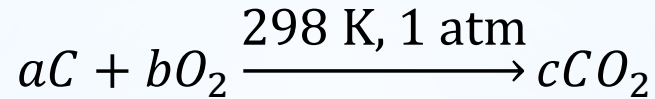# Engineering Thermodynamics

Heat Effects of Chemical Reactions

Enthalpy change for reactions involving compounds

Enthalpy of formation of a compound at standard conditions is obtained from the literature as standard enthalpy of formation
$\Delta H^o{}_{298}(CO_2(g)) = -393690$ J/mole at 298 K

$$aC + bO_2 \xrightarrow{\text{298 K, 1 atm}} cCO_2$$

Elements are assigned 0 enthalpy of formation

Enthalpy of a reaction involving compounds is calculated using Hess' law:
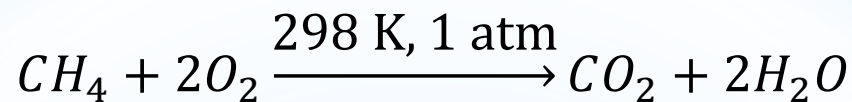
$$\Delta H_{Rxn} = \sum \Delta H_{products} - \sum \Delta H_{reactants}$$

The enthalpy changes are calculated from standard enthalpies of formation if the reaction occurs at standard conditions

$$\sum \Delta H_{products} = \sum \Delta H^o{}_{298}(products)$$

$$\sum \Delta H_{reactants} = \sum \Delta H^o{}_{298}(reactants)$$

Consider the chemical reaction:

$$CH_4 + 2O_2 \xrightarrow{\text{298 K, 1 atm}} CO_2 + 2H_2O$$

$\Delta H_{Rxn} = \Delta H^o{}_{298}$
$= (\Delta H^o{}_{298}(CO_2) + 2\Delta H^o{}_{298}(H_2O)) - (\Delta H^o{}_{298}(CH_4) + 2\Delta H^o{}_{298}(O_2))$

$\Delta H^o{}_{298}(CO_2) = \Delta H^o{}_{298}(CO_2) + \Delta H^o{}_{298}(C) + \Delta H^o{}_{298}(O_2)$

Similarly,

$\Delta H^o{}_{298}(H_2O) = \Delta H^o{}_{298}(H_2O) - \Delta H^o{}_{298}(H_2) - \dfrac{1}{2}\Delta H^o{}_{298}(O_2)$

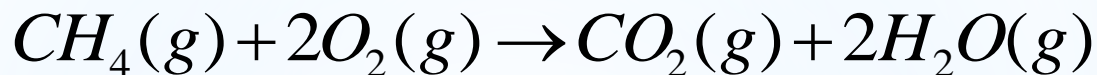$\Delta H^o{}_{298}(CH_4) = \Delta H^o{}_{298}(CH_4) - \Delta H^o{}_{298}(C) - 2\Delta H^o{}_{298}(H_2)$

So $\Delta H_{Rxn} = \Delta H^o{}_{298} = \Delta H^o{}_{298}(CO_2) + 2\Delta H^o{}_{298}(H_2O) - \Delta H^o{}_{298}(CH_4)$

$$\Delta H^o{}_{298} = \sum \Delta H^o{}_{298}(products) - \sum \Delta H^o{}_{298}(reactants)$$
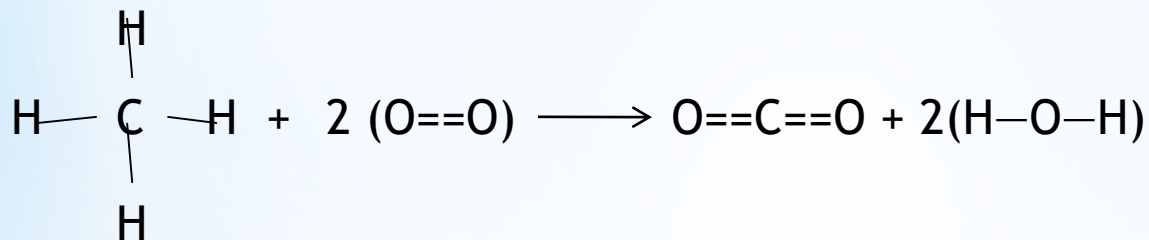
Molecular interpretation of enthalpy change

Enthalpy change of systems involving gaseous compounds may be explained using bond enthalpies

Consider the reaction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Bond configuration for above reaction:

Each bond has certain H*

O==O -414 kJ, C==O -498 kJ, O—H -741 kJ, C—H -464 kJ

ΔH°= ΔH*(bonds made) – ΔH*(bonds broken)
ΔH°= 2*(-498)+4(-741)-2(-414)-4(-464) = -686 kJ

Hess' Law and its applications

Enthalpy change accompanying a chemical reaction is the same whether it takes place in one or several stages since enthalpy is a state function
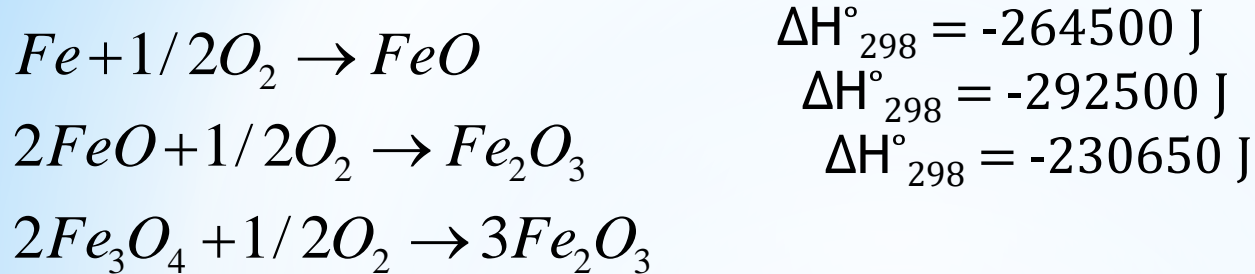
$$A \xrightarrow{\;\;\Delta H\;\;} B$$

with vertical steps:
- A → X (step 1)
- X → Y (step 2)
- Y → Z (step 3)
- Z → B (step 4)
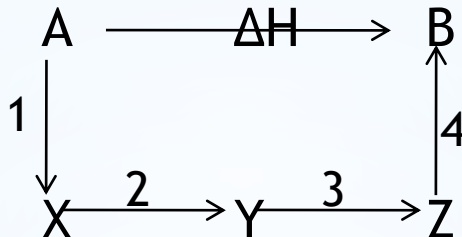
$\Delta H° = \Delta H°(1) + \Delta H°(2) + \Delta H°(3) + \Delta H°(4)$

Reaction	Enthalpy change
A→X	$\Delta H°(1)$
X→Y	$\Delta H°(2)$
Y→Z	$\Delta H°(3)$
Z→B	$\Delta H°(4)$
A→B	$\Delta H°$

Hess' law is useful for calculating the unknown enthalpy change of a reaction using known reactions

Hess' Law and its applications

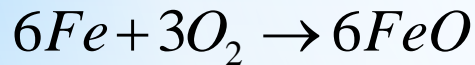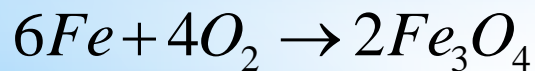Example – Calculate the standard enthalpy of formation of solid Fe_3O_4 from the following enthalpy data

$$Fe + 1/2 O_2 \rightarrow FeO$$
$$2FeO + 1/2 O_2 \rightarrow Fe_2O_3$$
$$2Fe_3O_4 + 1/2 O_2 \rightarrow 3Fe_2O_3$$

$\Delta H°_{298} = -264500 \text{ J}$
$\Delta H°_{298} = -292500 \text{ J}$
$\Delta H°_{298} = -230650 \text{ J}$

Main Reaction
$$3Fe + 2O_2 \rightarrow Fe_3O_4 \qquad \Delta H°_{298} = ?$$
Add the reactions in the following order to obtain the net reaction

$$6Fe + 3O_2 \rightarrow 6FeO$$

$$6FeO + 3/2 O_2 \rightarrow 3Fe_2O_3$$

$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + 1/2 O_2$$

Net reaction:
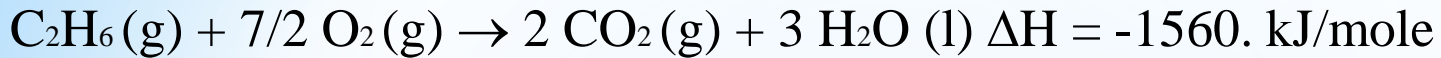$$6Fe + 4O_2 \rightarrow 2Fe_3O_4$$

$$3Fe + 2O_2 \rightarrow Fe_3O_4$$

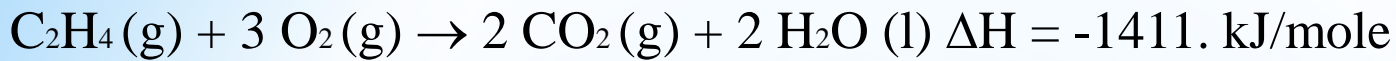$\Delta H = 6 \Delta H_1 + 3 \Delta H_2 - \Delta H_3$
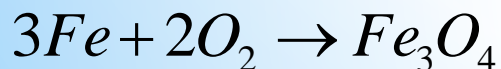
$\Delta H/2 = -1117240 \text{ J/mole}$

