PROBLEM SET 4

Problem 6

	$\Delta H^\circ_{reaction}$ (kJ mol^{-1})
$Fe(s) + CO(g) \rightarrow FeO(s) + C(graphite)$	-155.8
$CO_2(s) \rightarrow CO(g) + 1/2\ O_2(g)$	282.98
$C(graphite) + O_2(g) \rightarrow CO_2(g)$	-393.51
$Fe(g) + 1/2\ O_2(g) \rightarrow FeO(s)$	$\Delta H^\circ_f = -266.3$ kJ mol^{-1}

	$\Delta H^\circ_{reaction}$ (kJ mol^{-1})
$2Fe(g) + 3CO(g) \rightarrow Fe_2O_3(s) + 3C(graphite)$	-492.6
$3C(graphite) + 3O_2(g) \rightarrow 3CO_2(g)$	-3×393.51
$3CO_2(g) \rightarrow 3CO(g) + 3/2O_2(g)$	3×282.98
$2Fe(g) + 3/2O_2(g) \rightarrow Fe_2O_3(s)$	$\Delta H^\circ_f = -824.2$ kJ mol^{-1}

Problem 7

$$\Delta H^\circ_f(\mathrm{NO}, g, 840K) = \Delta H^\circ_f(\mathrm{NO}, g, 298.15K) + \int_{298.15}^{650} \Delta C_P\left(\frac{T}{K}\right) d\frac{T}{K}$$

$$\Delta C_P = C_{P,m}(\mathrm{NO}, g) - \frac{1}{2}C_{P,m}(\mathrm{N_2}, g) - \frac{1}{2}C_{P,m}(\mathrm{O_2}, g)$$

$$= (29.86 - 0.5\times 29.13 - 0.5\times 29.38)\ \mathrm{J\,K^{-1}mol^{-1}}$$

$$= 0.605\ \mathrm{J\,K^{-1}mol^{-1}}$$

$$\Delta H^\circ_f(\mathrm{NO}, g, 840\ \mathrm{K}) = \Delta H^\circ_f(\mathrm{NO}, g, 298.15\ \mathrm{K}) + \left[\int_{298.15}^{650} 0.605\, d\frac{T}{K}\right] \mathrm{J\,mol^{-1}}$$

$$= \Delta H^\circ_f(\mathrm{NO}, g, 298.15\ \mathrm{K}) + 0.328\ \mathrm{kJ\,mol^{-1}} = 91.3\ \mathrm{kJ\,mol^{-1}} + 0.328\ \mathrm{kJ\,mol^{-1}} = 91.6\ \mathrm{kJ\,mol^{-1}}$$

Problem 8

$$\Delta H^\circ_{reaction}(650K) = \Delta H^\circ_{reaction}(298.15K) + \int_{298.15}^{650} \Delta C_P\left(\frac{T}{\mathrm{K}}\right) d\frac{T}{\mathrm{K}}$$

$$\Delta C_P = 5C_{P,m}(\mathrm{N_2},g) + 6C_{P,m}(\mathrm{H_2O},g) - 4C_{P,m}(\mathrm{NH_3},g) - 6C_{P,m}(\mathrm{NO},g)$$

$$= \begin{bmatrix} (5\times30.81 + 6\times33.80 - 4\times29.29 - 6\times33.58) \\ -(5\times0.01187 + 6\times0.00795 + 4\times0.01103 - 6\times0.02593)\dfrac{T}{\mathrm{K}} \\ +(5\times2.3968 + 6\times2.8228 - 4\times4.2446 - 6\times5.3326)\times10^{-5}\dfrac{T^2}{\mathrm{K}^2} \\ -(5\times1.0176 + 6\times1.3115 - 4\times2.7706 - 6\times2.7744)\times10^{-8}\dfrac{T^3}{\mathrm{K}^3} \end{bmatrix} \mathrm{J\,K^{-1}mol^{-1}}$$

$$\int_{298.15}^{650} \Delta C_P\left(\frac{T}{\mathrm{K}}\right) d\frac{T}{\mathrm{K}} = \left[38.21 + 0.00441\frac{T}{\mathrm{K}} - 2.0053\times10^{-4}\frac{T^2}{\mathrm{K}^2} + 1.4772\times10^{-8}\frac{T^3}{\mathrm{K}^3}\right] \mathrm{J\,K^{-1}mol^{-1}}$$

$$= \left[\int_{298.15}^{650}\left(38.21 + 0.00441\frac{T}{\mathrm{K}} - 2.0053\times10^{-4}\frac{T^2}{\mathrm{K}^2} + 1.4772\times10^{-8}\frac{T^3}{\mathrm{K}^3}\right) d\frac{T}{\mathrm{K}}\right] \mathrm{J\,mol^{-1}}$$

