

Thermochemistry

- **Thermochemistry**: the study of energy (in the form of heat) changes that accompany physical & chemical changes
- heat flows from high to low (hot → cool)
- **endothermic reactions**: absorb energy in the form of heat; show a positive value for quantity of heat ($q > 0$)
- **exothermic reactions**: release energy in the form of heat; show a negative value for quantity of heat ($q < 0$)

Magnitude of Heat Flow:

- units of heat energy:
 $1 \text{ kcal} = 1000 \text{ cal} = 1 \text{ Cal (nutritional)}$
 $1 \text{ kJ} = 1,000 \text{ J}$
 $1 \text{ calorie} = 4.184 \text{ J}$
 $1 \text{ kcal} = 4.184 \text{ kJ}$
- The relationship between magnitude of heat flow, q , and temperature change, Δt , is:

$$q = c \cdot \Delta T$$

q = magnitude of heat
 c = heat capacity ($\text{J}/^\circ\text{C}$) of a calorimeter
 Δt = change in temperature

- for a pure substance of mass m , the expression of q can be written as:

(constant state) $q = m \cdot c \cdot \Delta T$

q = magnitude of heat
 m = mass
 c = specific heat of substance ($\text{J}/\text{g} \cdot ^\circ\text{C}$)
 Δt = change in temperature

- **specific heat** = the amount of heat that must be added to a stated mass of liquid to raise its temp. by 1°C , with no change in state.

specific heat values (in $\text{J} / \text{g} \cdot ^\circ\text{C}$):

$\text{CO}_2 (\text{g}) = 0.843 \text{ J}/\text{g} \cdot ^\circ\text{C}$
 $\text{Cu} (\text{s}) = 0.382 \text{ J}/\text{g} \cdot ^\circ\text{C}$
 $\text{Fe} (\text{s}) = 0.446 \text{ J}/\text{g} \cdot ^\circ\text{C}$
 $\text{H}_2\text{O} (\text{l}) = 4.184 \text{ J}/\text{g} \cdot ^\circ\text{C}$

Examples:

1. How much heat is given off by a 50.0 g sample of copper when it cools from 80.0 to 50.0°C?

$$q = m \cdot c \cdot \Delta T$$

$$q = (50.0 \text{ g})(0.382 \text{ J/g}\cdot^\circ\text{C})(-30.0^\circ\text{C})$$

$$q = \boxed{-573 \text{ J}} \text{ (heat is given off)}$$

2. Iron has a specific heat of 0.446 J/g°C. When a 7.55 g piece of iron absorbs 10.33 J of heat, what is the change in temperature? If it was originally at room temp. (22.0°C), what is the final temperature?

$$q = m \cdot c \cdot \Delta T$$

$$10.33 \text{ J} = (7.55 \text{ g})(0.446 \text{ J/g}\cdot^\circ\text{C})(\Delta T)$$

$$\Delta T = 3.07^\circ\text{C} = T_f - 22.0^\circ\text{C}$$

$$T_f = \boxed{25.1^\circ\text{C}}$$

3. The specific heat of copper is 0.382 J/g°C. How much heat is absorbed by a copper plate with a mass of 135.5 g to raise its temperature from 25.0°C to oven temperature (420°F)?

$$^\circ\text{F} = (1.8)(^\circ\text{C}) + 32$$

$$420 = (1.8)(T_f) + 32$$

$$T_f = 215.6^\circ\text{C}$$

$$q = m \cdot c \cdot \Delta T$$

$$q = (135.5 \text{ g})(0.382 \text{ J/g}\cdot^\circ\text{C})(215.6^\circ\text{C} - 25.0^\circ\text{C})$$

$$q = \boxed{9870 \text{ J}}$$

Calorimetry

- to measure the heat flow in a reaction, it is carried out in a calorimeter.

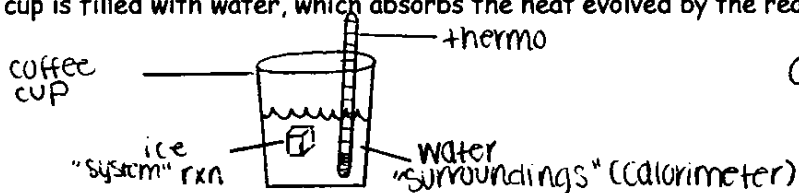
$$q_{\text{rxn}} = -q_{\text{calorimeter system}}$$

