Thermodynamics
tutorhour 6

How much heat is released during a chemical reaction?

If the reaction takes place under normal (laboratory) conditions, we may assume that the pressure is not influenced by the reaction.

$$Q_p = \Delta H$$

$\Delta_r H^\ominus$ is defined as the $\Delta_f H^\ominus$ (products) – $\Delta_f H^\ominus$ (reactants)
$\Delta_f H^\ominus$ (element) = 0

In formula:

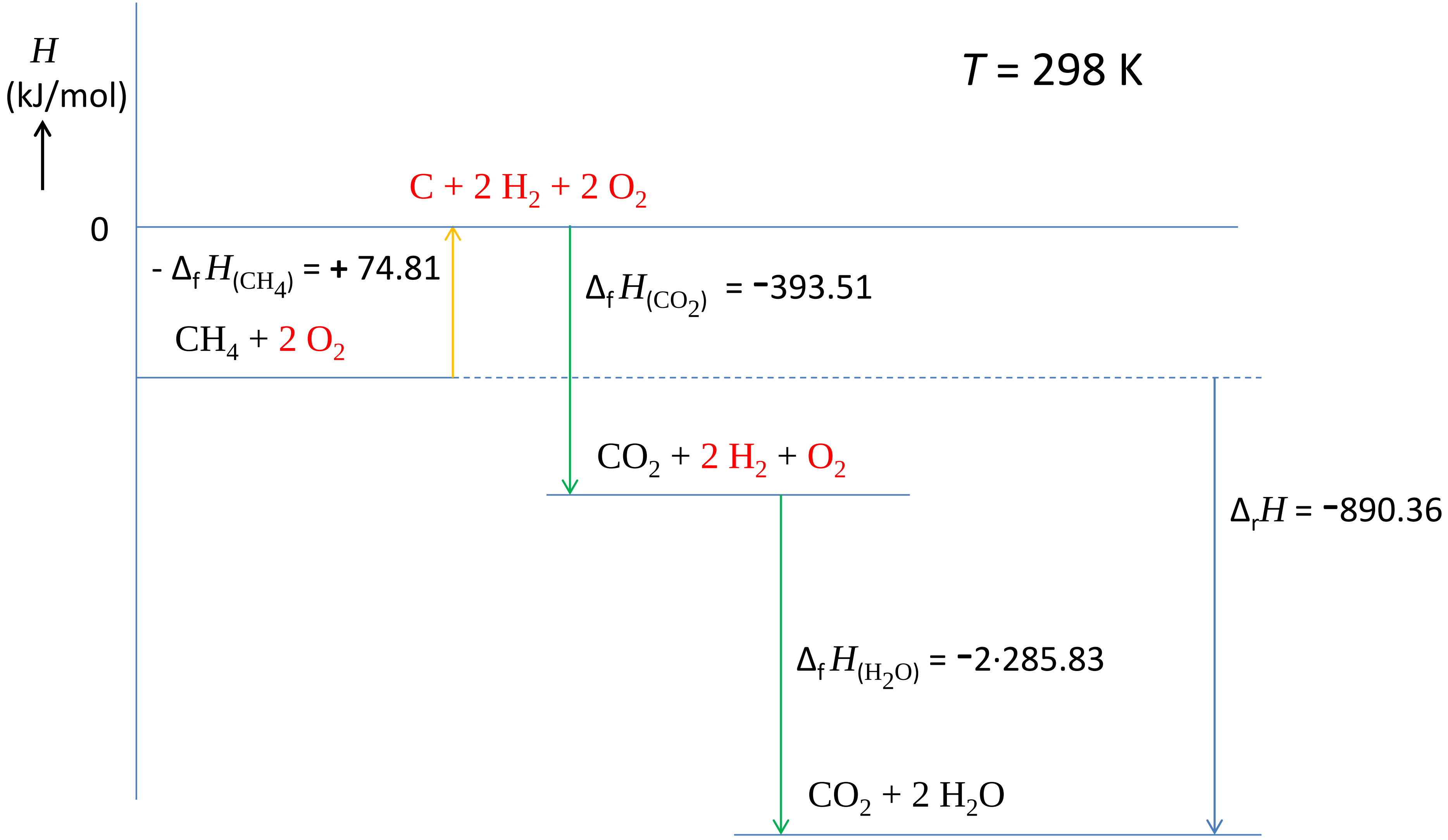
$$\Delta_\mathrm{r} H = \sum H_{\mathrm{f},products} - \sum H_{\mathrm{f},reactants}$$