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

$$\Delta H^\circ_{reaction}(298.15\ \mathrm{K}) = 5\Delta H^\circ_f(\mathrm{N_2},g) + 6\Delta H^\circ_f(\mathrm{H_2O},g) - 4\Delta H^\circ_f(\mathrm{NH_3},g) - 6\Delta H^\circ_f(\mathrm{NO},g)$$

$$\Delta H^\circ_{reaction}(298.15\ \mathrm{K}) = -6\times241.826\ \mathrm{kJ\,mol^{-1}} + 4\times45.94\ \mathrm{kJ\,mol^{-1}} - 6\times90.25\ \mathrm{kJ\,mol^{-1}} = -1809\ \mathrm{kJ\,mol^{-1}}$$

$$\Delta H^\circ_{reaction}(650\ \mathrm{K}) = -1809\ \mathrm{kJ\,mol^{-1}} - 1.775\ \mathrm{kJ\,mol^{-1}} = -1810\ \mathrm{kJ\,mol^{-1}}$$

Problem 10

$CH_4(g) \rightarrow C(g) + 4H(g)$

$$\Delta H^\circ_{reaction} = 4\Delta H^\circ_f(\mathrm{H},g) + \Delta H^\circ_f(\mathrm{C},g) - \Delta H^\circ_f(\mathrm{CH_4},g)$$

$$= 4\times218.0\ \mathrm{kJ\,mol^{-1}} + 716.7\ \mathrm{kJ\,mol^{-1}} + 74.6\ \mathrm{kJ\,mol^{-1}} = 1663\ \mathrm{kJ\,mol^{-1}}$$

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

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

Problem 13

$$\Delta H^{\circ}_{reaction}(300\text{ K}) = \Delta H^{\circ}_{reaction}(1000\text{ K}) + \int_{1000\text{ K}}^{300\text{K}} \Delta C_P(T)\,dT$$

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

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

Problem 15

For the reaction $2H_2O(l) \rightarrow 2H_2O(g)$

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

For the reaction $CH_3COOH(l) + 2O_2(g) \rightarrow 2H_2O(l) + 2CO_2(g)$

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

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

	$\Delta H^{\circ}_{reaction}$ (391.4 K) (kJ mol^{-1})
$CH_3COOH(l) + 2O_2(g) \rightarrow 2H_2O(l) + 2CO_2(g)$	-867.6 kJ mol^{-1}
$CH_3COOH(g) \rightarrow CH_3COOH(l)$	-24.4 kJ mol^{-1}
$2H_2O(l) \rightarrow 2H_2O(g)$	2×39.911 kJ mol^{-1}
$CH_3COOH(g) + 2O_2(g) \rightarrow 2H_2O(g) + 2CO_2(g)$	$\Delta H^{\circ}_{reaction} = -812.2$ kJ mol^{-1}

Problem 18

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

$SiF_4(g) \rightarrow Si(s) + 2F_2(g)$	$\Delta H^\circ_{reaction} = 1614.9\ \text{kJ mol}^{-1}$
$2F_2(g) \rightarrow 4F(g)$	$\Delta H^\circ_{reaction} = 4 \times 79.4\ \text{kJ mol}^{-1}$
$Si(s) \rightarrow Si(g)$	$\Delta H^\circ_{reaction} = 450\ \text{kJ mol}^{-1}$
$SiF_4(g) \rightarrow Si(g) + 4F(g)$	$\Delta H^\circ_{reaction} = 2382\ \text{kJ mol}^{-1}$

$$\text{Average Si–F bond enthalpy in } SiF_4 = \frac{2382\ \text{kJ mol}^{-1}}{4} = 596\ \text{kJ mol}^{-1}$$

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

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

Average single bond enthalpy in $SiCl_4$

$SiCl_4(g) \rightarrow Si(s) + 2Cl_2(g)$	$\Delta H^\circ_{reaction} = 657.0\ \text{kJ mol}^{-1}$
$Si(s) \rightarrow Si(s)$	$\Delta H^\circ_{reaction} = 450\ \text{kJ mol}^{-1}$
$2Cl_2(g) \rightarrow 4Cl(g)$	$\Delta H^\circ_{reaction} = 4\times 121.3\ \text{kJ mol}^{-1}$
$SiCl_4(g) \rightarrow Si(s) + 4Cl(g)$	$\Delta H^\circ_{reaction} = 1592\ \text{kJ mol}^{-1}$

