Energy Balances with Reaction

In any reaction between stable molecules, energy is required to break the reactant chemical bonds and energy is released when the product bonds form.

If the energy required is less than the energy released, the reaction is **exothermic.** If the energy required is more than the energy released, the reaction is **endothermic**. The net energy for a chemical reaction is called **heat of reaction**.

The large enthalpy changes commonly associated with chemical reactions can play major roles in the design and operation of chemical processes. An energy balance on a reactor tells the process engineer how much heating (for endothermic reactions) or cooling (for exothermic reactions) the reactor requires in order to operate at the desired conditions.

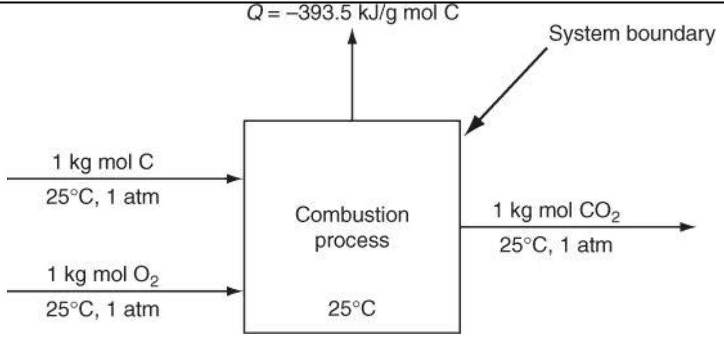
Heats of Formation

To include energy changes caused by a reaction in the energy balance, we make use of a quantity called the standard heat of formation (enthalpy). **The standard heat of formation** ($\Delta\hat{H}_f^o$) is the name given to the special enthalpy change associated with the formation of 1 mol of a compound from its constituent elements and products in their standard state of 25°C and 1 atm.

- The values for the standard heats of formation are negative for exothermic reactions and positive for endothermic reactions.
- The standard heat of formation of an elemental species (e.g., O_2, H_2) is zero, (i.e the heat of formation of an element in its natural state is defined as zero).
- The standard heat of formation will not be affected by high temperature and pressure because it by definition is at 25°C and 1 atm.
- The reversing the direction of a reaction equation does not reverse the sign of the heat of formation of a compound

Example 1: the enthalpy change that occurs for the reaction of carbon and oxygen to form carbon dioxide at 25°C and 1 atm.

$$C(s) + O_2(g) \rightarrow CO_2(g)$$



Solution

If you simplify the general energy balance, for the isothermal process (steady-state, flow, no KE or PE, etc.), you get the standard heat of formation of CO_2, calculated from:

$$-393.5\ \text{kJ/kg mol CO}_2 = Q = \Delta H = (1)\Delta\hat{H}^{o}_{f,CO_2} - (1)\Delta\hat{H}^{o}_{f,C} - (1)\Delta\hat{H}^{o}_{f,O_2}$$

$$= (1)\Delta\hat{H}^{o}_{f,CO_2} - 0 - 0 = \Delta\hat{H}^{o}_{f,CO_2}$$

Example 2: to get for $CH_2(NH_3)COOH$ (glycine), the smallest amino acid, with write the balanced chemical equation:

$$CH_2(NH_3)COOH(s) + 15/2\,O_2(g) \rightarrow 2CO_2(g) + 5/2\,H_2O(g) + HNO_3(g)$$

$$\Delta H^{o}_{f,\text{glycine solid}} + \Delta H^{o}_{f,O_2} = (2)\Delta H^{o}_{f,CO_2} + (5/2)\Delta H^{o}_{f,H_2O} + (1)\Delta H^{o}_{f,HNO_3}$$

$$\Delta\hat{H}^{o}_{f,\text{glycine solid}} + 0 = (2)(-393.51) + (5/2)(-241.826) + (1)(-173.23)$$

$$= -1202.08\ \text{kJ/g mol}$$

1. Enthalpy of Reaction

The heat of reaction or enthalpy of reaction $\Delta H_r(T,p)$ is the enthalpy change for a process in which stoichiometric quantities of reactants at temperature T and pressure P react completely in a single reaction to form products at the same temperature and pressure.