Example –
Calculate ΔH for the reaction C_2H_4 (g) + H_2 (g) = C_2H_6 (g), from the following data

C_2H_4 (g) + 3 O_2 (g) → 2 CO_2 (g) + 2 H_2O (l) ΔH = -1411. kJ/mole

C_2H_6 (g) + 7/2 O_2 (g) → 2 CO_2 (g) + 3 H_2O (l) ΔH = -1560. kJ/mole

H_2 (g) + 1/2 O_2 (g) → H_2O (l) ΔH = -285.8 kJ/mole

Example –
Calculate ΔH for the reaction $4 NH_3 (g) + 5 O_2 (g) = 4 NO (g) + 6 H_2O (g)$, from the following data

$N_2 (g) + O_2 (g) = 2 NO (g)$ $\Delta H = -180.5$ kJ

$N_2 (g) + 3 H_2 (g) = 2 NH_3 (g)$ $\Delta H = -91.8$ kJ

$2 H_2 (g) + O_2 (g) = 2 H_2O (g)$ $\Delta H = -483.6$ kJ
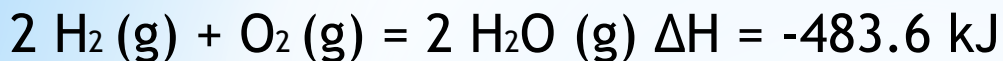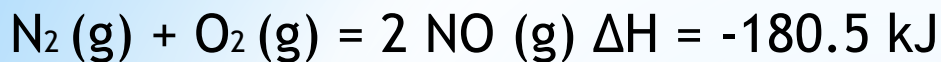
Isothermal enthalpy change for reactions <u>not</u> occuring at 298 K

Consider a general reaction with components at the same temperature different than 298 K:

$$aA(T) + bB(T) \xrightarrow{\Delta H_T} cC(T) + dD(T)$$
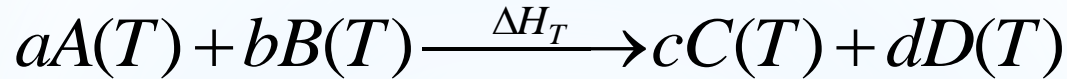
ΔH°_{298} are tabulated for components

$$\Delta H = c\Delta H_C + d\Delta H_D - a\Delta H_A - b\Delta H_B$$

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \qquad \frac{d\Delta H}{dT} = c\frac{dH_C}{dT} + d\frac{dH_D}{dT} - a\frac{dH_A}{dT} - b\frac{dH_B}{dT}$$

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P = cC_{PC} + dC_{PD} - aC_{PA} - bC_{PB}$$

$$\boxed{\Delta C_P = \sum C_{P(prod.)} - \sum C_{P(react.)}}$$

Isothermal enthalpy change for reactions _not_ occuring at 298 K

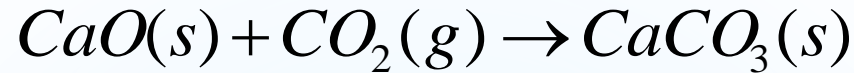ΔH values for chemical reactions can be determined from ΔH°$_{298}$ values:

$$\int_{\Delta H_{298}}^{\Delta H_T} d\Delta H = \int_{298}^{T} \Delta C_P dT$$

$$\Delta H_T - \Delta H_{298}^{o} = \int_{298}^{T} \Delta C_P dT \qquad \text{Kirchoff equation}$$

ΔH$_T$ can also be calculated from the enthalpy increment equations:

$$\Delta H_T = \Delta H_{298}^{o} + \sum (H_T - H_{298})_{prod.} - \sum (H_T - H_{298})_{react.}$$

Example – Find the net heat available or required when the following reaction takes place at 800 K