- it is possible to calculate the amt. of heat absorbed or evolved in a reaction if you know the heat capacity, C_{cal} , and the temp. change, ΔT , of the calorimeter:

$$q_{\text{rxn}} = -C_{\text{cal}} \cdot \Delta T$$

Coffee Cup Calorimeter

- the cup is filled with water, which absorbs the heat evolved by the reaction, so:



$$q_{\text{ice}} = m_w \cdot C_w \cdot \Delta T$$

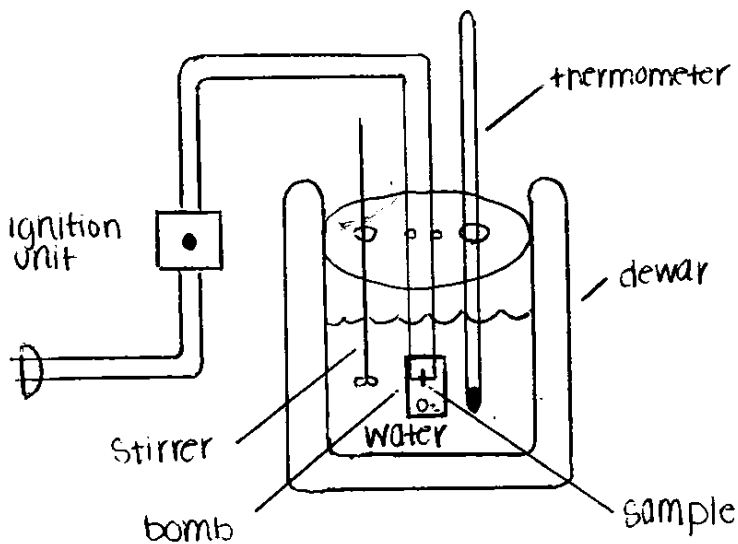
Example: When 1.00 g of ammonium nitrate, NH_4NO_3 , is added to 50.0 g of water in a coffee cup calorimeter, it dissolves, $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq})$, and the temperature of the water drops from 25.00°C to 23.32°C . Calculate q for the reaction system.

$$q_{\text{cal}} = m_w \cdot C_w \cdot \Delta T$$

$$q_{\text{cal}} = (50.0\text{g})(4.18\text{J/g}\cdot^\circ\text{C})(-1.68^\circ\text{C})$$

$$q_{\text{cal}} = -351\text{J (water releases heat)}$$

$$q_{\text{rxn}} = -q_{\text{cal}} = -(-351\text{J}) = 351\text{J (endothermic)}$$

Bomb Calorimeter:

Examples:

1. The reaction between hydrogen and chlorine, $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$, can be studied in a bomb calorimeter. It is found that when a 1.00 g sample of H_2 reacts completely, the temp. rises from 20.00°C to 29.82°C . Taking the heat capacity of the calorimeter to be $9.33 \text{ kJ}/^\circ\text{C}$, calculate the amount of heat evolved in the reaction.

$$q_{\text{cal}} = (9.33 \text{ kJ}/^\circ\text{C})(29.82^\circ\text{C} - 20.00^\circ\text{C})$$

$$q_{\text{cal}} = 91.6 \text{ kJ}$$

$$q_{\text{rxn}} = -q_{\text{cal}} = \boxed{-91.6 \text{ kJ}}$$

2. When 1.00 mol of caffeine ($\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$) is burned in air, $4.96 \times 10^3 \text{ kJ}$ of heat is evolved. Five grams of caffeine is burned in a bomb calorimeter. The temperature is observed to increase by 11.37°C . What is the heat capacity of the calorimeter in $\text{J}/^\circ\text{C}$?

$$q_{\text{cal}} = -q_{\text{rxn}} = -(-128 \text{ kJ}) = 128 \text{ kJ}$$

$$q_{\text{rxn}} = \frac{4.96 \times 10^3 \text{ kJ}}{1 \text{ mol } \text{C}_8\text{H}_{10}\text{N}_4\text{O}_2} \times \frac{5.00 \text{ g}}{194.0 \text{ g}} = -128 \text{ kJ}$$

$$128 \text{ kJ} = (C_{\text{cal}})(11.37^\circ\text{C})$$

$$C_{\text{cal}} = 11.2 \text{ kJ}/^\circ\text{C} = \boxed{11250 \text{ J}/^\circ\text{C}}$$

3. When twenty milliliters of ethyl ether, $\text{C}_4\text{H}_{10}\text{O}$, ($d=0.714 \text{ g/mL}$) is burned in a bomb calorimeter, the temperature rises from 24.7°C to 88.9°C . The calorimeter heat capacity is $10.34 \text{ kJ}/^\circ\text{C}$.

