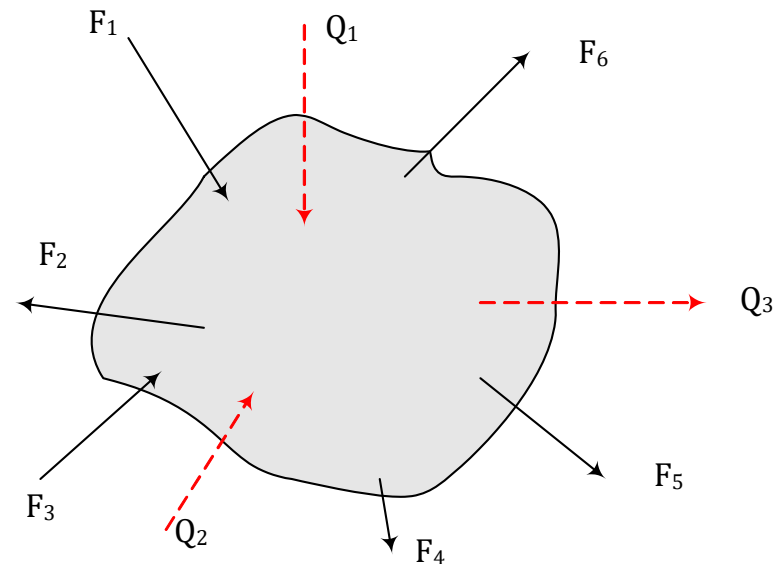


Comments Transient Energy Balances



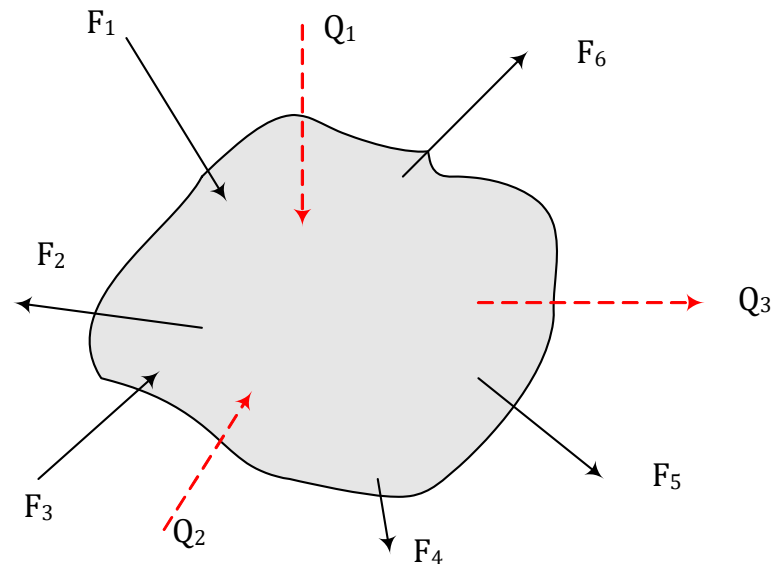
General form of the “stuff” balance equation

$$\left\{ \begin{array}{c} \text{Rate of} \\ \text{Accumulation} \end{array} \right\} = \left\{ \begin{array}{c} \text{Rate} \\ \text{In} \end{array} \right\} - \left\{ \begin{array}{c} \text{Rate} \\ \text{Out} \end{array} \right\} + \left\{ \begin{array}{c} \text{Rate of} \\ \text{Generation} \end{array} \right\} - \left\{ \begin{array}{c} \text{Rate of} \\ \text{Consumption} \end{array} \right\}$$



Word form of the energy balance equation

$$\left\{ \begin{array}{c} \text{Rate of} \\ \text{Accumulation} \end{array} \right\} = \left\{ \begin{array}{c} \text{Convection} \\ \text{Energy In} \end{array} \right\} - \left\{ \begin{array}{c} \text{Convection} \\ \text{Energy Out} \end{array} \right\} \pm \left\{ \begin{array}{c} \text{Heat Across} \\ \text{Boundary} \end{array} \right\} \pm \left\{ \begin{array}{c} \text{Work Across} \\ \text{Boundary} \end{array} \right\}$$