For example: the combustion of methane

$$\mathrm{CH_4(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(l)}$$

$$\Delta_r H = -(-74.81) - 2\cdot 0 + (-393.51) + 2\cdot(-285.83) = -890.36\ \text{kJ/mol}\ \mathrm{CH_4}$$

The combustion of methane in an enthalpy diagram:



H (kJ/mol)

T = 298 K

$C + 2\ H_2 + 2\ O_2$

0

$-\ \Delta_f H_{(CH_4)} = +\ 74.81$

$CH_4 + 2\ O_2$

$\Delta_f H_{(CO_2)} = -393.51$

$CO_2 + 2\ H_2 + O_2$

$\Delta_r H = -890.36$

$\Delta_f H_{(H_2O)} = -2 \cdot 285.83$

$CO_2 + 2\ H_2O$

In the data section of Atkins one can find $\Delta_f H^\ominus$ at 298 K.
Often reactions occur at another temperature, in which case a correction is needed.

For example:

Substance S is being heated from T_A (below melting point) to T_X (above boiling point). The heat needed for this process can be calculated using this formula:

A common approximation:

c_p is constant over a certain temperature interval.
In such cases, c_p can be placed in front of the integral sign:

$$\Delta H = \int_{T_1}^{T_2} c_p \mathrm{d}T = c_p \Delta T$$

$\Delta S^{\ominus}$ can be treated similarly:

$$\Delta S = \int \frac{\mathrm{d}Q^{rev}}{T} \quad \text{and} \quad \mathrm{d}Q^{rev} = c_p \mathrm{d}T \qquad \Delta G = \Delta H - T\Delta S$$

at melting and boiling point: $\Delta G = 0 = \Delta H - T\Delta S$

The cummulative entropy change is then:

$$\Delta S = \int_{T_A}^{T_{fus}} \frac{c_{p,solid}}{T} \mathrm{d}T + \frac{\Delta_{fus} H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{c_{p,liquid}}{T} \mathrm{d}T + \frac{\Delta_{vap} H}{T_{vap}} + \int_{T_{vap}}^{T_X} \frac{c_{p,gas}}{T} \mathrm{d}T$$

Again, assume c_p to be constant over a certain temperature interval, so c_p can be placed in front of the integral sign:

$$\Delta S = \int_{T_i}^{T_f} \frac{c_p}{T} \mathrm{d}T = c_p \int_{T_i}^{T_f} \frac{1}{T} \mathrm{d}T = c_p \ln \frac{T_f}{T_i}$$

