SKF2213: CHEMICAL ENGINEERING THERMODYNAMICS

HEAT EFFECTS

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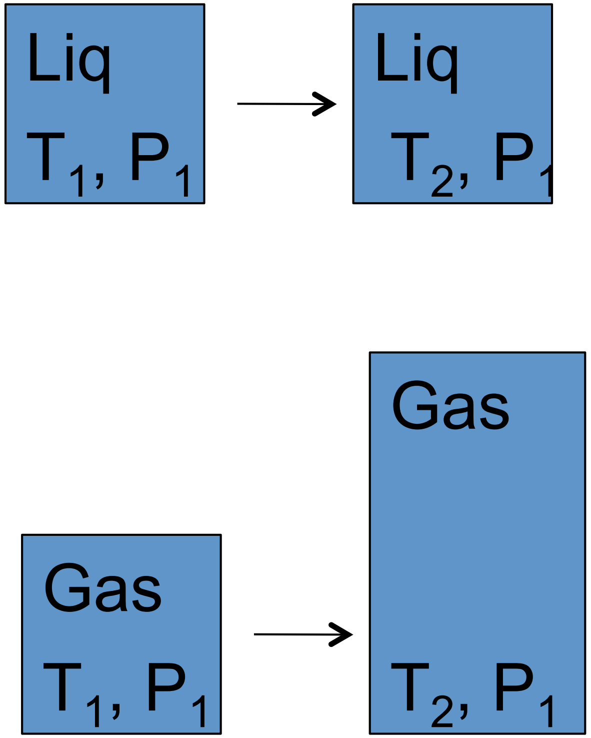
- Almost all chemical processes involve heat transfer.

- Heat is a path function and it is an energy in transition (we do not store heat, we transfer it!).

- Type of heat transfer effects.
  - Sensible heat
  - Latent heat
  - Heat of reaction
  - Heat of mixing/solution

Sensible Heat Effect

- Information on process,
  - Pure substance
  - Closed system
  - Constant pressure
  - Initial conditions: T_1 and P_1
  - Final conditions: T_2 and P_1
  - No reaction
  - No phase change



- Energy balance for closed system.

$$\partial Q + \partial W = dU + dE_K + dE_P \qquad \partial Q + \partial W = dU \qquad \partial Q - PdV = dU$$

- Also,

$$H = U + PV$$
$$dH = dU + PdV + \cancel{VdP}$$

- For constant P

$$dH = dU + PdV$$
$$dU = dH - PdV$$

- Substitute and integrate

$$Q = \Delta H$$

- So how do we determine ΔH?

- F = 2-1+1 = 2
- *Let H = H(T,P)*

$$dH = \left(\frac{\delta H}{\delta T}\right)_p dT + \left(\frac{\delta H}{\delta P}\right)_T dP$$

$$dH = C_p dT + \cancel{\left(\frac{\delta H}{\delta P}\right)_T dP}$$

- For isobaric process

$$dH = C_p dT$$

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} C_p dT$$

- So this equation for *ΔH* is only valid for isobaric process and no change of phase.

- If the process is not isobaric,

  the equation is also valid for ideal gas

  Also applicable for liquid and solid as *H* is not highly dependent on pressure

- Similarly, let *U = U(T,V)*

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dU = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

- For isochoric process

$$dU = C_v dT$$

$$\Delta U = U_2 - U_1 = \int C_v dT$$

- So this equation for *ΔU* is only valid for isochoric process and single phase.

