

## PROBLEM SET 4

### Problem 6

	$\Delta H_{\text{reaction}}^{\circ}$ (kJ mol <sup>-1</sup> )
$\text{Fe}(s) + \text{CO}(g) \rightarrow \text{FeO}(s) + \text{C}(\text{graphite})$	-155.8
$\text{CO}_2(s) \rightarrow \text{CO}(g) + 1/2 \text{O}_2(g)$	282.98
$\text{C}(\text{graphite}) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$	-393.51
$\text{Fe}(g) + 1/2 \text{O}_2(g) \rightarrow \text{FeO}(s)$	$\Delta H_f^{\circ} = -266.3 \text{ kJ mol}^{-1}$
$\Delta H_{\text{reaction}}^{\circ}$ (kJ mol <sup>-1</sup> )	
$2\text{Fe}(g) + 3\text{CO}(g) \rightarrow \text{Fe}_2\text{O}_3(s) + 3\text{C}(\text{graphite})$	-492.6
$3\text{C}(\text{graphite}) + 3\text{O}_2(g) \rightarrow 3\text{CO}_2(g)$	-3×393.51
$3\text{CO}_2(g) \rightarrow 3\text{CO}(g) + 3/2\text{O}_2(g)$	3×282.98
$2\text{Fe}(g) + 3/2\text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s)$	$\Delta H_f^{\circ} = -824.2 \text{ kJ mol}^{-1}$

### Problem 7

$$\Delta H_f^{\circ}(\text{NO}, g, 840\text{K}) = \Delta H_f^{\circ}(\text{NO}, g, 298.15\text{K}) + \int_{298.15}^{650} \Delta C_p \left( \frac{T}{\text{K}} \right) d \frac{T}{\text{K}}$$

$$\begin{aligned} \Delta C_p &= C_{p,m}(\text{NO}, g) - \frac{1}{2} C_{p,m}(\text{N}_2, g) - \frac{1}{2} C_{p,m}(\text{O}_2, g) \\ &= (29.86 - 0.5 \times 29.13 - 0.5 \times 29.38) \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 0.605 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta H_f^{\circ}(\text{NO}, g, 840\text{K}) &= \Delta H_f^{\circ}(\text{NO}, g, 298.15\text{K}) + \left[ \int_{298.15}^{650} 0.605 d \frac{T}{\text{K}} \right] \text{ J mol}^{-1} \\ &= \Delta H_f^{\circ}(\text{NO}, g, 298.15\text{K}) + 0.328 \text{ kJ mol}^{-1} = 91.3 \text{ kJ mol}^{-1} + 0.328 \text{ kJ mol}^{-1} = 91.6 \text{ kJ mol}^{-1} \end{aligned}$$

### Problem 8

$$\Delta H_{\text{reaction}}^{\circ}(650\text{K}) = \Delta H_{\text{reaction}}^{\circ}(298.15\text{K}) + \int_{298.15}^{650} \Delta C_p \left( \frac{T}{\text{K}} \right) d \frac{T}{\text{K}}$$

$$\Delta C_p = 5C_{p,m}(\text{N}_2, g) + 6C_{p,m}(\text{H}_2\text{O}, g) - 4C_{p,m}(\text{NH}_3, g) - 6C_{p,m}(\text{NO}, g)$$

$$= \begin{bmatrix} (5 \times 30.81 + 6 \times 33.80 - 4 \times 29.29 - 6 \times 33.58) \\ -(5 \times 0.01187 + 6 \times 0.00795 + 4 \times 0.01103 - 6 \times 0.02593) \frac{T}{\text{K}} \\ + (5 \times 2.3968 + 6 \times 2.8228 - 4 \times 4.2446 - 6 \times 5.3326) \times 10^{-5} \frac{T^2}{\text{K}^2} \\ -(5 \times 1.0176 + 6 \times 1.3115 - 4 \times 2.7706 - 6 \times 2.7744) \times 10^{-8} \frac{T^3}{\text{K}^3} \end{bmatrix} \text{J K}^{-1} \text{mol}^{-1}$$