- a. What is q for the calorimeter?

$$q_{\text{cal}} = (10.34 \text{ kJ}/^\circ\text{C})(88.9^\circ\text{C} - 24.7^\circ\text{C})$$

$$q_{\text{cal}} = \boxed{664 \text{ kJ}}$$

- b. What is q when 20.0 mL of ether is burned?

$$q_{\text{rxn}} = -q_{\text{cal}}$$

$$q_{\text{rxn}} = \boxed{-664 \text{ kJ}}$$

- c. What is q for the combustion of one mole of ethyl ether?

$$\frac{-664 \text{ kJ}}{20.0 \text{ mL } \text{C}_4\text{H}_{10}\text{O}} \times \frac{1 \text{ mL}}{0.714 \text{ g}} \times \frac{74 \text{ g}}{1 \text{ mol}} = -3.44 \times 10^3 \text{ kJ/mol}$$

Enthalpy

- Enthalpy = a type of chemical energy, sometimes referred to as "heat content"

- exothermic reactions:

$$q = \Delta H < 0 \text{ (negative values)}$$

- endothermic reactions:

$$q = \Delta H > 0 \text{ (positive values)}$$

Thermochemical Equations

- a chemical equation that shows the enthalpy (ΔH) is a thermochemical equation.

Rules of Thermochemistry:

Rule #1) The magnitude of ΔH is directly proportional to the amount of reactant or product.

Example: $H_2 + Cl_2 \rightarrow 2HCl \Delta H = -185 \text{ kJ}$

Calculate ΔH when 1.00 g of Cl_2 reacts.

$$\frac{-185 \text{ kJ}}{70.9 \text{ g}} = \frac{x}{1.00 \text{ g}}$$

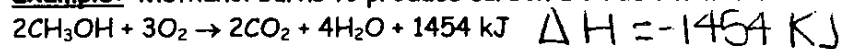
$$x = \boxed{-2.61 \text{ kJ}}$$

Example: When an ice cube weighing 24.6 g of ice melts, it absorbs 8.19 kJ of heat. Calculate ΔH when 1.00 mol of solid water melts.

$$\frac{8.19 \text{ kJ}}{24.6 \text{ g}} = \frac{x}{18.0 \text{ g}}$$

$$x = \boxed{5.99 \text{ kJ}}$$

Example: Methanol burns to produce carbon dioxide and water:

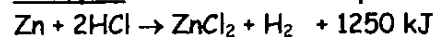


What mass of methanol is needed to produce 1820 kJ?

$$\frac{-1454 \text{ kJ}}{64.1 \text{ g}} = \frac{-1820 \text{ kJ}}{x}$$

$$x = \boxed{80.1 \text{ g}}$$

Example: How much heat is produced when 58.0 liters of hydrogen (at STP) are also produced?



$$\frac{-1250 \text{ kJ}}{22.4 \text{ L}} = \frac{x}{58.0 \text{ L}}$$

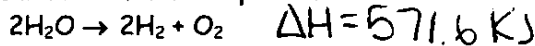
$$x = \boxed{-3240 \text{ kJ}}$$

Rule #2) ΔH for a reaction is equal in the magnitude but opposite in sign to ΔH for the reverse reaction. (If 6.00 kJ of heat absorbed when a mole of ice melts, then 6.00 kJ of heat is given off when 1.00 mol of liquid water freezes)

Ex: Given:



Calculate ΔH for the equation:

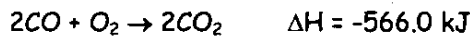


x2; FIIP

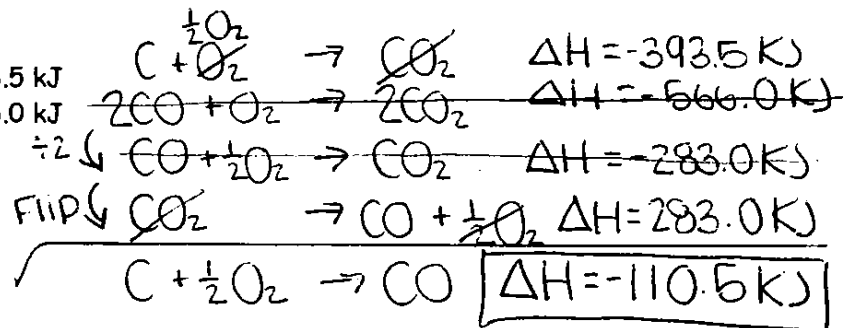
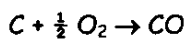
Rule #3) The value of ΔH for a reaction is the same whether it occurs in one step or in a series of steps. ΔH for the overall equation is the sum of the ΔH 's for the individual equations:

Hess's Law: $\Delta H = \Delta H_1 + \Delta H_2 + \dots$

Example: Given:



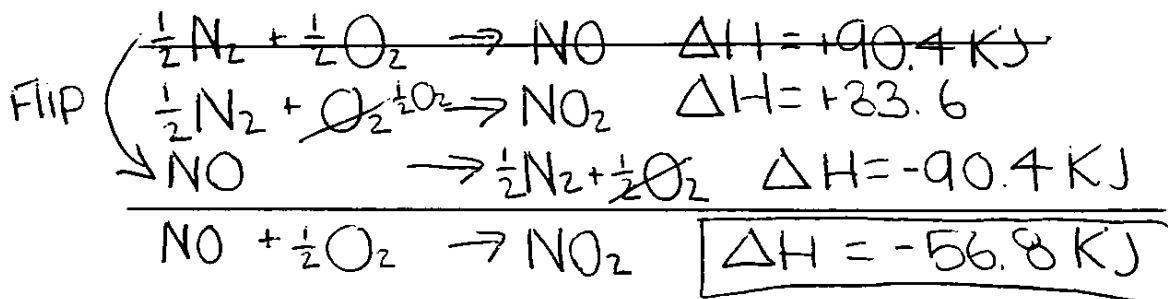
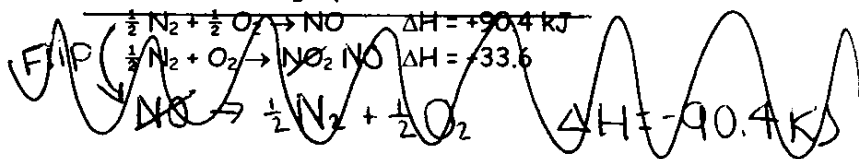
Calculate ΔH for the reaction:



Example: Find the heat of reaction (enthalpy) for the following reaction



Given the following equations....



Heat Transfer in Liquids and Solids

- **specific heat** = the amt of heat that must be added to a stated mass of a substance to raise its temp by 1°C, with no change in state.

Ex: How much heat is released by 250.0 g of H₂O as it cools from 85.0°C to 40.0°C? (specific heat of water = 4.18 J/g°C)

$$q = m \cdot c \cdot \Delta T$$

$$q = (250.0g)(4.18 J/g \cdot ^\circ C)(40.0^\circ C - 85.0^\circ C)$$

$$q = -47025 \approx -47000 \text{ J} = \boxed{-47.0 \text{ KJ}}$$

- **heat of vaporization:** the amt of heat that must be added to 1 g of a liquid at its boiling point to convert it to vapor with no change in temp.

$$q = mH_{\text{vap}}$$

- heat of vaporization of water = 2260 J/g

Ex: How much heat energy is required to bring 135.5 g of water at 55.0°C to its boiling point (100°C) and then vaporize it?

$$q = m \cdot c \cdot \Delta T$$

$$q_{55 \rightarrow 100} = (135.5g)(4.18 J/g \cdot ^\circ C)(45.0^\circ C) = 255 \text{ KJ}$$

$$q_{\text{vap}} = (135.5g)(2260 \text{ J/g}) = 306 \text{ KJ}$$

$$q_{\text{Total}} = \boxed{332 \text{ KJ}}$$

- **heat of fusion:** the amt of heat needed to melt 1 g of a solid at its melting point.

- heat of fusion of ice = 334 J/g $q = mH_{\text{fus}}$

- When substances change state, they often have different specific heats:

specific heat of ice = 2.09 J/g°C
 specific heat of water = 4.18 J/g°C
 specific heat of steam = 2.03 J/g°C

Ex: How much heat energy is required to convert 15.0 g of ice at -12.5°C to steam at 123.0°C?