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$$

Substance	ΔH^o_{298} (kJ/mole)	C_P (J/mole K)
CaO(s)	-634.3	$49.62+4.52*10^{-3}*T-6.95*10^5*T^{-2}$
CO_2(g)	-393.5	$44.14+9.04*10^{-3}*T-8.54*10^5*T^{-2}$
$CaCO_3$(s)	-1206.7	$104.52+21.92*10^{-3}*T-25.94*10^5*T^{-2}$

$$\Delta H^o_{298} = \Delta H^o_{298}(CaCO_3) - \Delta H^o_{298}(CaO) - \Delta H^o_{298}(CO_2)$$

= -1206.7 - 634.3 + 393.5 = -178.9 kJ

$$\Delta C_P = C_{P(CaCO_3)} - C_{P(CaO)} - C_{P(CO_2)}$$

= $10.76 + 8.36*10^{-3}*T-10.45*10^5*T^{-2}$ J/K

$$\Delta H^o_{800} = -178900 + \int_{298}^{800}(10.76+8.36*10^{-3}T-10.45*10^5T^{-2})dT$$

$$\Delta H^o_{800} = -178900 + 5505 = -173395 \quad J$$

Alternatively ΔH$_T$ can be calculated from Hess' law

$$CaO(800) + CO_2(800) \xrightarrow{\Delta H_{800}} CaCO_3(800)$$

$$1 \downarrow \qquad 2 \downarrow \qquad \qquad 4 \uparrow$$

$$CaO(298) + CO_2(298) \xrightarrow[3]{\Delta H_{298}} CaCO_3(298)$$
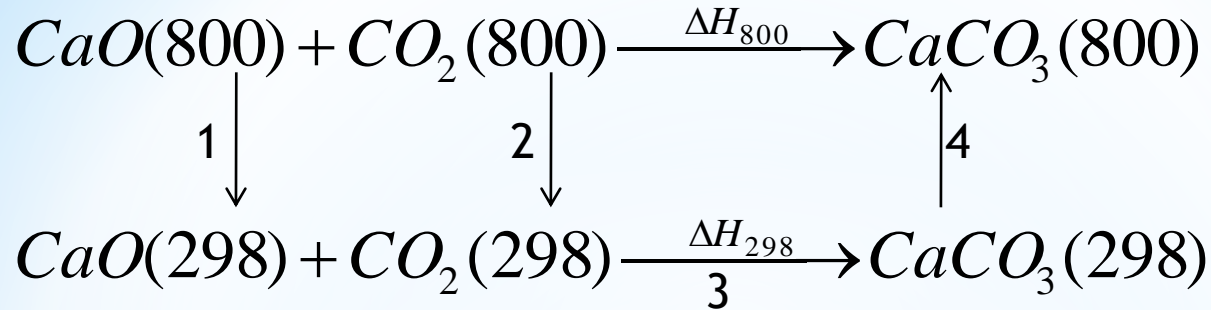
$$\Delta H_1 = \int_{800}^{298} C_{P(CaO)} dT$$

$$\Delta H_2 = \int_{800}^{298} C_{P(CO_2)} dT$$

$$\Delta H_3 = \Delta H_{298}^o$$

$$\Delta H_4 = \int_{298}^{800} C_{P(CaCO_3)} dT$$

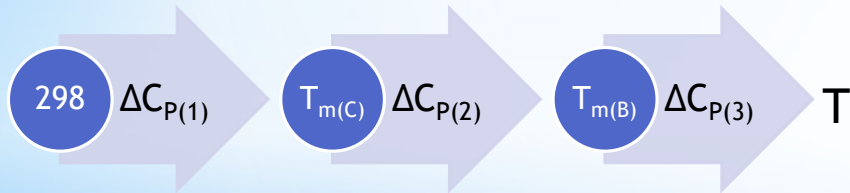$$\Delta H_T = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$$

Isothermal enthalpy change involving phase change

Consider a general reaction with components at the same temperature different than 298 K where liquid B and C phases are solid at 298 K:

$$aA(s)(T) + bB(l)(T) \xrightarrow{\Delta H_T} cC(l)(T) + dD(s)(T)$$

Kirschoff equation can be used to calculate ΔH°_T :

$$\Delta H_T = \Delta H^{o}_{298} + \int_{298}^{T} \Delta C_P dT$$

298 $\Delta C_{P(1)}$ $T_{m(C)}$ $\Delta C_{P(2)}$ $T_{m(B)}$ $\Delta C_{P(3)}$ T

Component C transforms to liquid at $T_{m(C)}$
Component B transforms to liquid at $T_{m(B)}$
ΔC_P seperated into 3 ranges