$$\int_{298.15}^{650} \Delta C_p \left( \frac{T}{\text{K}} \right) d \frac{T}{\text{K}} = \left[ 38.21 + 0.00441 \frac{T}{\text{K}} - 2.0053 \times 10^{-4} \frac{T^2}{\text{K}^2} + 1.4772 \times 10^{-8} \frac{T^3}{\text{K}^3} \right] \text{J K}^{-1} \text{mol}^{-1}$$

$$= \left[ \int_{298.15}^{650} \left( 38.21 + 0.00441 \frac{T}{\text{K}} - 2.0053 \times 10^{-4} \frac{T^2}{\text{K}^2} + 1.4772 \times 10^{-8} \frac{T^3}{\text{K}^3} \right) d \frac{T}{\text{K}} \right] \text{J mol}^{-1}$$

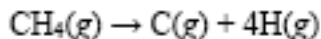
$$= (13.444 - 0.736 - 16.585 + 0.630) \text{kJ mol}^{-1} = -1.775 \text{J mol}^{-1}$$

$$\Delta H_{\text{reaction}}^{\circ}(298.15\text{K}) = 5\Delta H_f^{\circ}(\text{N}_2, g) + 6\Delta H_f^{\circ}(\text{H}_2\text{O}, g) - 4\Delta H_f^{\circ}(\text{NH}_3, g) - 6\Delta H_f^{\circ}(\text{NO}, g)$$

$$\Delta H_{\text{reaction}}^{\circ}(298.15\text{K}) = -6 \times 241.826 \text{kJ mol}^{-1} + 4 \times 45.94 \text{kJ mol}^{-1} - 6 \times 90.25 \text{kJ mol}^{-1} = -1809 \text{kJ mol}^{-1}$$

$$\Delta H_{\text{reaction}}^{\circ}(650\text{K}) = -1809 \text{kJ mol}^{-1} - 1.775 \text{kJ mol}^{-1} = -1810 \text{kJ mol}^{-1}$$

### Problem 10



$$\Delta H_{\text{reaction}}^{\circ} = 4\Delta H_f^{\circ}(\text{H}, g) + \Delta H_f^{\circ}(\text{C}, g) - \Delta H_f^{\circ}(\text{CH}_4, g)$$

$$= 4 \times 218.0 \text{kJ mol}^{-1} + 716.7 \text{kJ mol}^{-1} + 74.6 \text{kJ mol}^{-1} = 1663 \text{kJ mol}^{-1}$$

$$\text{Average Bond Enthalpy} = \frac{1663 \text{kJ mol}^{-1}}{4} = 415.8 \text{kJ mol}^{-1}$$

$$\text{Relative Error} = 100 \times \frac{415.8 \text{kJ mol}^{-1} - 411 \text{kJ mol}^{-1}}{415.8 \text{kJ mol}^{-1}} = 1.2\%$$

**Problem 13**

$$\Delta H_{\text{reaction}}^{\circ}(300 \text{ K}) = \Delta H_{\text{reaction}}^{\circ}(1000 \text{ K}) + \int_{1000 \text{ K}}^{300 \text{ K}} \Delta C_p(T) dT$$

For this problem, the heat capacities are assumed to be independent of  $T$ .

$$\begin{aligned} \Delta H_{\text{reaction}}^{\circ}(300 \text{ K}) &= \Delta H_{\text{reaction}}^{\circ}(1000 \text{ K}) + \Delta C_p \Delta T \\ &= -123.77 \text{ kJ mol}^{-1} + [2C_{p,m}(\text{NH}_3, g) - C_{p,m}(\text{N}_2, g) - 3C_{p,m}(\text{H}_2, g)] [-700 \text{ K}] \\ &= -123.77 \text{ kJ mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times [2 \times 4.217 - 3.502 - 3 \times 3.466] [-700 \text{ K}] \\ &= -91.96 \text{ kJ mol}^{-1} \end{aligned}$$

**Problem 15**

For the reaction  $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2\text{O}(g)$