Average single bond enthalpy in SiCl4 = $\dfrac{1592\ \text{kJ mol}^{-1}}{4} = 398\ \text{kJ mol}^{-1}$

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

Average Si–Cl bond energy in $SiCl_4$ = $\dfrac{1582\ \text{kJ mol}^{-1}}{4} = 396\ \text{kJ mol}^{-1}$

Average single bond enthalpy in CF_4

$CF_4(g) \rightarrow C(s) + 2F_2(g)$	$\Delta H^\circ_{reaction} = 925\ \text{kJ mol}^{-1}$
$C(s) \rightarrow C(s)$	$\Delta H^\circ_{reaction} = 716.7\ \text{kJ mol}^{-1}$
$2F_2(g) \rightarrow 4F(g)$	$\Delta H^\circ_{reaction} = 4\times 79.4\ \text{kJ mol}^{-1}$
$CF_4(g) \rightarrow C(s) + 4F(g)$	$\Delta H^\circ_{reaction} = 1959\ \text{kJ mol}^{-1}$

Average single bond enthalpy in CF_4 = $\dfrac{1959\ \text{kJ mol}^{-1}}{4} = 489\ \text{kJ mol}^{-1}$

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

Average C–F bond energy in CF_4 = $\dfrac{1949\ \text{kJ mol}^{-1}}{4} = 487\ \text{kJ mol}^{-1}$

Average single bond enthalpy in NF_3

$NF_3(g) \rightarrow 1/2N_2(g) + 3/2F_2(g)$	$\Delta H^\circ_{reaction} = 125\ \text{kJ mol}^{-1}$
$1/2N_2(g) \rightarrow N(g)$	$\Delta H^\circ_{reaction} = 472.7\ \text{kJ mol}^{-1}$
$3/2F_2(g) \rightarrow 3F(g)$	$\Delta H^\circ_{reaction} = 3\times 79.4\ \text{kJ mol}^{-1}$

$NF_3(g) \rightarrow N(g) + 3F(g)$ $\Delta H^\circ_{reaction} = 836\ kJ\ mol^{-1}$

Average single bond enthalpy in $NF_3 = \dfrac{836\ kJ\ mol^{-1}}{3} = 279\ kJmol^{-1}$

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

$= 836\ kJ\ mol^{-1} - 3 \times 8.314\ J\ mol^{-1}\ K^{-1} \times 298.15\ K = 828\ kJ\ mol^{-1}$

Average N–F bond energy in $NF_3 = \dfrac{828\ kJ\ mol^{-1}}{3} = 276\ kJ\ mol^{-1}$

Average single bond enthalpy in OF_2

$OF_2(g) \rightarrow 1/2O_2(g) + F_2(g)$	$\Delta H^\circ_{reaction} = 22\ kJ\ mol^{-1}$
$1/2O_2(g) \rightarrow O(g)$	$\Delta H^\circ_{reaction} = 249.2\ kJ\ mol^{-1}$
$F_2(g) \rightarrow 2F(g)$	$\Delta H^\circ_{reaction} = 2 \times 79.4\ kJ\ mol^{-1}$
$OF_2(g) \rightarrow O(g) + 2F(g)$	$\Delta H^\circ_{reaction} = 430\ kJ\ mol^{-1}$

Average single bond enthalpy in $OF_2 = \dfrac{430\ kJ\ mol^{-1}}{2} = 215\ kJ\ mol^{-1}$

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

$= 430\ kJ\ mol^{-1} - 2 \times 8.314\ J\ mol^{-1}\ K^{-1} \times 298.15\ K = 425\ kJ\ mol^{-1}$

Average O–F bond energy in $OF_2 = \dfrac{425\ kJ\ mol^{-1}}{2} = 213\ kJ\ mol^{-1}$

Average single bond enthalpy in HF

$HF(g) \rightarrow 1/2H_2(g) + F_2(g)$	$\Delta H^\circ_{reaction} = 271\ kJ\ mol^{-1}$
$\frac{1}{2}H_2(g) \rightarrow H(g)$	$\Delta H^\circ_{reaction} = 218\ kJ\ mol^{-1}$
$\frac{1}{2}F_2(g) \rightarrow F(g)$	$\Delta H^\circ_{reaction} = 79.4\ kJ\ mol^{-1}$
$HF(g) \rightarrow H(g) + F(g)$	$\Delta H^\circ_{reaction} = 568\ kJ\ mol^{-1}$

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

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

$= 568\ kJ\ mol^{-1} - 1 \times 8.314\ J\ mol^{-1}\ K^{-1} \times 298.15\ K = 565\ kJ\ mol^{-1}$