Isothermal enthalpy change involving phase change

$$aA(s)(T) + bB(l)(T) \xrightarrow{\Delta H_T} cC(l)(T) + dD(s)(T)$$

| 298 | $\Delta C_{P(1)}$ | $T_{m(C)}$ | $\Delta C_{P(2)}$ | $T_{m(B)}$ | $\Delta C_{P(3)}$ |
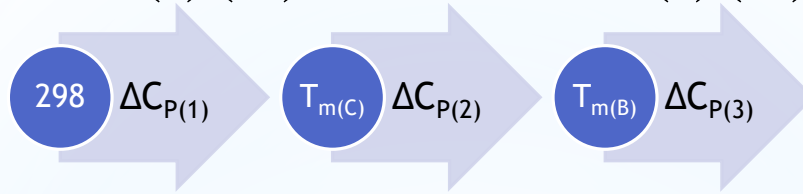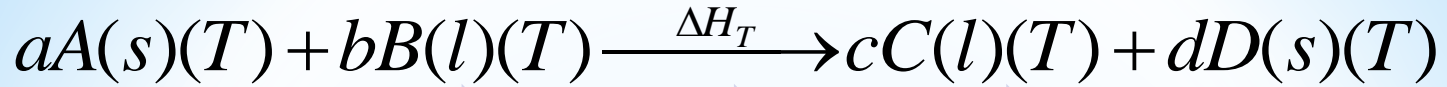
$$\Delta C_P^I = cC_{P(C(s))} + dC_{P(D(s))} - aC_{P(A(s))} - bC_{P(B(s))}$$

$$\Delta C_P^{II} = cC_{P(C(l))} + dC_{P(D(s))} - aC_{P(A(s))} - bC_{P(B(s))}$$

$$\Delta C_P^{III} = cC_{P(C(l))} + dC_{P(D(s))} - aC_{P(A(s))} - bC_{P(B(l))}$$

Therefore

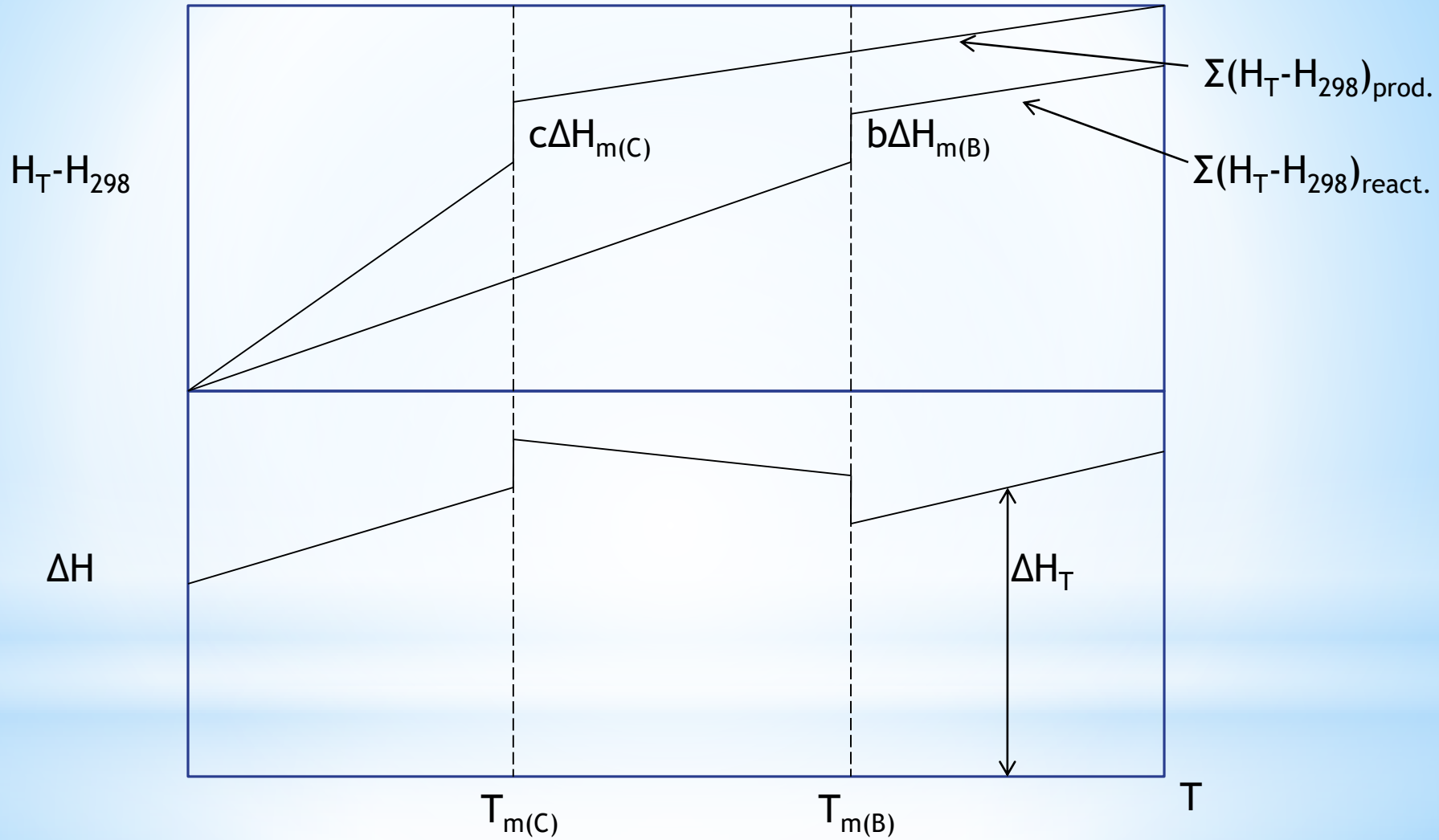$$\Delta H_T = \Delta H_{298}^o + \int_{298}^{Tm(C)} \Delta C_P^I dT + c\Delta H_{m(C)} + \int_{Tm(C)}^{Tm(B)} \Delta C_P^{II} dT - b\Delta H_{m(B)} + \int_{Tm(B)}^{T} \Delta C_P^{III} dT$$
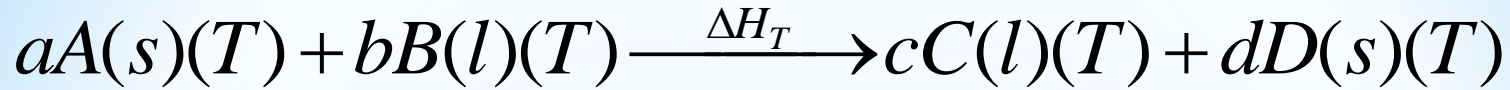
Since H_T-H_{298} enthalpy increment equations incorporate phase changes,