The standard heat of reaction ΔH_r^o is the heat of reaction when both reactants and products are at a specified reference temperature and pressure, usually 25°C and 1 atm.

Observations Related to Heats of Reaction

- If $\Delta H_r(T,p) < 0$ the reaction is exothermic at T and P.
- If $\Delta H_r(T,p) > 0$ the reaction is endothermic at T and P.
- At low and moderate pressures $\Delta H_r(T,p)$ is nearly independent of pressure, $\Delta H_r(T)$.
- The value of the heat of reaction depends on how the stoichiometric equation is written: e.g. $\Delta H_r(T,p)$ for $A \rightarrow B$ is half of $\Delta H_r(T,p)$ for $2A \rightarrow 2B$ (definition of $\Delta H_r(T,p)$).
- The value of the heat of reaction depends on the states of aggregation (gas, liquid or solid) of the reactants and products:

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H^o_{r,n} = -890.3 \text{ kJ/mol}$$

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)} \qquad \Delta H^o_{r,n} = -802.3 \text{ kJ/mol}$$

In general, for complete reaction,

$$\Delta H^o_{\text{rxn}} = \left(\sum_i^{\text{Products}} v_i \Delta \hat{H}^o_{f,i} - \sum_i^{\text{Reactants}} |v_i| \Delta \hat{H}^o_{f,i} \right) = \sum_i^{\text{All Species}} v_i \Delta \hat{H}^o_{f,i}$$

where νi is the stoichiometric coefficient in the reaction equation.

Hess's Law

If the stoichiometric equation for reaction 1 can be obtained by algebraic operation (multiplication by constants, addition and subtraction) on stoichiometric equations for reactions 2, 3, …., then the $\Delta H_{r1}{}^o(T,p)$ can be obtained by performing the same operations on the heats of reactions $\Delta H_{r2}{}^o(T,p)$, $\Delta H_{r3}{}^o(T,p)$ …

Example Hess's Law

The standard heats of the following reactions have been determined experimentally:

$$C_2H_6 + 3.5\,O_2 \longrightarrow 2CO_2 + 3H_2O \qquad \Delta H^o_{r1,n} = -1559.8 \text{ kJ/mol}$$

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H^o_{r2,n} = -393.5 \text{ kJ/mol}$$

$$\mathrm{H}_2 + 0.5O_2 \longrightarrow H_2O \qquad \Delta H^o_{r3,n} = -285.8 \text{ kJ/mol}$$

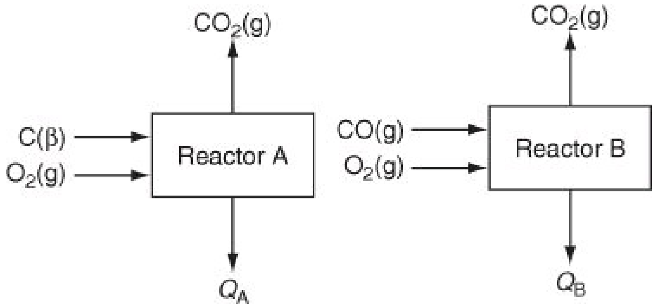
Use Hess's law and the given heats of reaction to determine the standard heat of reaction $\Delta H_{r4}{}^{o}(T,p)$ for:

$$2C+\ 3H_2 \longrightarrow C_2H_6 \qquad \Delta H^o_{r4,n} = ?\ \text{kJ/mol}$$

$$\begin{aligned}\Delta H^o_{r4,n} &= 2\times\Delta H^o_{r2,n} + 3\times\Delta H^o_{r3,n} - \Delta H^o_{r1,n}\\ &= 2\times(-393.5)+3\times(-285.8)-(-1559.8)\\ &= -84.6\ \text{kJ/mol}\end{aligned}$$

Example 3: Use of Heat Transfer Measurements to Get a Heat of Formation

Suppose that you want to find the standard heat of formation of CO from experimental data. Can you prepare pure CO from the reaction of C and O2 and measure the heat transfer? This would be far too difficult. It would be easier experimentally to find first the heat of reaction at standard conditions for the two reactions shown below for the flow process as shown in Figure below (assuming you had some pure CO to start with).