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

Problem 19

a) The C–H bond in CH_4
b) The C–C single bond in C_2H_6
c) The C=C double bond in C_2H_4

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

a) $CH_4(g) \rightarrow C(g) + 4H(g)$

$$\Delta H^\circ_{reaction} = 4\Delta H^\circ_f(\mathrm{H}, g) + 4\Delta H^\circ_f(\mathrm{C}, g) - 4\Delta H^\circ_f(\mathrm{CH_4}, g)$$
$$= 4\times 218.0 \text{ kJ mol}^{-1} + 716.7 \text{ kJ mol}^{-1} + 74.6 \text{ kJ mol}^{-1}$$
$$=1663 \text{ kJ mol}^{-1}$$

Average C–H bond enthalpy in CH_4 = $\dfrac{1663 \text{ kJ mol}^{-1}}{4}$ = 416 kJ mol^{-1}

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

Average C–H bond energy in CH_4 = $\dfrac{1654 \text{ kJ mol}^{-1}}{4}$ = 413 kJ mol^{-1}

b) $C_2H_6(g) \rightarrow 2C(g) + 6H(g)$

$$\Delta H^\circ_{reaction} = 6\Delta H^\circ_f(\mathrm{H}, g) + 2\Delta H^\circ_f(\mathrm{C}, g) - \Delta H^\circ_f(\mathrm{C_2H_6}, g)$$
$$= 6\times 218.0 \text{ kJ mol}^{-1} + 2\times 716.7 \text{ kJ mol}^{-1} + 84.0 \text{ kJ mol}^{-1}$$
$$= 2825 \text{ kJ mol}^{-1}$$

$\Delta H^\circ_{reaction}$ = 6 × C–H bond enthalpy + C–C bond enthalpy

C–C bond enthalpy = 2825 kJ mol^{-1} – 6 × 416 kJ mol^{-1}
= 329 kJ mol^{-1}

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

ΔU° = 6 × C–H bond energy + C–C bond energy

C–C bond energy = 2808 kJ mol^{-1} – 6 × 413 kJ mol^{-1}
≈ 329 kJ mol^{-1}

c) $C_2H_4(g) \rightarrow 2C(g) + 4H(g)$

$$\Delta H^\circ_{reaction} = 2\Delta H^\circ_f(\mathrm{C}, g) + 4\Delta H^\circ_f(\mathrm{H}, g) - \Delta H^\circ_f(\mathrm{C_2H_4}, g)$$
$$= 2\times 716.7\ \mathrm{kJ\ mol^{-1}} + 4\times 218\ \mathrm{kJ\ mol^{-1}} - 52.4\ \mathrm{kJ\ mol^{-1}}$$
$$= 2253\ \mathrm{kJ\ mol^{-1}}$$

$\Delta H^\circ_{reaction}$ = 4 × C–H bond enthalpy + C=C bond enthalpy

C=C bond enthalpy = 2253 kJ mol^{-1} – 4 × 416 kJ mol^{-1}

= 589 kJ mol^{-1}

$$\Delta U^\circ = \Delta H^\circ - \Delta nRT$$
$$= 2253\ \mathrm{kJ\ mol^{-1}} - 5\times 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}} \times 298.15\ \mathrm{K} = 2240\ \mathrm{kJ\ mol^{-1}}$$

ΔU° = 4 × C–H bond energy + C=C bond energy

C–C bond energy = 2240 kJ mol^{-1} – 4 × 413 kJ mol^{-1}

= 588 kJ mol^{-1}

Problem 21

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

For the reaction $C_6H_5COOH(s) + \frac{15}{2}O_2(g) \rightarrow 7CO_2(g) + 3H_2O(l)$, $\Delta n = -\frac{1}{2}$

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

$$C_{calorimeter} = \frac{-\frac{m_s}{M_s}\Delta U_R - \frac{m_{H_2O}}{M_{H_2O}} C_{H_2O,m}\Delta T}{\Delta T}$$

$$= \frac{\frac{1.350\ \mathrm{g}}{122.13\ \mathrm{g\ mol^{-1}}}\times 3228.11\times 10^3\ \mathrm{J\ mol^{-1}} - \frac{1.240\times 10^3\ \mathrm{g}}{18.02\ \mathrm{g\ mol^{-1}}}\times 75.291\ \mathrm{J\ mol^{-1}\ K^{-1}}\times 3.45\ ^\circ\mathrm{C}}{3.45\ ^\circ\mathrm{C}}$$

$$= 5.16\times 10^3\ \mathrm{J\ ^\circ C^{-1}}$$

Problem 22

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

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

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

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

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

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

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