$$\Delta H_T = \Delta H_{298}^o + \sum (H_T - H_{298})_{prod.} - \sum (H_T - H_{298})_{react.}$$

Isothermal enthalpy change involving phase change

Another alternative method that can be used in enthalpy computations for chemical reactions that involve phase transformations is the application of Hess' law
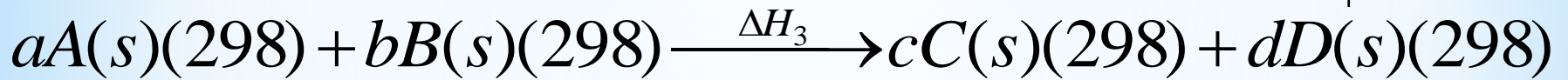
$$aA(s)(T) + bB(l)(T) \xrightarrow{\Delta H_T} cC(l)(T) + dD(s)(T)$$

$$\downarrow 1 \qquad \downarrow 2 \qquad\qquad\qquad \uparrow 4 \qquad \uparrow 5$$

$$aA(s)(298) + bB(s)(298) \xrightarrow{\Delta H_3} cC(s)(298) + dD(s)(298)$$

$$\Delta H_T = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$$

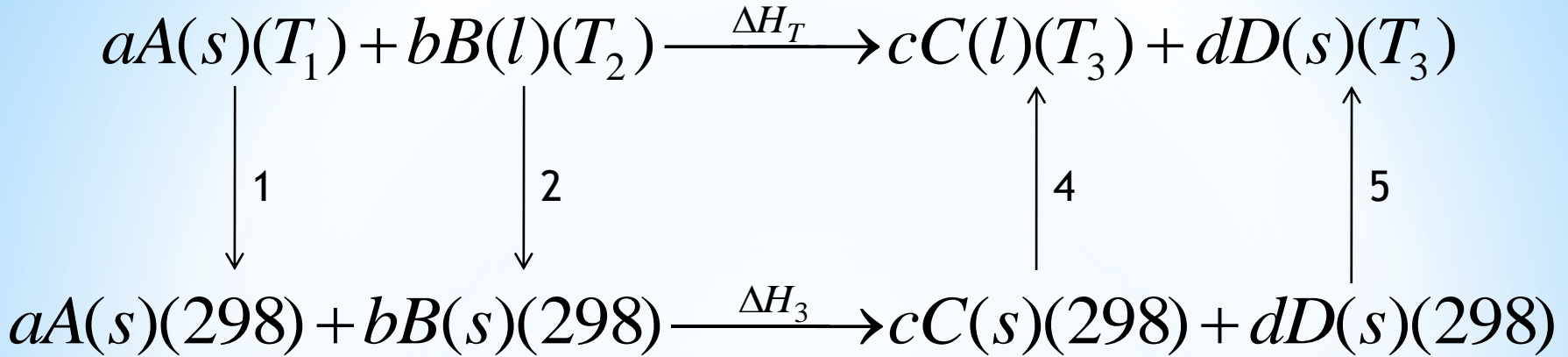$$\Delta H_1 = a \int_T^{298} C_{P(A(s))} dT$$