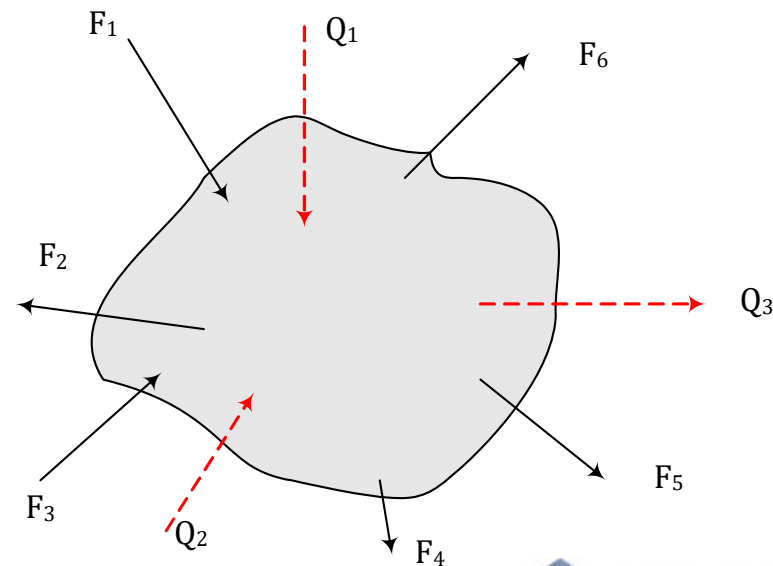


Transient energy balance equation

$$\frac{dE}{dt} = \sum_{i:\text{inlet}} \dot{E}_i - \sum_{j:\text{outlet}} \dot{E}_j + \sum_k \dot{Q}_k - \sum_m \dot{W}_{s,m}$$

$$\frac{d(U + \mathcal{K} + \mathcal{P})}{dt} = \sum_{i:\text{inlet}} \rho_i F_i \hat{H}_i - \sum_{j:\text{outlet}} \rho_j F_j \hat{H}_j + \sum_k \dot{Q}_k - \sum_m \dot{W}_{s,m}$$

$$\frac{d(\rho \hat{H} V)}{dt} \approx \frac{d(\rho \hat{U} V)}{dt} = \sum_{i:\text{inlet}} \rho_i F_i \hat{H}_i - \sum_{j:\text{outlet}} \rho_j F_j \hat{H}_j + \sum_k \dot{Q}_k - \sum_m \dot{W}_{s,m}$$



Where does heat of reaction come from?

Use of heat capacity for enthalpy

The enthalpy form of the energy balance is the same whether or not there is a chemical reaction, heat of mixing, heat of absorption, etc.

These effects are artifacts of describing the enthalpy of a mixture using the heat capacity.

$$\left(\frac{\partial \tilde{H}}{\partial T}\right)_p \equiv \tilde{C}_p \quad \Rightarrow \quad \tilde{H} - \tilde{H}_{ref} = \int_{T_{ref}}^T \tilde{C}_p dT \approx \tilde{C}_p (T - T_{ref})$$
$$\hat{H} - \hat{H}_{ref} = \int_{T_{ref}}^T \hat{C}_p dT \approx \hat{C}_p (T - T_{ref})$$

Where does heat of reaction come from?

Use of heat capacity for enthalpy

No reaction:

$$\rho V \frac{d\hat{H}_1}{dt} = \rho F \hat{H}_0 - \rho F \hat{H}_1 + Q$$

$$\rho V \hat{C}_p \frac{dT_1}{dt} = \rho F \left[\hat{C}_p (T_0 - T_{ref}) + H_{ref} \right] - \rho F \left[\hat{C}_p (T_1 - T_{ref}) + H_{ref} \right] + Q$$

$$\rho V \hat{C}_p \frac{dT_1}{dt} = \rho F \hat{C}_p (T_0 - T_1) + Q$$

With chemical reaction, the reference enthalpies are different:

$$\rho V \hat{C}_p \frac{dT_1}{dt} = \rho F \left[\hat{C}_p (T_0 - T_{ref}) + \hat{H}_{ref,0} \right] - \rho F \left[\hat{C}_p (T_1 - T_{ref}) + \hat{H}_{ref,1} \right] + Q$$

$$\rho V \hat{C}_p \frac{dT_1}{dt} = \rho F \hat{C}_p (T_0 - T_1) + \rho F \left[\hat{H}_{ref,0} - \hat{H}_{ref,1} \right] + Q$$

Where does heat of reaction come from?