Answers

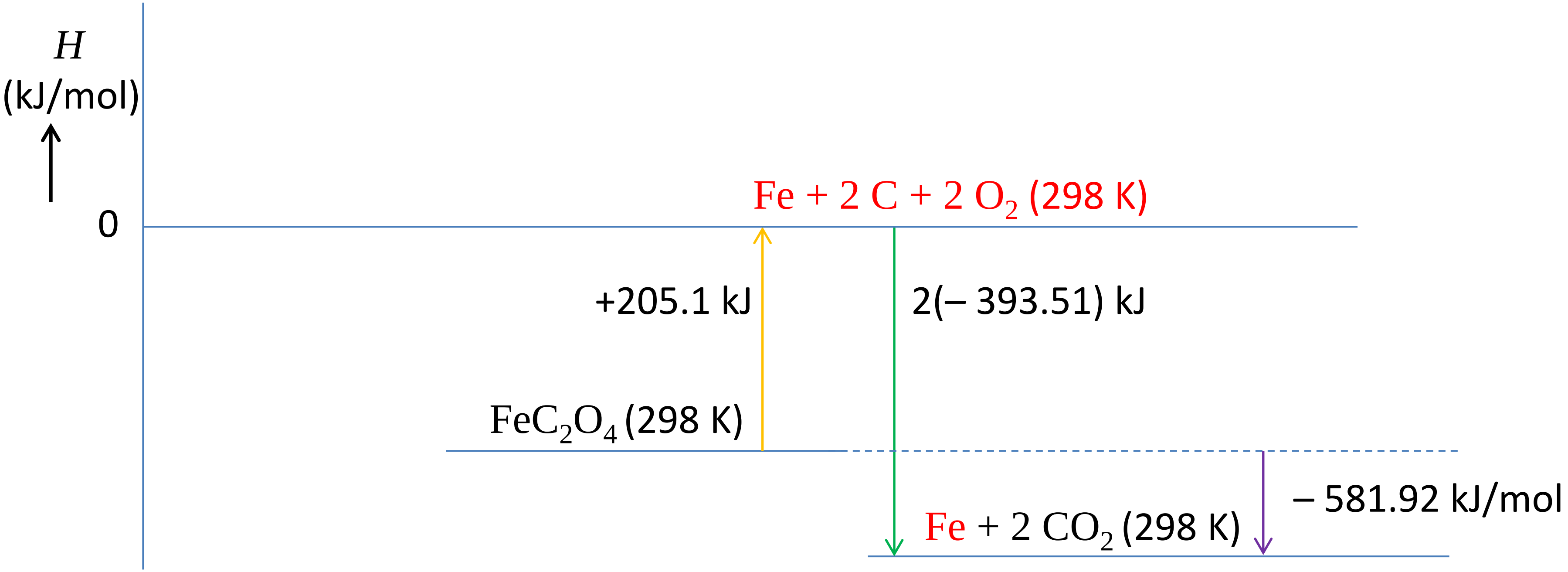
Question 1

a) $FeC_2O_4 \longrightarrow Fe + 2\ CO_2$

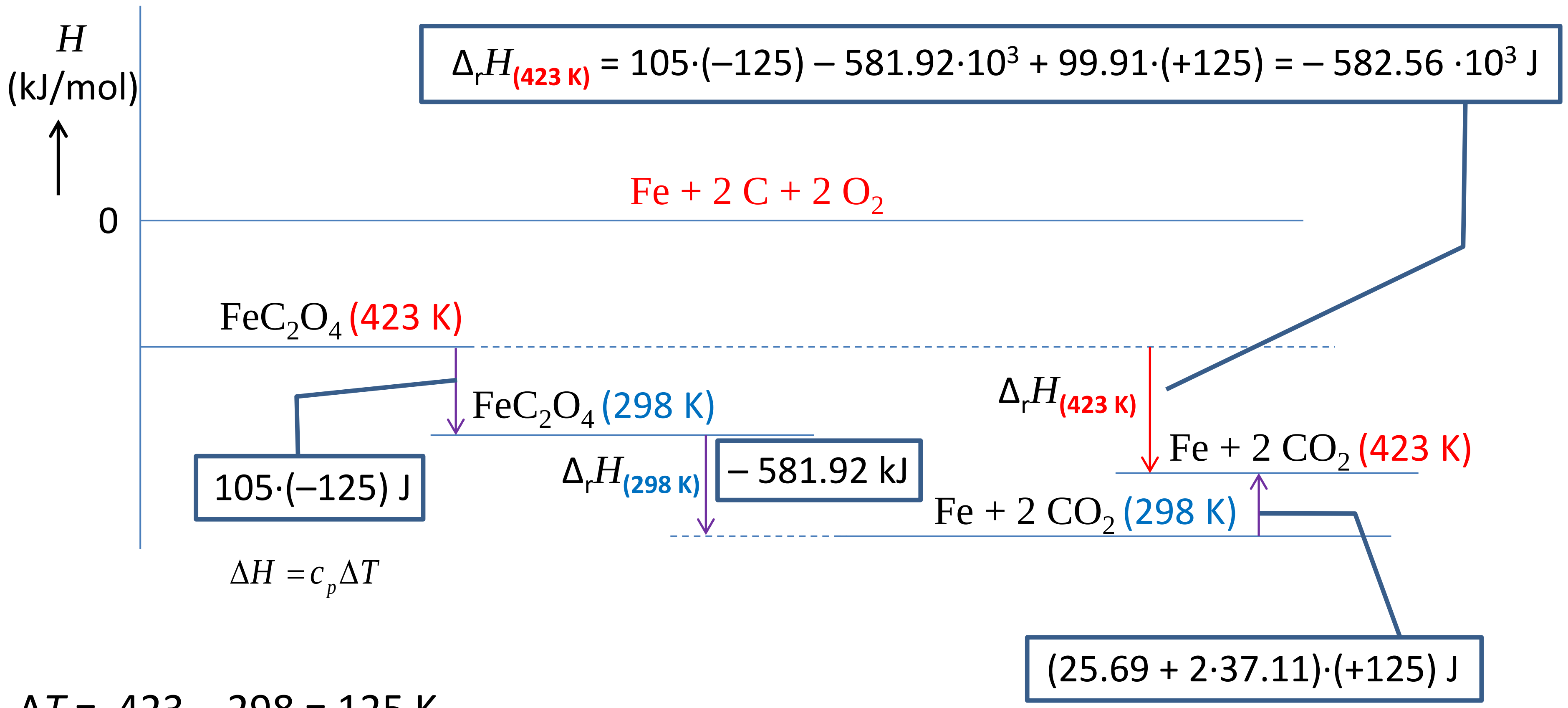
b) Given: $\Delta_f H_{(298\text{ K}, FeC_2O_4)} = -205.1$ kJ mol^{-1} and $\Delta_f H_{(298\text{ K}, CO_2)} = -393.51$ kJ mol^{-1}