$$\Delta H_2 = b \left[\int_T^{T_{m(B)}} C_{P(B(l))} dT - \Delta H_{m(B)} + \int_{T_{m(B)}}^{298} C_{P(B(s))} dT \right]$$

$$\Delta H_3 = \Delta H_{298}^o$$

$$\Delta H_4 = c \left[\int_{298}^{T_{m(C)}} C_{P(C(s))} dT + \Delta H_{m(C)} + \int_{T_{m(C)}}^{T} C_{P(B(l))} dT \right]$$

$$\Delta H_5 = d \int_{298}^{T} C_{P(D(s))} dT$$

Non-isothermal chemical processes

$$aA(s)(T_1) + bB(l)(T_2) \xrightarrow{\Delta H_T} cC(l)(T_3) + dD(s)(T_3)$$

| 1 | 2 | 4 | 5 |

$$aA(s)(298) + bB(s)(298) \xrightarrow{\Delta H_3} cC(s)(298) + dD(s)(298)$$

$$\Delta H_T = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$$

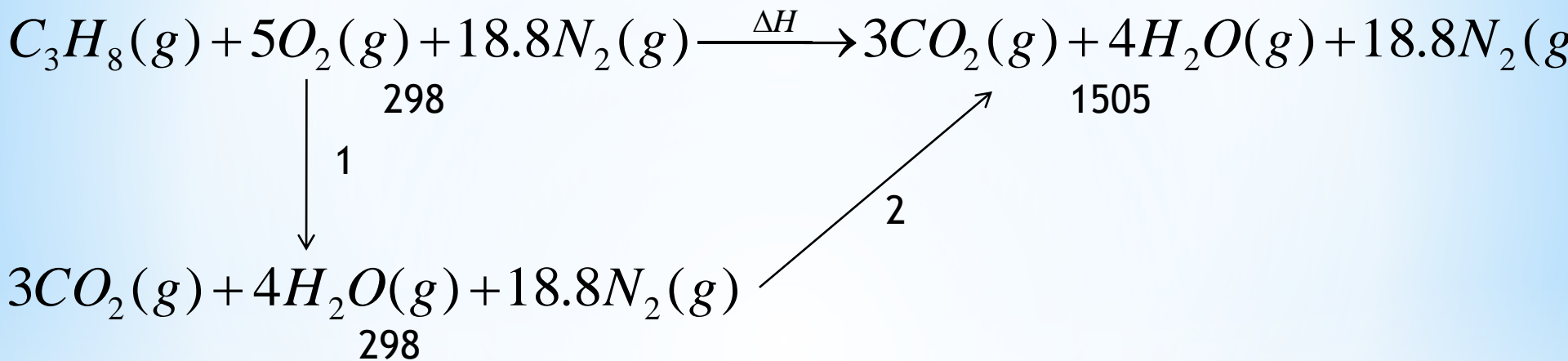$$\Delta H_1 = a\int_{T_1}^{298} C_{P(A(s))}dT = -a(H_{T_1} - H_{298})_{A(s)}$$

$$\Delta H_2 = b\left[\int_{T_2}^{T_{m(B)}} C_{P(B(l))}dT - \Delta H_{m(B)} + \int_{T_{m(B)}}^{298} C_{P(B(s))}dT\right] = -b(H_{T2} - H_{298})_{B(l)}$$

$$\Delta H_3 = \Delta H_{298}^o = \sum H_{298(prod.)}^o - \sum H_{298(react.)}^o$$