$$\text{ice } q = (15.0g)(2.09 J/g \cdot ^\circ C)(12.5^\circ C) = 391.875 \text{ J}$$

$$q_{\text{fus}} = (15.0g)(334 J/g) = 5010 \text{ J}$$

$$\text{water } q = (15.0g)(4.18 J/g \cdot ^\circ C)(100^\circ C - 0^\circ C) = 6270 \text{ J}$$

$$q_{\text{vap}} = (15.0g)(2260 J/g) = 33900 \text{ J}$$

$$\text{steam } q = (15.0g)(2.03 J/g \cdot ^\circ C)(123.0^\circ C - 100^\circ C) = 700.35 \text{ J}$$

$$\boxed{4523 \text{ KJ}}$$

Enthalpies of Formation

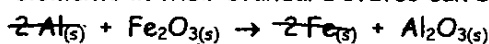
enthalpy change (delta) ΔH_f° = enthalpy of formation
 Standard conditions (25°C, 1atm)
 formation

- usually exothermic
- see table 8.3 for ΔH_f° value
- enthalpy of formation of an element in its stable state = 0
- these can be used to calculate ΔH° for a reaction
- standard enthalpy change, ΔH° , for a given thermochemical equation is = to the sum of the standard enthalpies of formation of the product - the standard enthalpies of formation of the reactants.

$$\Delta H_{rxn}^\circ = \sum n_p \Delta H_f^\circ (\text{products}) - \sum n_r \Delta H_f^\circ (\text{reactants})$$

sum of (sigma) moles

- elements in their standard states can be omitted:



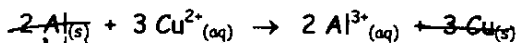
$$\Delta H_{rxn} = \sum (\Delta H_f^\circ \text{ products}) - \sum (\Delta H_f^\circ \text{ reactants})$$

$$\Delta H_{rxn} = \Delta H_f^\circ \text{Al}_2\text{O}_3 - \Delta H_f^\circ \text{Fe}_2\text{O}_3$$

$$\Delta H_{rxn} = (-1676 \text{ kJ}) - (-822.1 \text{ kJ})$$

$$\Delta H_{rxn} = -853.9 \text{ kJ} \approx -854 \text{ kJ}$$

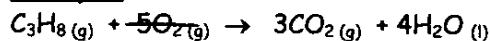
- the coefficient of the products and reactants in the thermochemical equation must be taken into account:



$$\Delta H_{rxn} = 2(-531.0 \text{ kJ}) - 3(64.8 \text{ kJ})$$

$$\Delta H_{rxn} = -1256.4 \text{ kJ}$$

Example: Calculate ΔH for the combustion of one mole of propane:



$$\Delta H_{rxn} = [3(-393.5 \text{ kJ}) + 4(-285.8 \text{ kJ})] - (-103.8 \text{ kJ})$$

$$\Delta H_{rxn} = -2219.9 \text{ kJ}$$

Example: The thermochemical equation for the combustion of benzene,

C_6H_6 , is:



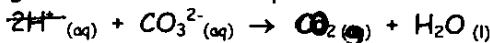
$$\Delta H^\circ = -3267.4 \text{ kJ}$$

$$-3267.4 \text{ kJ} = [6(-393.5 \text{ kJ}) + 3(-285.8 \text{ kJ})] - (\Delta H_f^\circ \text{C}_6\text{H}_6)$$

$$-49 \text{ kJ} = -\Delta H_f^\circ \text{C}_6\text{H}_6$$

$$\Delta H_f^\circ \text{C}_6\text{H}_6 = 49 \text{ kJ}$$

Example: When hydrochloric acid is added to a solution of sodium carbonate, carbon dioxide gas is formed. The equation for the reaction is:



Calculate ΔH° for this thermochemical equation.

$$\Delta H_{rxn} = (-393.5 \text{ kJ}) + (-285.8 \text{ kJ}) - (-677.1 \text{ kJ})$$

$$\Delta H_{rxn} = -2.2 \text{ kJ}$$

Thermodynamics

• THERMODYNAMICS = the study of energy changes that accompany physical and chemical changes.

• Enthalpy (H): the total energy "stored" within a substance

• Enthalpy change (ΔH): a comparison of the total enthalpies of the product & reactants

• Exothermic reactions/changes: release energy in the form of heat; have negative ΔH values.