Use of two convenient reactions to determine the heat of formation for an inconvenient reaction:

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad Q = -393.51\ \text{kJ/g mol C} \equiv \Delta\hat{H}_A \qquad (a)$$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad Q = -282.99\ \text{kJ/g mol CO} \equiv \Delta\hat{H}_B \qquad (b)$$

Basis: 1 g mol each of C and CO

According to Hess's law, you subtract Reaction (b) from Reaction (a), subtract the corresponding , and rearrange the compounds to form the desired chemical equation:

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad \text{(c)}$$

For which the net heat of reaction per gram mole of CO is the heat of formation of CO:

$$\Delta\hat{H}^{o}_{f,\,CO} = -393.51 - (-282.99) = -110.52 \text{ kJ/g mol CO}$$

Example: Calculation of the Standard Heat of Reaction from the Standard Heats of Formation

Calculate ΔH^{o}_{rxn} for the following reaction of 4 g mol of NH_3 and 5 g mol of O_2:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Tabulated data:	$NH_3(g)$	$O_2(g)$	$NO(g)$	$H_2O(g)$
$\Delta\hat{H}^{o}_{f}$ per mol at 25°C and 1 atm (kJ/g mol)	–46.191	0	+90.374	–241.826

Solution

To calculate (25°C, 1 atm) for 4 g mol of NH_3, assuming complete reaction:

$$\Delta H^{o}_{rxn} = [4(90.374) + 6(2241.826)] + [(-5)(0) + (-4)\ \ (-46.191)] = -904.696 \text{ kJ}$$

Therefore, the heat of reaction per mole of NH_3 is:

$$\Delta H^{o}_{rxn} = \frac{904.646 \text{ kJ}}{4 \text{ g mol } NH_3} = -226.174 \text{ kJ/g mol } NH_3$$

Heats of Combustion

The standard heat of combustion of a substance is the heat of the combustion of that substance with oxygen to yield specified products, with both reactants and products at reference temperature and pressure.

Standard heats of reactions that involve only combustible substances and combustion products can be calculated from tabulated standard heats of combustion.

$$\Delta H^0_{r,n} = -\sum_i \nu_i \Delta H^o_{ci} = \sum_{\text{reactants}} |\nu_i| \Delta H^o_{ci} - \sum_{\text{products}} |\nu_i| \Delta H^o_{ci}$$

Note that this formula is similar to that used to determine from heats of formation, except that in this case the negative of the sum is taken.

If any of the reactants or products are themselves combustion products (e.g., CO_2, H_2O, SO_2) their heat of combustion is set to 0.

Example Involving Heats of Combustion

Calculate the standard heat of reaction for the dehydrogenation of ethane $C_2H_6 \rightarrow C_2H_4 + H_2$

$$\left(\Delta H^o_c\right)_{C_2H_6} = -1559.9\ \text{kJ} \cdot \text{mol}^{-1} \quad \left(\Delta H^o_c\right)_{C_2H_4} = -1411.0\ \text{kJ} \cdot \text{mol}^{-1} \quad \left(\Delta H^o_c\right)_{H_2} = -285.84\ \text{kJ} \cdot \text{mol}^{-}$$

$$\Delta H^0_{r,n} = -\sum_i \nu_i \Delta H^o_{ci} = \sum_{\text{reactants}} |\nu_i| \Delta H^o_{ci} - \sum_{\text{products}} |\nu_i| \Delta H^o_{ci}$$

$$\Delta H^0_{r,n} = \left(\Delta H^o_c\right)_{C_2H_6} - \left(\Delta H^o_c\right)_{C_2H_4} - \left(\Delta H^o_c\right)_{H_2}$$

$$\Delta H^0_{r,n} = -1559.9 + 1411.0 + 285.84 = 136.9\ \text{kJ} \cdot \text{mol}^{-1}$$