Use of heat capacity for enthalpy

What if the reactants have different heat capacities than the products?

$$\rho V \frac{d(\hat{C}_{p1} T_1)}{dt} = \rho F [\hat{C}_{p0} (T_0 - T_{ref}) + \hat{H}_{ref,0}] - \rho F [\hat{C}_{p1} (T_1 - T_{ref}) + \hat{H}_{ref,1}] + Q$$

$$\rho V \frac{d(\hat{C}_{p1} T_1)}{dt} = \rho F [\hat{C}_{p0} (T_0 - T_{ref}) - \hat{C}_{p1} (T_1 - T_{ref})] + \rho F [\hat{H}_{ref,0} - \hat{H}_{ref,1}] + Q$$

Where does heat of reaction come from?

Enthalpy of formation as reference enthalpy

Total enthalpy is component average of individual enthalpies (if no mixing effect)

$$H = \sum_{i=1}^N m_i \hat{H}_i = \sum_{i=1}^N n_i \tilde{H}_i \quad \Rightarrow \quad C_p = \sum_{i=1}^N m_i \hat{C}_{pi} = \sum_{i=1}^N n_i \tilde{C}_{pi}$$

For constant heat capacities for each chemical species

$$\frac{dH_1}{dt} = \dot{H}_0 - \dot{H}_1 + Q$$

$$\frac{dH_1}{dt} = \sum_{i=1}^N \dot{n}_{i,0} \tilde{H}_{i,0} - \sum_{i=1}^N \dot{n}_{i,1} \tilde{H}_{i,1} + Q$$

$$\frac{dH_1}{dt} = \sum_{i=1}^N \dot{n}_{i,0} \tilde{C}_{p,i} (T_0 - T_{ref}) - \sum_{i=1}^N \dot{n}_{i,1} \tilde{C}_{p,i} (T_1 - T_{ref}) + \sum_{i=1}^N (\dot{n}_{i,0} - \dot{n}_{i,1}) (\Delta \tilde{H}_F)_i + Q$$

Where does heat of reaction come from?

Heat of formation or combustion as reference

Reference state enthalpies can be the enthalpy of formation or the heat of combustion

- Take care whether the heat of combustion is reported as a negative or positive value (positive value consistent with report as heating value)

Can separate the terms for the reacting & non-reacting species

- Written with heat of combustion as negative value

$$\frac{dH_1}{dt} = \sum_{i=1}^{N_{\text{Reacting}}} \dot{n}_{i,0} \tilde{C}_{p,i} (T_0 - T_{\text{ref}}) - \sum_{i=1}^{N_{\text{Reacting}}} \dot{n}_{i,1} \tilde{C}_{p,i} (T_1 - T_{\text{ref}}) + \sum_{i=1}^{N_{\text{Reacting}}} (\dot{n}_{i,0} - \dot{n}_{i,1}) (\Delta \tilde{H}_c)_i$$
$$+ \sum_{i=1}^{N_{\text{Nonreacting}}} \dot{n}_{i,0} \tilde{C}_{p,i} (T_0 - T_1) + Q$$

Latent heat effects

There are other latent heat effects that look like “generation” terms
– changes in enthalpy not due to temperature changes

Heats associated with phase change, e.g., vaporization
(solidification, dissolution, absorption, etc. are similar)

$$\begin{aligned}\int_{T_0}^{T_1} dH &= \int_{T_0}^{T_{\text{vap}}} \tilde{C}_{p,L} dT + (\Delta H)_{\text{vap}} + \int_{T_{\text{vap}}}^{T_1} \tilde{C}_{p,V} dT \\ &= \tilde{C}_{p,L} (T_{\text{vap}} - T_0) + (\Delta H)_{\text{vap}} + \tilde{C}_{p,L} (T_1 - T_{\text{vap}})\end{aligned}$$

Heat of mixing

$$\tilde{H} = \sum_{i=1}^N x_i \tilde{H}_i + (\Delta H)_{\text{mix}} \approx \sum_{i=1}^N x_i \tilde{H}_i + x_R (\Delta \tilde{H})_{\text{mix},R}$$