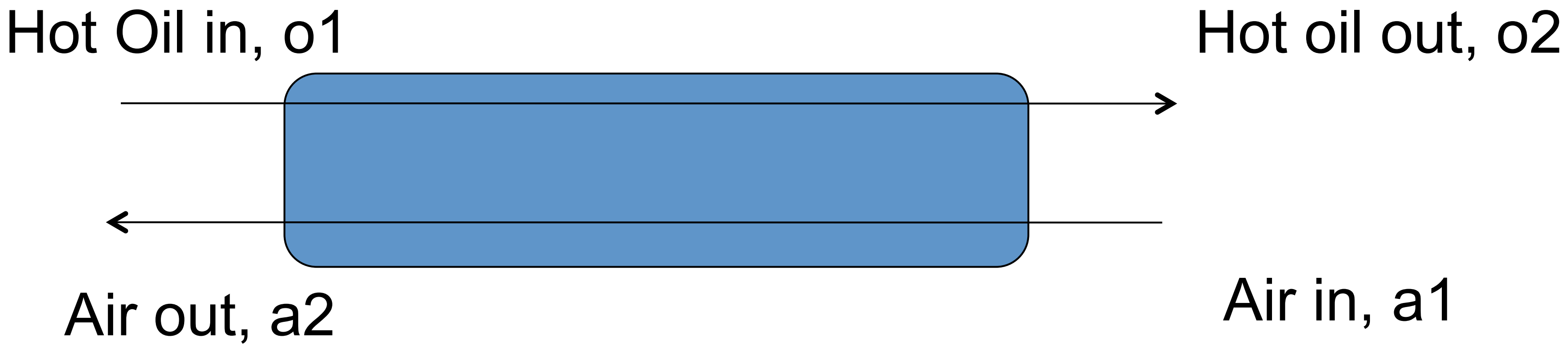
- If the process is not isochoric,

  The equation is also valid for ideal gas

  Also applicable for liquid and solid as *U* is not highly dependent on specific volume

Example

- Hot oil at T_{o1} is supplied to a heater to heat air entering at T_{a1}. The oil exits at T_{o2} and the air heater is totally insulated.
- Do the energy balance in order to determine the outlet air temperature, T_{a2}.



Steady state energy balance for open system:

$$\dot{Q} + \dot{W} = \sum\left(mH\right)_2 - \sum\left(mH\right)_1 + \Delta E_K + \Delta E_P$$

$$0 + 0 = \sum\left(mH\right)_2 - \sum\left(mH\right)_1 + 0 + 0$$

$$0 = \dot{m}_o H_{o2} + \dot{m}_a H_{a2} - \dot{m}_o H_{o1} - \dot{m}_a H_{a1}$$

$$\dot{m}_o (H_{o2} - H_{o1}) + \dot{m}_a (H_{a2} - H_{a1}) = 0$$

Assume air is an ideal gas:

$$\dot{m}_o \int_{T_o}^{T} C_{po}^{l} dT + \dot{m}_a \int_{T_o}^{T} C_{pa}^{ig} dT = 0$$

Assume constant C_P:

$$\dot{m}_o C_{po}^{l} (T_{o2} - T_{o1}) + \dot{m}_a C_{pa}^{ig} (T_{a2} - T_{a1}) = 0$$

$$\dot{m}_o C_{po}^{l} (T_{o2} - T_{o1}) = -\dot{m}_a C_{pa}^{ig} (T_{a2} - T_{a1})$$

Solve for T_{a2}

Heat Capacity

- A function of temperature

$$\frac{C_p}{R} = A + BT + CT^2 + DT^{-2} \qquad (4.4)$$

- *A,B,C* and *D are* constants for heat capacity and values for ideal gas, solid and liquid are tabulated in Table C1, C2, C3 respectively

- In this textbook, the tabulated constants are for C_p/R. The units for C_P depends on the unit for R.

Mean Heat Capacity

- To simplify calculation, let us define mean heat capacity as,

$$\langle C_p \rangle_H = \frac{\int_{T_o}^{T} C_p \, dT}{T - T_o}$$

$$\langle C_p \rangle_H = \frac{R\int_{T_o}^{T} (A + BT + CT^2 + DT^{-2})\, dT}{T - T_o}$$

$$\frac{\langle C_p \rangle_H}{R} = A + \frac{B}{2} T_o(\tau + 1) + \frac{C}{3} T_o^2(\tau^2 + \tau + 1) + \frac{D}{\tau T_o^2} \equiv MCPH(T0, T; A, B, C, D)$$

- Where *MCPH* is a subroutine function and $\tau = \frac{T}{T_o}$

- Since

$$\left\langle C_p \right\rangle_H = \frac{\int_{T_o}^{T} C_p \, dT}{T - T_o}$$

Hence,

$$\Delta H = \left\langle C_p \right\rangle_H \left(T - T_0 \right)$$

- We could also write,

$$\Delta H = \langle C_p \rangle_H (T_2 - T_1) \qquad \tau = \frac{T_2}{T_1}$$

$$\Delta H = R\left[A + \frac{B}{2}T_1(\tau + 1) + \frac{C}{3}T_1^2(\tau^2 + \tau + 1) + \frac{D}{\tau T_1^2}\right](\mathrm{T}_2 - \mathrm{T}_1)$$