Example: In the manufacture of sulphuric acid SO_2 is oxidised to SO_3 in a catalytic converter. The feed to the converter is 9.0 % (v/v) SO_2, 10.1 % O_2, and 80.9 % N_2, and 80 % of the SO_2 is converted to SO_3. The feed enters at 698 K. Use the following data to estimate the temperature of the exit stream from the converter. Assume the heat losses are negligible.

At 298 K heat of formation of SO_2 = −297 MJ·kmol^{-1}

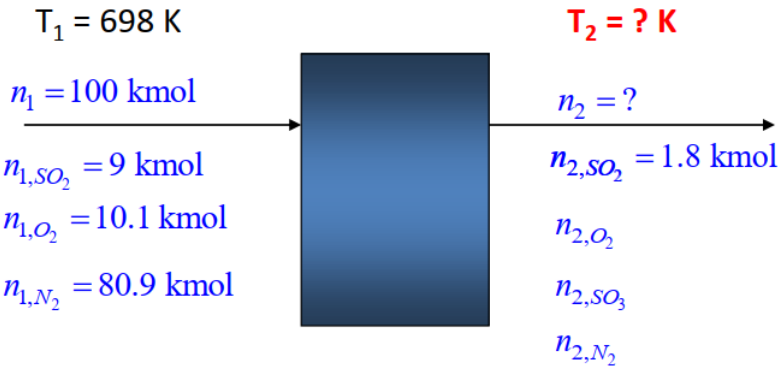
At 298 K heat of formation of SO_3 = −394 MJ·kmol^{-1}

$$C_{P,N_2} = 31.56 \frac{\text{kJ}}{\text{kmol K}} \qquad C_{P,SO_2} = 52.46 \frac{\text{kJ}}{\text{kmol K}}$$

$$C_{P,O_2} = 33.54 \frac{\text{kJ}}{\text{kmol K}} \qquad C_{P,SO_3} = 77.63 \frac{\text{kJ}}{\text{kmol K}}$$

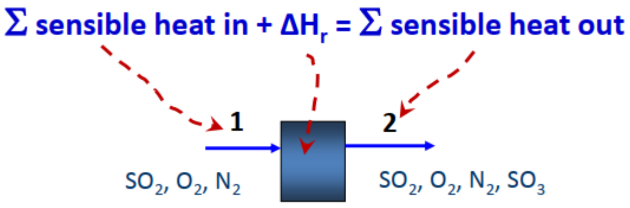
Stoichiometric equation: $SO_2 + ½O_2 \rightarrow SO_3$

- **Basis:** 100 kmol feed
- **T_{ref}** = 298 K
- Assume ideal gas, i.e. mol % = vol %



$$X_{SO_2} = \frac{n_{1,SO_2} - n_{2,SO_2}}{n_{1,SO_2}} = 0.8 \quad \Rightarrow \quad n_{2,SO_2} = 1.8 \text{ kmol}$$

Heat balance



Σ sensible heat in + ΔH_r = Σ sensible heat out

$$\text{Heat}_{\text{in}} = \sum_{\text{reactants}} n_{1,i} \cdot C_{P,i} \cdot \left(T_1 - T_{ref}\right)$$

$$\text{Heat}_{\text{in}} = n_{1,SO_2} \cdot C_{P,SO_2} \cdot \left(T_1 - T_{ref}\right) + n_{1,O_2} \cdot C_{P,O_2} \cdot \left(T_1 - T_{ref}\right) + n_{1,N_2} \cdot C_{P,N_2} \cdot \left(T_1 - T_{ref}\right)$$