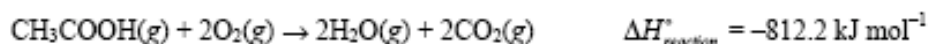
$$\begin{aligned} \Delta H_{\text{reaction}}^{\circ}(391.4 \text{ K}) &= \Delta H_{\text{reaction}}^{\circ}(373.15 \text{ K}) + [C_{p,m}(\text{H}_2\text{O}(g)) - C_{p,m}(\text{H}_2\text{O}(l))] \Delta T \\ &= 40.656 \text{ kJ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} [4.038 - 9.055] \times [391.4 \text{ K} - 373.15 \text{ K}] \\ &= 39.911 \text{ kJ mol}^{-1} \end{aligned}$$

For the reaction  $\text{CH}_3\text{COOH}(l) + 2\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) + 2\text{CO}_2(g)$

$$\begin{aligned} \Delta H_{\text{reaction}}^{\circ}(391.4 \text{ K}) &= \Delta H_{\text{reaction}}^{\circ} + \Delta C_p \Delta T \\ &= -871.5 \text{ kJ mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} [2 \times 4.46 + 2 \times 9.055 - 14.9 - 2 \times 3.53] \times [391.4 \text{ K} - 298 \text{ K}] \\ &= -867.6 \text{ kJ mol}^{-1} \end{aligned}$$

The table above can now be rewritten with all enthalpy values given at 391.4 K.

	$\Delta H_{\text{reaction}}^{\circ}(391.4 \text{ K})$ (kJ mol <sup>-1</sup> )
$\text{CH}_3\text{COOH}(l) + 2\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) + 2\text{CO}_2(g)$	-867.6 kJ mol <sup>-1</sup>
$\text{CH}_3\text{COOH}(g) \rightarrow \text{CH}_3\text{COOH}(l)$	-24.4 kJ mol <sup>-1</sup>
$2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2\text{O}(g)$	$2 \times 39.911$ kJ mol <sup>-1</sup>



**Problem 18**

The average single bond enthalpy Si-F is calculated as follows:



$$\text{Average Si-F bond enthalpy in SiF}_4 = \frac{2382 \text{ kJ mol}^{-1}}{4} = 596 \text{ kJ mol}^{-1}$$

$$\Delta U^{\circ} = \Delta H^{\circ} - \Delta nRT$$

$$= 2382 \text{ kJ mol}^{-1} - 4 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 2372 \text{ kJ mol}^{-1}$$

### Average single bond enthalpy in SiCl<sub>4</sub>



$$\text{Average single bond enthalpy in SiCl}_4 = \frac{1592 \text{ kJ mol}^{-1}}{4} = 398 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta U^{\circ} &= \Delta H^{\circ} - \Delta nRT \\ &= 1592 \text{ kJ mol}^{-1} - 4 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 1582 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Average Si-Cl bond energy in SiCl}_4 = \frac{1582 \text{ kJ mol}^{-1}}{4} = 396 \text{ kJ mol}^{-1}$$

### Average single bond enthalpy in CF<sub>4</sub>



$$\text{Average single bond enthalpy in CF}_4 = \frac{1959 \text{ kJ mol}^{-1}}{4} = 489 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta U^{\circ} &= \Delta H^{\circ} - \Delta nRT \\ &= 1959 \text{ kJ mol}^{-1} - 4 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 1949 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Average C-F bond energy in CF}_4 = \frac{1949 \text{ kJ mol}^{-1}}{4} = 487 \text{ kJ mol}^{-1}$$

### Average single bond enthalpy in NF<sub>3</sub>



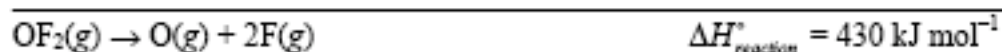
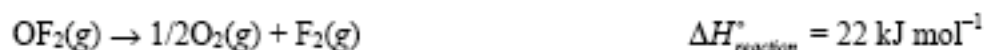


$$\text{Average single bond enthalpy in NF}_3 = \frac{836 \text{ kJ mol}^{-1}}{3} = 279 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta U^{\circ} &= \Delta H^{\circ} - \Delta nRT \\ &= 836 \text{ kJ mol}^{-1} - 3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 828 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Average N-F bond energy in NF}_3 = \frac{828 \text{ kJ mol}^{-1}}{3} = 276 \text{ kJ mol}^{-1}$$