- Heat capacity for ideal mixture,

$$C_{P_{mix}}^{ig} = \sum y_i C_{p_i}^{ig} \qquad \text{Ideal gas mixture}$$

$$C_{P_{mix}}^{id} = \sum x_i C_{p_i} \qquad \text{Ideal solution}$$

- Example 4.2

Solution for Q is straight forward if T_1 and T_2 are known

$$Q = \Delta H = R\left[A + \frac{B}{2}T_1(\tau + 1) + \frac{C}{3}T_1^2(\tau^2 + \tau + 1) + \frac{D}{\tau T_1^2}\right](\mathrm{T}_2 - \mathrm{T}_1)$$

- Example 4.3

Solution for T_2 is by iteration if T_1 and Q (or ΔH) are known

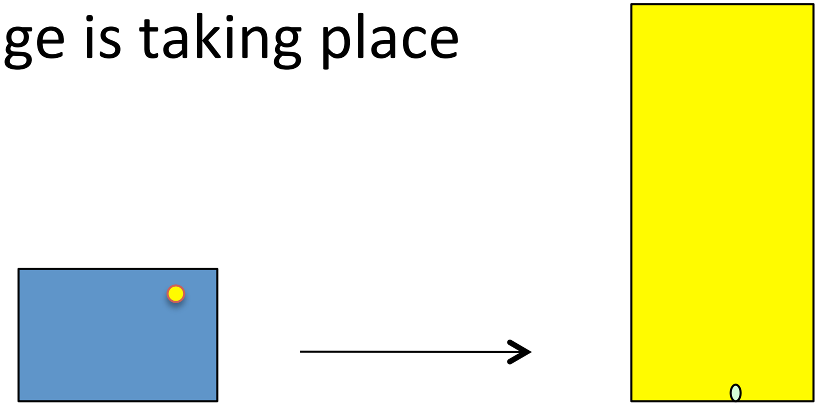
$$T_2 = \frac{\Delta \mathrm{H}}{R\left[A + \frac{B}{2}T_1(\tau+1) + \frac{C}{3}T_1^2(\tau^2+\tau+1) + \frac{D}{\tau T_1^2}\right]} + T_1$$

Latent Heat of Vaporization

- Information on process
  - Pure substance
  - Initial condition is saturated liquid at T_1 (or T_1^{sat}) and P_1 (or P_1^{sat})

    (first bubble appears)
  - Final condition is saturated vapor at T_1 and P_1

    (last drop of liquid (dew) is to disappear))
  - Phase change is taking place



First bubble appears

Last drop of liquid is about to disappear

- Energy Balance Closed System

$$\partial Q + \partial W = dU + dE_K + dE_P$$
$$\partial Q + \partial W = dU$$
$$\partial Q - PdV = dU$$
$$\partial Q = dU + PdV = dH$$

$Q = \Delta H$, this is delta H of vaporization at temperature T_1

note,

$Q = \Delta H_n$, this is delta H of vaporization at normal boiling point

- Degree of freedom, *F=2-2+1=1*
  - Once we specified one thermodynamic properties, other properties will depends on this.

- For example, saturated H_2O at a specified $T=150^oC$.

a) We can use Clapeyron equation to estimate ΔH_{vap}

$$\Delta H_{vap} = T\Delta V \frac{dP^{sat}}{dT} \qquad (4.11)$$

To used eqn 4.11, we need data for P_{sat}, T_{sat}, $V_{sat\ liq}$ and $V_{sat\ vap}$

b) or from steam table we get,

$$P^{sat}, H_v^{sat}, H_l^{sat}$$

so

$$\Delta H_{vap} = H_v^{sat} - H_l^{sat}$$

- At normal boiling point (T_n) we could estimate ΔH_{vap} by simple equation known as Riedel equation,

$$\frac{\Delta H_{vap,n}}{RT_n} = \frac{1.092(\ln P_c - 1.013)}{0.930 - T_{r_n}} \qquad (4.12)$$

- Example, for water

$$\Delta H_n = RT_n \frac{1.092(\ln P_c - 1.013)}{0.930 - T_{r_n}}$$

$$\Delta H_n = 8.314 \frac{J}{mol.K} 373.15K \frac{1.092(\ln 220.5 - 1.013)}{0.930 - \frac{373.15}{647.5}} \frac{1mol}{18g}$$

$$\Delta H_n = 2328 \frac{J}{g}$$

Now, compare with the value from steam table

- Also Trouton's Rule and Chen's Equation (see Felder's Textbook)

- If we know ΔH_{vap1} at T_1, we could estimate ΔH_{vap2} at T_2 using Watson equation,

$$\frac{\Delta H_{vap}}{\Delta H_{vap1}} = \left(\frac{1 - T_r}{1 - T_{r1}}\right)^{0.38} = \left(\frac{T_c - T}{T_c - T_1}\right)^{0.38} \qquad (4.13)$$

- So we could combine Riedel and Watson *equations to solve for* ΔH_{vap2}*, whereby* ΔH_{vap1} *is* ΔH_n and T_{r1} is T_{rn}.