$\Delta_r H_{(298\text{ K})} = -(-205.1) + 0 + 2\cdot(-393.51) = -581.92$ kJ/mol

In an enthalpy diagram:



c) $\Delta_r H_{(423\ K)}$ = ...? In the same enthalpy diagram:



$\Delta_r H_{(423\ K)} = 105\cdot(-125) - 581.92\cdot10^3 + 99.91\cdot(+125) = -582.56\cdot10^3$ J

H (kJ/mol)

0

$Fe + 2\ C + 2\ O_2$

FeC_2O_4 (423 K)

FeC_2O_4 (298 K)

$105\cdot(-125)$ J

$\Delta H = c_p \Delta T$

$\Delta_r H_{(298\ K)}$

– 581.92 kJ

$\Delta_r H_{(423\ K)}$

$Fe + 2\ CO_2$ (423 K)

$Fe + 2\ CO_2$ (298 K)

$(25.69 + 2\cdot37.11)\cdot(+125)$ J

d) Given: $\Delta T = 423 - 298 = 125$ K

and $c_{p,m(FeC_2O_4)} = 105$ J K^{-1} mol^{-1}, $c_{p,m(Fe)} = 25.69$ J K^{-1} mol^{-1}, $c_{p,m(CO_2)} = 37.11$ J K^{-1} mol^{-1}

So: $\Delta_r H_{(423\ K)} = -582.56$ kJ

e) Enthalpy difference: $\Delta_r H_{(298\ K)} - \Delta_r H_{(423\ K)} = -581.92 - (-582.56) = 0.64$ kJ

As a percentage of $\Delta_r H_{(298\ K)}$: $(0.64 / 581.92) \times 100\ \% = 0.11\ \%$

Question 2

$$\Delta H = \cancel{\int_{T_A}^{T_{fus}} c_{p,solid}\,\mathrm{d}T} + \cancel{\Delta_{fus}H} \boxed{+ \int_{T_i}^{T_{vap}} c_{p,liquid}\,\mathrm{d}T + \Delta_{vap}H + \int_{T_{vap}}^{T_X} c_{p,gas}\,\mathrm{d}T}$$