#### Average single bond enthalpy in OF<sub>2</sub>

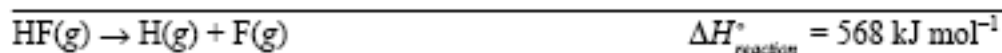
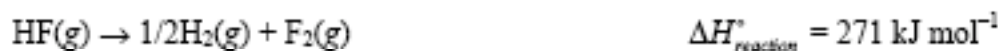


$$\text{Average single bond enthalpy in OF}_2 = \frac{430 \text{ kJ mol}^{-1}}{2} = 215 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta U^{\circ} &= \Delta H^{\circ} - \Delta nRT \\ &= 430 \text{ kJ mol}^{-1} - 2 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 425 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Average O-F bond energy in OF}_2 = \frac{425 \text{ kJ mol}^{-1}}{2} = 213 \text{ kJ mol}^{-1}$$

#### Average single bond enthalpy in HF



$$\text{Average single bond enthalpy in HF} = 568 \text{ kJ mol}^{-1}$$

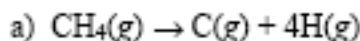
$$\begin{aligned} \Delta U^{\circ} &= \Delta H^{\circ} - \Delta nRT \\ &= 568 \text{ kJ mol}^{-1} - 1 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 565 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Average single bond energy in HF} = 565 \text{ kJ mol}^{-1}$$

**Problem 19**

- a) The C–H bond in CH<sub>4</sub>
- b) The C–C single bond in C<sub>2</sub>H<sub>6</sub>
- c) The C=C double bond in C<sub>2</sub>H<sub>4</sub>

Use your result from part (a) to solve parts (b) and (c).

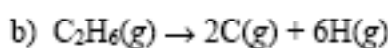


$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= 4\Delta H_f^{\circ}(\text{H}, g) + \Delta H_f^{\circ}(\text{C}, g) - 4\Delta H_f^{\circ}(\text{CH}_4, g) \\ &= 4 \times 218.0 \text{ kJ mol}^{-1} + 716.7 \text{ kJ mol}^{-1} - 4 \times 74.6 \text{ kJ mol}^{-1} \\ &= 1663 \text{ kJ mol}^{-1}\end{aligned}$$

$$\text{Average C–H bond enthalpy in CH}_4 = \frac{1663 \text{ kJ mol}^{-1}}{4} = 416 \text{ kJ mol}^{-1}$$

$$\begin{aligned}\Delta U^{\circ} &= \Delta H^{\circ} - \Delta nRT \\ &= 1663 \text{ kJ mol}^{-1} - 3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 1654 \text{ kJ mol}^{-1}\end{aligned}$$

$$\text{Average C–H bond energy in CH}_4 = \frac{1654 \text{ kJ mol}^{-1}}{4} = 413 \text{ kJ mol}^{-1}$$



$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= 2\Delta H_f^{\circ}(\text{C}, g) + 6\Delta H_f^{\circ}(\text{H}, g) - \Delta H_f^{\circ}(\text{C}_2\text{H}_6, g) \\ &= 2 \times 716.7 \text{ kJ mol}^{-1} + 6 \times 218.0 \text{ kJ mol}^{-1} - 84.0 \text{ kJ mol}^{-1} \\ &= 2825 \text{ kJ mol}^{-1}\end{aligned}$$

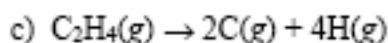
$$\Delta H_{\text{reaction}}^{\circ} = 6 \times \text{C–H bond enthalpy} + \text{C–C bond enthalpy}$$

$$\begin{aligned}\text{C–C bond enthalpy} &= 2825 \text{ kJ mol}^{-1} - 6 \times 416 \text{ kJ mol}^{-1} \\ &= 329 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta U^{\circ} &= \Delta H^{\circ} - \Delta nRT \\ &= 2825 \text{ kJ mol}^{-1} - 7 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 2808 \text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta U^{\circ} = 6 \times \text{C–H bond energy} + \text{C–C bond energy}$$

$$\begin{aligned}\text{C–C bond energy} &= 2808 \text{ kJ mol}^{-1} - 6 \times 413 \text{ kJ mol}^{-1} \\ &\approx 329 \text{ kJ mol}^{-1}\end{aligned}$$



