{H}^{\circ} \approx \mathbf{- 1 4 6} \mathbf{~ k J}$ )
c) Given that the Gibbs free energy of formation of $\mathrm{Ag}^{+}(\mathrm{aq})$ at 298 K is $+77 \mathrm{~kJ} / \mathrm{mol}$, calculate $\Delta \mathrm{G}^{\circ}{ }_{298}$ and $\varepsilon^{\circ}{ }_{298}$ for the half-reaction

$$
\mathrm{Ag}(\mathrm{~s})+\mathrm{l}^{-}(\mathrm{aq}) \longrightarrow \mathrm{Agl}(\mathrm{~s})+\mathrm{e}^{-}
$$

$\left(\varepsilon^{\circ}{ }_{298}=+0.18 \mathrm{~V}\right.$ and $\left.\Delta \mathrm{G}^{\circ}{ }_{298}=-18 \mathrm{~kJ}\right)$