(only from liquid to gas)

c_p is constant for the temperature interval: $\int_{T_i}^{T_f} c_p\,\mathrm{d}T = c_p \Delta T$

$\Delta H = c_{p,m(CH_3OH,liquid)} \cdot \Delta T + \Delta_{vap}H + c_{p,m(CH_3OH,gas)} \cdot \Delta T$

$\Delta H = 81.6 \cdot (65 - 0) + 38.0 \cdot 10^3 + 43.9 \cdot (100 - 65) = 44.84$ kJ

$$\Delta S = \cancel{\int_{T_A}^{T_{fus}} \frac{c_{p,solid}}{T}\,\mathrm{d}T} + \cancel{\frac{\Delta_{fus}H}{T_{fus}}} \boxed{+ \int_{T_i}^{T_{vap}} \frac{c_{p,liquid}}{T}\,\mathrm{d}T + \frac{\Delta_{vap}H}{T_{vap}} + \int_{T_{vap}}^{T_X} \frac{c_{p,gas}}{T}\,\mathrm{d}T}$$

c_p is constant for the temperature interval: $\int_{T_i}^{T_f} \frac{c_p}{T}\,\mathrm{d}T = c_p \int_{T_i}^{T_f} \frac{1}{T}\,\mathrm{d}T = c_p \ln\frac{T_f}{T_i}$

$\Delta S = c_{p,m(CH_3OH,liquid)} \cdot \ln (T_f / T_i) + \Delta_{vap}H / T_{vap} + c_{p,m(CH_3OH,gas)} \cdot \ln (T_f / T_i)$

$\Delta S = 81.6 \cdot \ln(338/273) + 38.0 \cdot 10^3/338 + 43.9 \cdot \ln(373/338) = 134.2$ J/K

Question 3

a) $\Delta_r G^{\Theta}_{(298\ \text{K})} = -\,\Delta_f G^{\Theta}_{(\text{NH}_3)} - \Delta_f G^{\Theta}_{(\text{HCl})} + \Delta_f G^{\Theta}_{(\text{NH}_4\text{Cl})}$

$= -\,(-\,16.45) - (-\,95.30) -\ 202.87 = -\,91.12\ \text{kJ/mol}$

b) Assumption: ΔH and ΔS are independent of the temperature, so

$\Delta_r G^{\Theta}_{(T)} = \Delta_r H^{\Theta}_{(298\ \text{K})} - T\Delta_r S^{\Theta}_{(298\ \text{K})}$

$\Delta_r H^{\Theta}_{(298\ \text{K})} = -\,\Delta_f H^{\Theta}_{(\text{NH}_3)} - \Delta_f H^{\Theta}_{(\text{HCl})} + \Delta_f H^{\Theta}_{(\text{NH}_4\text{Cl})}$

$= -\,(-\,46.11) - (-\,92.31) -\ 314.43 = -\,176.01\ \text{kJ/mol}$

$\Delta_r S^{\Theta}_{(298\ \text{K})} = -\,\Delta S_m{}^{\Theta}{}_{(\text{NH}_3)} - \Delta S_m{}^{\Theta}{}_{(\text{HCl})} + \Delta S_m{}^{\Theta}{}_{(\text{NH}_4\text{Cl})}$

$= -\,(192.45) - (186.91) + 94.6 = -\,284.76\ \text{J/mol·K}$

$\Delta_r G^{\Theta}_{(423\ \text{K})} = \Delta_r H^{\Theta}_{(298\ \text{K})} - (423)\Delta_r S^{\Theta}_{(298\ \text{K})}$

$= -\,176.01 \cdot 10^3 - 423 \cdot (-\,284.76) = -\,55.56\ \text{kJ/mol}$

c) Gibbs free energy difference:

$\Delta_r G^{\Theta}_{(423\ \text{K})} - \Delta_r G^{\Theta}_{(298\ \text{K})} = -\,55.56 - (-\,91.12) = 35.56\ \text{kJ/mol}$

As a percentage of $\Delta_r G^{\Theta}_{(298\ \text{K})}$: $(35.56 / 91.12) \times 100\ \% = 39\ \%$