Heat of Reaction

- Information on process
  - Feeds (e.g. A_1, A_2) are reactants
  - Outlets are products (e.g. A_3, A_4) of the reaction
  - Heat is released or absorbed during the process
  - Exothermic reaction: ΔH is negative
  - Endothermic reaction: ΔH is positive

Stoichiometric reaction,

$$|v_1|A_1 + |v_2|A_2 \rightarrow |v_3|A_3 + |v_4|A_4$$

Where $|v_i|$ is stoichiometric coefficient

- Where the value of v_i is positive for products and negative for reactants.

$$\text{e.g.}\quad CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$|-1|CH_4 + |-2|O_2 \rightarrow |1|CO_2 + |2|H_2O$$

Energy balance for steady-state open system with stoichiometric reaction,

$$
\begin{aligned}
Q &= \Delta H \\
&= |v_3| H_3 + |v_4| H_4 - |v_2| H_2 - |v_1| H_1 \\
&= \sum v_i H_i
\end{aligned}
$$

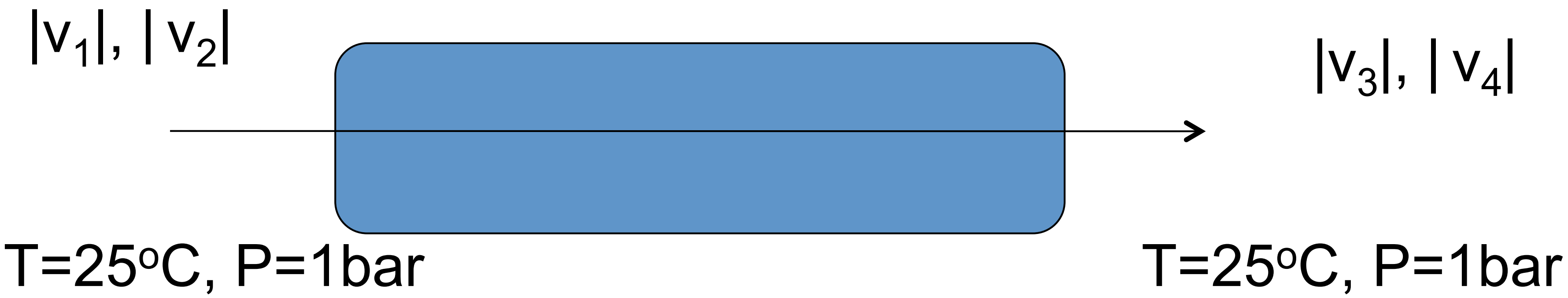
Standard Heat of Reaction $\Delta H^o{}_T$

- Defined as the enthalpy change from a stoichiometric reaction where the reactants entering at standard state (T=T and P=1 bar, specified phase (*g, l, s*)) and the products are also at specified phases and the same standard state.

- Rewrite energy balance as,

$$Q = \Delta H^o_T = \sum v_i H^o_i$$

- There are many references for tabulated data for ΔH^{o}_{298} for commonly found reactions.



$|v_1|, |v_2|$

$|v_3|, |v_4|$

T=25°C, P=1bar

T=25°C, P=1bar

Ex. of Standard Heat of Reaction at T=298.15K, ΔH^o_{298}

Note: The value of standard heat of reaction depends on stoichiometric coefficients as written