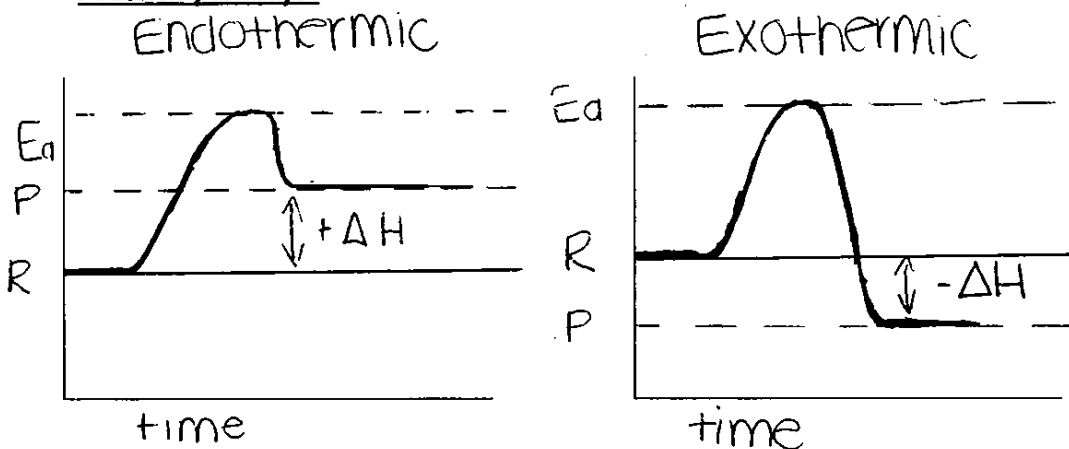


• Endothermic reactions/changes: absorb energy in the form of heat; have positive ΔH values.



• Changes that involve a decrease in enthalpy are favored!

Reaction pathways:



• Entropy (S): the measure of the degree of disorder in a system; in nature, things tend to increase in entropy, or disorder.

$$\Delta S = S_{\text{products}} - S_{\text{reactants}}$$

• all physical & chemical changes involve a change in entropy, or ΔS. (remember that high entropy is favorable)

• enthalpy and entropy are DRIVING FORCES for spontaneous reactions (rxns that *happen* at normal conditions)

• it is the interplay of these 2 driving forces that determines whether or not a physical or chemical change will actually happen.

- **Free Energy (G):** relates enthalpy and entropy in a way that indicates which predominates; the quantity of energy that is available or stored to do work or cause change.

$$\Delta G = \Delta H - T\Delta S$$

where:

ΔG = change in free energy (kJ)
 ΔH = change in enthalpy (kJ)
 T = absolute temp (K)
 ΔS = change in entropy (kJ/K)

ΔG : pos value means change is NOT spon.

ΔG : neg value means change IS spon.

Relating Enthalpy and Entropy to Spontaneity

Example of reaction	ΔH	ΔS	Spontaneity
$2K + 2H_2O \rightarrow 2KOH + H_2$	-	+	always
$H_2O_{(g)} \rightarrow H_2O_{(l)}$	-	-	@ low temps
$H_2O_{(s)} \rightarrow H_2O_{(l)}$	+	+	@ high temps
$16CO_2 + 18H_2O \rightarrow 2C_8H_{18} + 25O_2$	+	-	never

Examples:

1) For the decomposition of $O_3(g)$ to $O_2(g)$: $2O_{3(g)} \rightarrow 3O_{2(g)}$
 $\Delta H = -285.4 \text{ kJ/mol}$ and $\Delta S = 137.55 \text{ J/mol}\cdot\text{K}$ at 25°C .

ON TEST

a) Calculate ΔG for the reaction.

$$\Delta G = (-285.4 \text{ kJ/mol}) - (289 \text{ K})(0.13755 \text{ kJ/mol}\cdot\text{K})$$

$$\Delta G = -326.4 \text{ kJ}$$

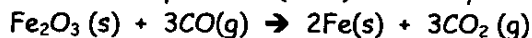
b) Is the reaction spontaneous?

yes

c) Is ΔH or ΔS (or both) favorable for the reaction?

Both ΔS & ΔH are favorable (both are driving forces)

2) What is the minimum temperature (in $^\circ\text{C}$) necessary for the following reaction to occur spontaneously?



$\Delta H = +144.5 \text{ kJ/mol}$; $\Delta S = +24.3 \text{ J/K}\cdot\text{mol}$

(Hint: assume $\Delta G = -0.1 \text{ kJ/mol}$)

$$\Delta G = \Delta H - T\Delta S$$

$$-0.1 \text{ kJ/mol} = (144.5 \text{ kJ/mol}) - (T)(0.0243 \text{ kJ/K}\cdot\text{mol})$$

$$T = 5950.6 \text{ K} \approx 5951 \text{ K} \approx 5680 \text{ K}$$

$$5950 \text{ K} - 273 \text{ K} = 5677 \text{ }^\circ\text{C}$$