How to calculate the effect of heat of reaction

Heat of reaction effects are determined by the indirect path:

- Determine enthalpy change to take reactants to reference temperature
- Determine the change in enthalpy @ reference temperature
- Determine enthalpy change to take products from the reference temperature

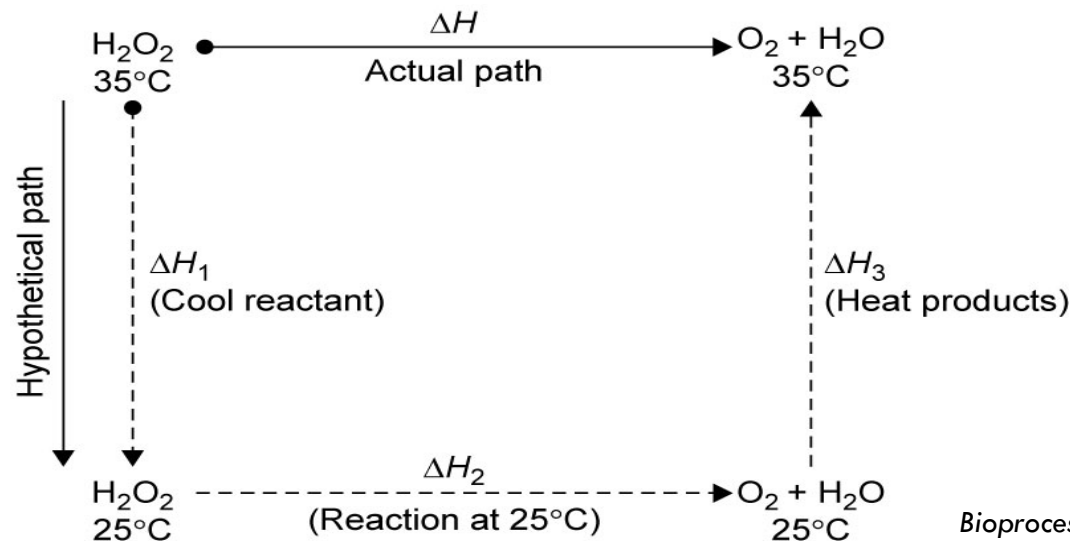


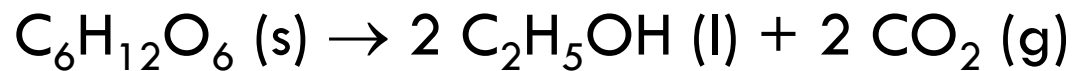
Figure 5.2

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Calculating heat of reaction from heats of combustion (values in Table C.8)

Use the heat of combustion as the reference

Example: Glucose \rightarrow Ethanol



Compound (state)	ΔH_c^0
$\text{C}_6\text{H}_{12}\text{O}_6 (\text{s})$	-2805.0 kJ/mol
$\text{C}_2\text{H}_5\text{OH} (\text{l})$	-1366.8 kJ/mol
$\text{CO}_2 (\text{g})$	0 kJ/mol

$$\begin{aligned}\Delta \tilde{H}_{rxn}^0 &= \sum_{\text{reactants}} n_i \Delta \tilde{H}_c^0 - \sum_{\text{products}} n_i \Delta \tilde{H}_c^0 \\ &= [1 \cdot (-2805.0)] - [2 \cdot (-1366.8) + 2 \cdot (0)] \\ &= -71.4 \frac{\text{kJ}}{\text{mol glucose}}\end{aligned}$$