$$\tfrac{1}{2}N_2(g)+\tfrac{3}{2}H_2(g)\rightarrow NH_3(g)$$

$$\Delta H^o_{298}=-46110\,\frac{J}{\text{mol NH}_3\text{ produced}}$$

$$\Delta H^o_{298}=-46110\,\frac{J}{\tfrac{3}{2}\text{mol H}_2\text{ reacted}}$$

$$\Delta H^o_{298}=-46110\,\frac{J}{\tfrac{1}{2}\text{mol N}_2\text{ reacted}}$$

$$N_2(g)+3H_2(g)\rightarrow 2NH_3(g)$$

$$\Delta H^o_{298}=-92220\,\frac{J}{\text{2mol NH}_3\text{ produced}}$$

$$\Delta H^o_{298}=-92220\,\frac{J}{\text{3mol H}_2\text{ reacted}}$$

$$\Delta H^o_{298}=-92220\,\frac{J}{\text{mol N}_2\text{ reacted}}$$

- However, tabulation of all possible reactions are not practical.
- Furthermore, not all reactions can take place at 298K
- So, how to calculate standard heat of reaction?

Standard Heat of Formation $\Delta H^o_{f,i}$ of species *i*

- For formation of 1 mol of compound A_i from its elements (*E*),

$$|\nu_1| E_1 + |\nu_2| E_2 \rightarrow A_i$$

$$\Delta H^o_{f298,i} = H^o_i - \sum \cancelto{}{|\nu_e|} H^o_e = H^o_i$$

- Here H^o_i is calculated with reference to its elements' enthalpy (H^o_e) to be zero at standard state (T=298.15K)

- So we can calculate standard heat of reaction from standard heat of formation of the reactants and products

$$\Delta H^o_{298} = \sum \nu_i H^o_i$$

$$\downarrow$$

$$\Delta H^o_{298} = \sum \nu_{\mathrm{i}} \Delta H^o_{f\,298,i}$$

- Example of formation reaction,

$$C(s) + \tfrac{1}{2}O_2(g) + 2H_2(g) \rightarrow CH_3OH(l)$$

where

C, O_2, H_2 are elements

- Heat of formations are usually tabulated at 298.15K, such as in Table C4. $\Delta H^o_{f\,298}$

Example:

Calculation of std heat of rxn using std heat of formation,

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$$

$$\Delta H^o_{298} = \sum v_i H^o_i$$

$$\Delta H^o_{298} = \sum v_\mathrm{i} \Delta H^o_{f\,298,i}$$

$$\Delta H^o_{298} = v_{co2}\Delta H^o_{f\,298,co2} + v_{H2}\Delta H^o_{f\,298,H2} + v_{co}\Delta H^o_{f\,298,co} + v_{H2O}\Delta H^o_{f\,298,H2O}$$
$$= (-1)(-393509) + (-1)(0) + (1)(-110525) + (1)(-241818)$$

$$\Delta H^o_{298} = 41166 \frac{J}{\text{mol CO}_2 \text{ reacted}}$$

- Note:

  H_2O does not actually exist as gas at 25°C and 1 bar.

  This is hypothetical state of H_2O as an ideal gas at 25°C and 1 bar is used for convenience in calculation.

  Notice also the standard heat of formation of H_2O is tabulated for liquid as well as gas at the standard state (1bar, 25°C).

Standard Heat of Combustion

- Type of heat of reaction that is commonly encountered.
- A reaction between fuel and oxygen to produce water and carbon dioxide
- Reactants has higher chemical energy than the products, therefore the heat of combustion is negative.
- Data for heat of combustion at standard state are widely available

- We could calculate standard heat of reaction from standard heat of combustion as follows,

$$\Delta H^{o}_{298} = -\sum \nu_i \Delta H^{o}_{298,i}$$

Heat of combustion

- For example, for the following reaction,

$$4C(s) + 5H_2(g) \rightarrow C_4H_{10}(g)$$

$$\Delta H^{o}_{298} = -\left[(1)(-2877.4) + (-5)(-285.83) + (-4)(-393.51)\right]$$

$$\Delta H^{o}_{298} = -125.79 \frac{kJ}{\text{mol } \mathrm{C_4H_{10}} \text{ produced}}$$

- Note, coincidentally this is also standard heat of formation of n-Butane.