$$\text{Heat}_{\text{in}} = \left(n_{1,SO_2} \cdot C_{P,SO_2} + n_{1,O_2} \cdot C_{P,O_2} + n_{1,N_2} \cdot C_{P,N_2}\right) \cdot \left(T_1 - T_{ref}\right)$$

$$\text{Heat}_{\text{in}} = (9 \cdot 52.46 + 10.1 \cdot 33.54 + 80.9 \cdot 31.56) \cdot (698 - 298)$$

$$\text{Heat}_{\text{in}} = 1345639.2 \text{ kJ} = 1345.64 \text{ MJ}$$

Heat of reaction

$SO_2 + ½\, O_2 \rightarrow SO_3$

$\left(\Delta H_f^o\right)_{SO_3} = -\,394 \text{ MJ} \cdot \text{kmol}^{-1}$ $\left(\Delta H_f^o\right)_{SO_2} = -\,297 \text{ MJ} \cdot \text{kmol}^{-1}$

$$\Delta H_{r,n}^o = \sum_i \nu_i \Delta H_{fi}^o = \sum_{\text{products}} |\nu_i| \Delta H_{fi}^o - \sum_{\text{reactants}} |\nu_i| \Delta H_{fi}^o$$

$$\Delta H_{r,n}^o = \left(\Delta H_f^o\right)_{SO_3} - \left(\Delta H_f^o\right)_{SO_2} \Longrightarrow \Delta H_{r,n}^o = -97 \text{ MJ} \cdot \text{kmol}^{-1}$$

$\Delta H_r^o = n \cdot \Delta H_{r,n}^o = 7.2 \cdot (-97) = -698.4 \text{ MJ}$ *the total heat released in the reaction*

$$\text{Heat}_{\text{out}} = \sum_{\text{products}} n_{2,i} \cdot C_{P,i} \cdot \left(T_2 - T_{ref}\right)$$

$$\begin{aligned}\text{Heat}_{\text{out}} = {} & n_{2,SO_2} \cdot C_{P,SO_2} \cdot \left(T_2 - T_{ref}\right) + n_{2,O_2} \cdot C_{P,O_2} \cdot \left(T_2 - T_{ref}\right) + \\ & n_{2,N_2} \cdot C_{P,N_2} \cdot \left(T_2 - T_{ref}\right) + n_{2,SO_3} \cdot C_{P,SO_3} \cdot \left(T_2 - T_{ref}\right)\end{aligned}$$

$$\text{Heat}_{\text{out}} = \left(n_{2,SO_2} \cdot C_{P,SO_2} + n_{2,O_2} \cdot C_{P,O_2} + n_{2,N_2} \cdot C_{P,N_2} + n_{2,SO_3} \cdot C_{P,SO_3}\right) \cdot \left(T_2 - T_{ref}\right)$$

$$\text{Heat}_{\text{out}} = \left(1.8 \cdot 52.46 + 6.5 \cdot 33.54 + 80.9 \cdot 31.56 + 7.2 \cdot 77.63\right) \cdot \left(T_2 - 298\right)$$

$$\text{Heat}_{\text{out}} = 3424.6 \cdot \left(T_2 - 298\right) \text{ kJ}$$

$$\text{Heat}_{\text{out}} = 3.43 \cdot \left(T_2 - 298\right) \text{ MJ}$$

Heat Balance (neglecting heat losses)

$$\text{Heat}_{\text{in}} + \Delta H_r^o = \text{Heat}_{\text{out}} \quad \left\{ \begin{array}{l} \text{Heat}_{\text{in}} = 1345.64 \text{ MJ} \\ \Delta H_r^o = -698.4 \text{ MJ} \\ \text{Heat}_{\text{out}} = 3.43 \cdot \left(T_2 - 298\right) \text{ MJ} \end{array} \right.$$

$$1345.64 + \left(-698.4\right) = 3.43 \cdot \left(T_2 - 298\right)$$

$$T_2 = 486.7 \text{ K}$$

Answer: Under given conditions the temperature of the exit stream from the converter is 487 K.