Heat of reaction with cell growth

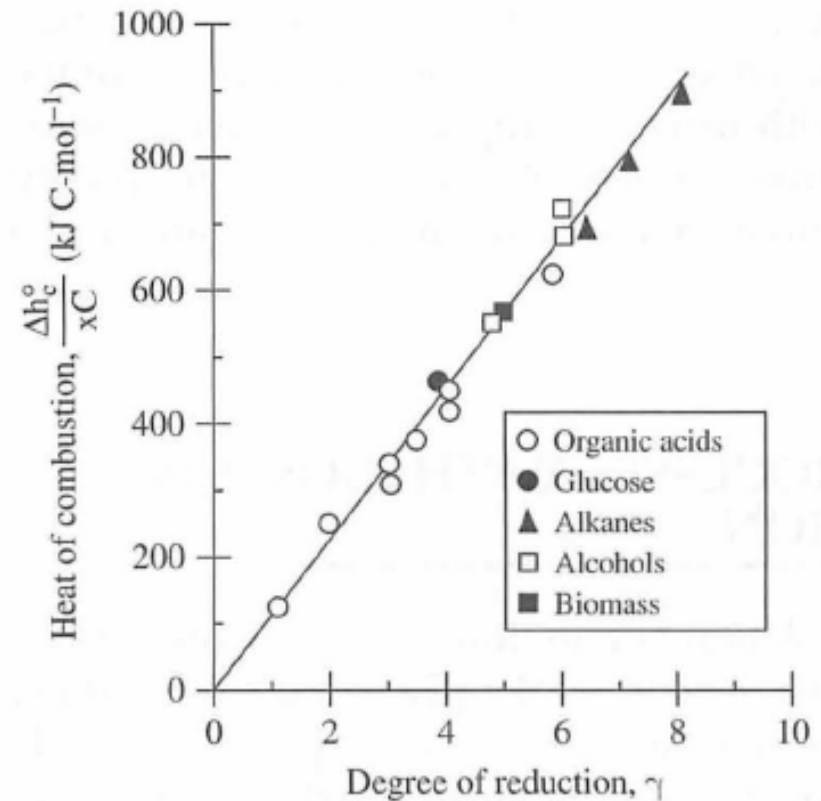
Estimated from available electrons

$$-\Delta\tilde{H}_c = -q \gamma x_c$$

$$q \approx 111 \text{ to } 115 \frac{\text{kJ}}{\text{g.mol}}$$

Heat of reaction with oxygen
as electron acceptor
(aerobic, combustion))

$$\Delta\tilde{H}_{rxn} = -460 \frac{\text{kJ}}{\text{g.mol O}_2}$$



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Heat of combustion for bacteria & yeast

Can be estimated as:

$$\left(\Delta\tilde{H}_c\right)_{bacteria} \approx -23.2 \frac{\text{kJ}}{\text{g}}$$

$$\left(\Delta\tilde{H}_c\right)_{yeast} \approx -21.2 \frac{\text{kJ}}{\text{g}}$$

For general biomass

(CH_{1.8}O_{0.5}N_{0.2}):

$$\left(\Delta\tilde{H}_c\right)_{biomass} \approx -21.3 \frac{\text{kJ}}{\text{g}}$$

TABLE 5.1 Heats of Combustion of Bacteria and Yeast

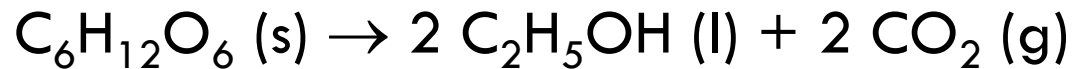
Organism	Substrate	Δh_c (kJ g ⁻¹)
BACTERIA		
<i>Escherichia coli</i>	glucose	-23.04 ± 0.06
	glycerol	-22.83 ± 0.07
<i>Enterobacter cloacae</i>	glucose	-23.22 ± 0.14
	glycerol	-23.39 ± 0.12
<i>Methylophilus methylotrophus</i>	methanol	-23.82 ± 0.06
<i>Bacillus thuringiensis</i>	glucose	-22.08 ± 0.03
YEAST		
<i>Candida lipolytica</i>	glucose	-21.34 ± 0.16
<i>Candida boidinii</i>	glucose	-20.14 ± 0.18
	ethanol	-20.40 ± 0.14
	methanol	-21.52 ± 0.09
<i>Kluyveromyces fragilis</i>	lactose	-21.54 ± 0.07
	galactose	-21.78 ± 0.10
	glucose	-21.66 ± 0.19
	glucose*	-21.07 ± 0.07
		-21.30 ± 0.10
	-20.66 ± 0.26	
	-21.22 ± 0.14	

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Calculating heat of reaction from heats of combustion (values in Table C.8)