Measurement of Heat of Combustion

- Bomb Calorimeter for liquid and solid fuel
- Boys Calorimeter for gas fuel

Temperature Dependence of $\Delta H^o{}_T$

- Most reactions in the industry occur at temperature other than standard state.
- For example, reactants enter a reactor at 200°C and the products exit 200°C, so std heat of reaction is $\Delta H^o_{473.15}$
- Since *H* is state function, we can use hypothetical path to determine $\Delta H^o_{473.15}$

Convenient path is through standard state at 298.15K,

$$\begin{tikzcd}
Rxts(473) \arrow[d, "\Delta H_{rxts}"'] & & \text{Prds}(473) \\
Rxts(298) \arrow[rr, "\Delta H^o_{298}"'] & & \text{Prds}(298) \arrow[u, "\Delta H_{prds}"']
\end{tikzcd}$$

$$\Delta H^o_{473} = \Delta H_{rxts} + \Delta H^o_{298} + \Delta H_{prds}$$

$$\Delta H^o_{473} = \text{Sensible Heat} + \text{Std Heat of Rxn at 298} + \text{Sensible Heat}$$

$$dH^{o}_{473} = \sum_{rxts\,473\rightarrow 298} n_i C_p dT + dH^{o}_{298} + \sum_{prd\,298\rightarrow 473} n_i C_p dT$$

$$dH^{o}_{473} = -\sum_{rxt\,298\rightarrow 473} n_i C_p dT + dH^{o}_{298} + \sum_{prd\,298\rightarrow 473} n_i C_p dT$$

$$dH^{o}_{473} = dH^{o}_{298} + \sum_{prd\,298\rightarrow 473} n_i C_p dT - \sum_{rxt\,298\rightarrow 473} n_i C_p dT$$

For stoichiometric reaction, $n_i = |v_i|$

$$dH^o_{473} = dH^o_{298} + \sum_{prd\,298\to 473} v_i C_p dT + \sum_{rxt\,298\to 473} v_i C_p dT$$

$$dH^o_{473} = dH^o_{298K} + \sum v_i C_p dT$$

$$dH^o_{473} = dH^o_{298K} + \Delta C^o_p dT$$

Where,

$< \Delta C^o_p >_H \quad \equiv$ Mean Heat Capacity for Reaction

and

$$< \Delta C^o_p >_H = R\left(\Delta A + \frac{\Delta B}{2} T_0(\tau + 1) + \frac{\Delta C}{3} T_0^2(\tau^2 + \tau + 1) + \frac{\Delta D}{\tau T_0^2} \right) \qquad (4.20)$$

and $\Delta M = \sum v_i M_i$, and $A, B, C,\ D$ are constants for heat capacity.

$So,$

$$\Delta H^{o}_{473} = \Delta H^{o}_{298} + < \Delta C^{o}_{p} >_{H} \left(T - T_{o}\right)$$

$$\Delta H^{o}_{473} = \Delta H^{o}_{298} + < \Delta C^{o}_{p} >_{H} \left(473.15 - 298.15\right)$$

In general, standard heat of reaction at temperature T,

$$\Delta H^{o}_{T} = \Delta H^{o}_{To} + < \Delta C^{o}_{p} >_{H} \left(T - T_{o}\right) \qquad (4.21)$$

$$\Delta H^{o}_{T} = \Delta H^{o}_{298} + < \Delta C^{o}_{p} >_{H} \left(T - 298\right)$$

Heat Effects of Industrial Reactions

- Most reaction in industry rarely occur at 25°C, 1bar and also not at stoichiometric proportion.
- Reactants always contains excess component.
- The reaction is not always go to completion (not 100% conversion)
- Outlet temperature is not the same as the inlet.
- Presence of inert materials
- More than one reactions may took place simultaneously

For example,

What is the maximum temperature that can be reached by the combustion of 1 mol of methane with 20% excess air? Both the methane and the air enter the burner at 25°C.

$$CH_4 + 2O_2 + 2\left(\frac{79}{21}\right)N_2 \rightarrow CO_2 + 2H_2O + 2\left(\frac{79}{21}\right)N_2$$

With 20% excess air,

$$CH_4 + 1.2(2O_2) + 1.2\left(2\left(\frac{79}{21}\right)N_2\right) \rightarrow CO_2 + 2H_2O + 1.2\left(2\left(\frac{79}{21}\right)N_2\right) + 0.2(2)O_2$$

$$CH_4 + 1.2(2O_2) + 1.2\left(2\left(\frac{79}{21}\right)N_2\right) \rightarrow CO_2 + 2H_2O + 1.2\left(2\left(\frac{79}{21}\right)N_2\right) + 0.2(2)O_2$$

- Basis of calculation: 1 mol CH4

Inlet	Outlet
1 mol CH4	1 mol CO2
2.4 mol O2	0.4 mol O2
9.03 mol N2	9.03 mol N2
	2 mol H2O