$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= 2\Delta H_f^{\circ}(\text{C}, g) + 4\Delta H_f^{\circ}(\text{H}, g) - \Delta H_f^{\circ}(\text{C}_2\text{H}_4, g) \\ &= 2 \times 716.7 \text{ kJ mol}^{-1} + 4 \times 218 \text{ kJ mol}^{-1} - 52.4 \text{ kJ mol}^{-1} \\ &= 2253 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= 4 \times \text{C-H bond enthalpy} + \text{C=C bond enthalpy} \\ \text{C=C bond enthalpy} &= 2253 \text{ kJ mol}^{-1} - 4 \times 416 \text{ kJ mol}^{-1} \\ &= 589 \text{ kJ mol}^{-1}\end{aligned}$$

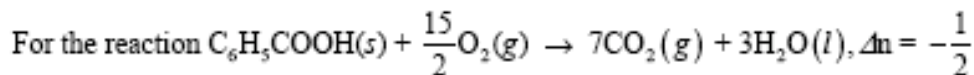
$$\begin{aligned}\Delta U^{\circ} &= \Delta H^{\circ} - \Delta nRT \\ &= 2253 \text{ kJ mol}^{-1} - 5 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 2240 \text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta U^{\circ} = 4 \times \text{C-H bond energy} + \text{C=C bond energy}$$

$$\begin{aligned}\text{C-C bond energy} &= 2240 \text{ kJ mol}^{-1} - 4 \times 413 \text{ kJ mol}^{-1} \\ &= 588 \text{ kJ mol}^{-1}\end{aligned}$$

### Problem 21

$$\Delta U_{\text{combustion}} = \Delta H_{\text{combustion}} - \Delta nRT$$



$$\Delta U_{\text{combustion}} = -3226.87 \text{ kJ mol}^{-1} - \frac{1}{2} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = -3228.11 \text{ kJ mol}^{-1}$$

$$\begin{aligned}C_{\text{calorimeter}} &= \frac{-\frac{m_s}{M_s} \Delta U_R - \frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} C_{\text{H}_2\text{O},m} \Delta T}{\Delta T} \\ &= \frac{\frac{1.350 \text{ g}}{122.13 \text{ g mol}^{-1}} \times 3228.11 \times 10^3 \text{ J mol}^{-1} - \frac{1.240 \times 10^3 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.291 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.45^{\circ} \text{C}}{3.45^{\circ} \text{C}} \\ &= 5.16 \times 10^3 \text{ J}^{\circ} \text{C}^{-1}\end{aligned}$$



**Problem 22**

$$0 = \frac{m_s}{M_s} \Delta H_{\text{solution,m}} + \frac{m_{H_2O}}{M_{H_2O}} C_{H_2O,m} \Delta T + C_{\text{calorimeter}} \Delta T$$

$$\Delta H_{\text{solution,m}} = - \frac{\left( \frac{225 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.291 \text{ J K}^{-1} \text{ mol}^{-1} \times 0.151^\circ \text{C} + 330 \text{ J K}^{-1} \times 0.151^\circ \text{C} \right)}{0.225 \text{ L} \times 0.200 \text{ mol L}^{-1}}$$

$$= -2.86 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta H_{\text{solution,m}} = 2\Delta H_{\text{solution,m}}(\text{Na}^+, \text{aq}) + \Delta H_{\text{solution,m}}(\text{SO}_4^{2-}, \text{aq}) - \Delta H_f(\text{Na}_2\text{SO}_4, \text{s})$$

$$= -2 \times 240.3 \times 10^3 \text{ J mol}^{-1} - 909.3 \times 10^3 \text{ J mol}^{-1} + 1387.1 \times 10^3 \text{ J mol}^{-1}$$

$$= -2.4 \times 10^3 \text{ J mol}^{-1}$$

$$\text{The relative error is } \frac{-2.86 \text{ kJ mol}^{-1} + 2.4 \text{ kJ mol}^{-1}}{-2.86 \text{ kJ mol}^{-1}} = 16\%$$