Use the heat of combustion as the reference

Example: Glucose \rightarrow Ethanol



Compound (state)	ΔH_c^0
$\text{C}_6\text{H}_{12}\text{O}_6 (\text{s})$	-2805.0 kJ/mol
$\text{C}_2\text{H}_5\text{OH} (\text{l})$	-1366.8 kJ/mol
$\text{CO}_2 (\text{g})$	0 kJ/mol

$$\begin{aligned}\Delta \tilde{H}_{rxn}^0 &= \sum_{\text{reactants}} n_i \Delta \tilde{H}_c^0 - \sum_{\text{products}} n_i \Delta \tilde{H}_c^0 \\ &= [1 \cdot (-2805.0)] - [2 \cdot (-1366.8) + 2 \cdot (0)] \\ &= -71.4 \frac{\text{kJ}}{\text{mol glucose}}\end{aligned}$$

Example energy balance – Continuous Ethanol Fermentation

Saccharomyces cerevisiae is grown anaerobically in continuous culture at 30°C. Glucose is used as the carbon source; ammonia is the nitrogen source. A mixture of glycerol and ethanol is produced.

Compound	In [kg/h]	Out [kg/h]
Glucose	36.0	
NH ₃	0.40	
Cells		2.81
Glycerol		7.94
Ethanol		11.9
CO ₂		13.6
Produced H ₂ O		0.15

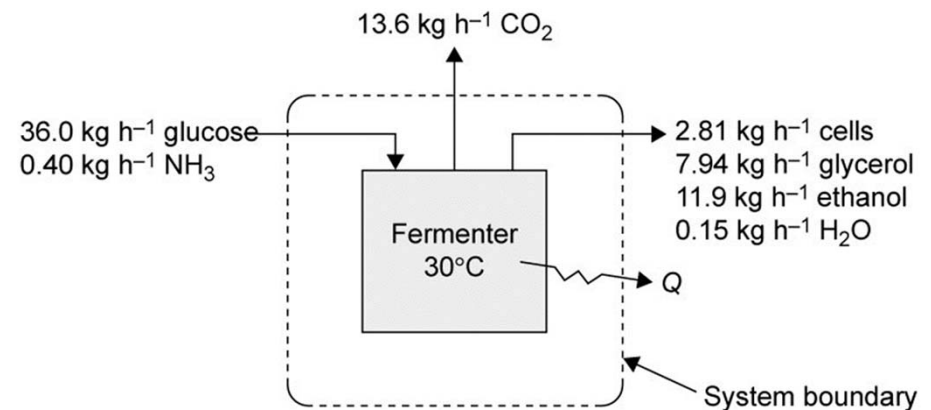


Figure 5.9

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What is the cooling requirement to keep @ 30°C?

Example energy balance – Continuous Ethanol Fermentation

We'll calculate the heat of reaction at the standard temperature (25°C) & assume this is close enough

- For more accuracy we would need to cool reactants to 25°C, calculate heat of reaction @ 25°C, & then heat up products to 30°C

Heat of reaction:

$$\begin{aligned} \Delta H_{\text{rxn}} &= -570000 - (-556025) \\ &= -13,977 \text{ kJ/h} \end{aligned}$$

Since negative this heat to be removed

Compound	In [kg/h]	Out [kg/h]	Mol Wt	ΔH_c [kJ/mol]	ΔH_c [kJ/kg]
Glucose	36		180	-2805.0	-15,583
NH ₃	0.4		17	-382.6	-22,506
Cells		2.81			-21,200
Glycerol		7.94	92	-1655.4	-17,993
Ethanol		11.9	46	-1366.8	-29,713
CO ₂		13.6		0	0
Produced H ₂ O		0.15		0	0
TOTAL	36.4	36.4			
$\Sigma m \Delta H_c$	-570,002	-556,025			

Other topics from supplemental text

Use of steam tables

- How much steam might be needed to heat a reactor or stream
- How much heat is carried away by evaporated water

Closing comments

Remember that the heat of reaction is energy released not energy generated

- Unless we are working with nuclear reactions we do not create nor destroy energy

Using heat of combustion (i.e., change in enthalpy upon combustion) is a valid reference state, just like enthalpy of formation

- Take care whether the values are reported as negative (consistent with ΔH_{rxn}) or positive (reported as heating value)
- For biological reactions make sure you choose the higher heating value (i.e., where any product water is in the liquid state)

Many times you can ignore the actual reactor temperature & just use the heat of reaction at standard conditions