- Energy balance

$$Q + \cancel{W_s} = \Delta H + \cancel{\Delta E_K} + \cancel{\Delta E_P}$$

$$\cancel{Q} = \Delta H$$

- Maximum temperature is when *Q=0*, so

$$\Delta H = 0$$

- Path

$$\begin{tikzcd}
 & & \text{Prd}\left(T_{out}\right) \\
Rxt(25^{o}C) \arrow[rr, "\Delta H^{o}_{298}"] & & \text{Prd}(25^{o}C) \arrow[u, "\Delta H_{prd}"']
\end{tikzcd}$$

- Energy balance becomes,

$$\Delta H = \Delta H^{o}_{298} + \Delta H_{prd} = 0$$

where

$$\Delta H^{o}_{298} = \sum v_i \Delta H^{o}_{298,f}$$

$$\Delta H^{o}_{298} = (1)(-393509) + (2)(-241818) + (-1)(-74520) + (-2)(0)$$

$$\Delta H^{o}_{298} = -802625 \frac{J}{Mol}$$

and

$$\Delta H_{prd} = \sum n_i \int_{T_1}^{T_2} C_p dT = \; < \Delta C^{o}_{p} >_H \left(T_2 - T_1\right)$$

$$\Delta H_{prd} = \sum n_i \int_{T_1}^{T_2} C_p dT = \quad < \Delta C_p^o >_H \left(T_2 - T_1\right)$$

$$\Delta H_{prd} = R\left(\Delta A + \frac{\Delta B}{2} T_1(\tau + 1) + \frac{\Delta C}{3} T_1^2 (\tau^2 + \tau + 1) + \frac{\Delta D}{\tau T_1^2}\right)\left(T_2 - T_1\right)$$

$\Delta M = \sum n_i M_i$ $\quad$ n_i is mol of each component in products.

Outlet
1 mol CO2
0.4 mol O2
9.03 mol N2
2 mol H2O

$$\Delta A = 1(5.457) + 0.4(3.639) + 9.03(3.28) + 2(3.47) = 43.471$$

$$\Delta B = [1(1.045) + 0.4(0.506) + 9.03(0.593) + 2(1.45)]x10^{-3} = 9.502x10^{-3}$$

$$\Delta D = [1(-1.157) + 0.4(-0.227) + 9.03(0.04) + 2(0.121)]x10^{5} = -0.645x10^{5}$$

For T_1=298K,

$$\Delta H_{prd} = R\left(43.471 + \frac{9.502x10^{-3}}{2}(298)(\tau + 1) - \frac{0.645x10^{5}}{\tau (298)^2}\right)\left(T_2 - 298\right)$$

Substitute into energy balance

$$\Delta H = \Delta H^o_{298} + \Delta H_{prd} = 0$$

$$\Delta H = -802625\frac{J}{Mol} + <\Delta C^o_p>_H \left(T_2 - 298\right) = 0$$

$$-802625\frac{J}{Mol} + 8.314\frac{J}{MolK}\left(43.471 + \frac{9.502x10^{-3}}{2}(298)(\tau+1) - \frac{0.645x10^5}{\tau(298)^2}\right)\left(T_2 - 298\right) = 0$$

$$T_2 = \frac{802625}{8.314\left(43.471 + \frac{9.502x10^{-3}}{2}(298)(\tau+1) - \frac{0.645x10^5}{\tau(298)^2}\right)} + 298$$

$$T_2 = \frac{96539}{\left(43.471 + 1.416(\tau+1) - \frac{0.7263}{\tau}\right)} + 298$$

$$T_2 = \frac{96539}{\left(43.471 + 1.416(\tau+1) - \frac{0.7263}{\tau}\right)} + 298$$

$$T_2 = 298 + \frac{96539}{\left(43.471 + 1.416\left(\frac{T_2}{298}+1\right) - \frac{0.7263}{\frac{T_2}{298}}\right)}$$

$$T_2 = 298 + \frac{96539}{\left(44.887 + 0.00475T_2 - \frac{216.437}{T_2}\right)}$$

- Solve by iteration (Use Excel or Casio fx-570)

  Answer: $T_2 = 2066K = 1793^oC$
- What will happen to the outlet temperature (T_2) if no excess air is used?

Reference

Smith J.M., Van Ness H.C. , and Abbott M. M. , Introduction to Chemical Engineering Thermodynamics, 7th Edition, McGraw Hill, New York, 2001.