$$\Delta H_4 = c\left[\int_{298}^{T_{m(C)}} C_{P(C(s))}dT + \Delta H_{m(C)} + \int_{T_{m(C)}}^{T_3} C_{P(C(l))}dT\right] = c(H_{T3} - H_{298})_{C(l)}$$

$$\Delta H_5 = d\int_{298}^{T_3} C_{P(D(s))}dT = d(H_{T3} - H_{298})_{D(s)}$$

Example – A furnace that is designed to melt silver/copper scrap is to be fired with propane and air. The propane vapor mixes with dry air at 298 K. Flue gases are expected to exit the furnace at 1505 K under steady state conditions. How long will a 45.5 kg container of propane maintain the furnace temperature if heat is conducted through the brickwork at the rate of 10000 kJ/hour ?
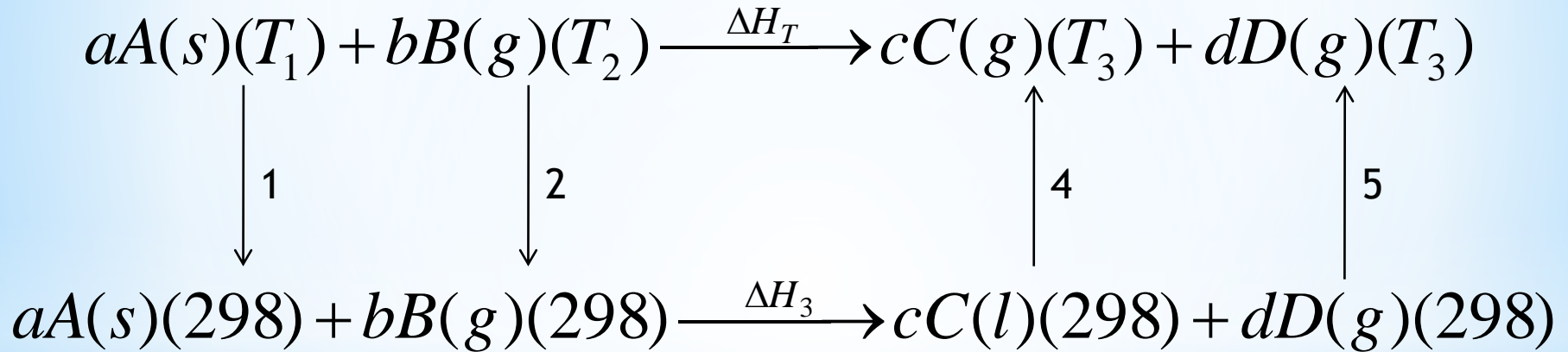
$$C_3H_8(g)+5O_2(g)+18.8N_2(g) \xrightarrow{\;\Delta H\;} 3CO_2(g)+4H_2O(g)+18.8N_2(g$$

298

1

1505

2

$$3CO_2(g)+4H_2O(g)+18.8N_2(g)$$

298

Substance	$H_T - H_{298}$ (J/mole)	ΔH^o_{298} (kJ/mole)	C_P (J/mole K)
$C_3H_8(g)$		-103.55	
$CO_2(g)$	$-16476+44.25*T+0.0044*T^2+8.62*10^5\ T^{-2}$	-393.5	$44.14+9.04*10^{-3}*T-8.54*10^5*T^{-2}$
$H_2O(l)$		-285.85	75.47
$H_2O(g)$	$34660+30.01*T+0.00536*T^2-0.33*10^5\ T^{-2}$	-241.95	$30.01+10.72*10^{-3}*T+0.33*10^5*T^{-2}$
$N_2(g)$	$-8502+27.88*T+0.00213*T^2$	--	$27.88+4.27*10^{-3}*T$

$\Delta H_v(H_2O)$ = 40897 J/mole

Air: 21% O_2 + 79% N_2

Flame temperature

The maximum temperature the gaseous products can reach upon proceeding of an exothermic reaction is called the flame temperature

The furnace is considered as adiabatic for no heat loss to the surroundings and maximum flame temperature

$$aA(s)(T_1) + bB(g)(T_2) \xrightarrow{\Delta H_T} cC(g)(T_3) + dD(g)(T_3)$$

$$\downarrow 1 \qquad \downarrow 2 \qquad \qquad \uparrow 4 \qquad \uparrow 5$$

$$aA(s)(298) + bB(g)(298) \xrightarrow{\Delta H_3} cC(l)(298) + dD(g)(298)$$

$$\Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_4 + \Delta H_5$$

$$\Delta H_4 = c\left[\int_{298}^{T_{m(C)}} C_{P(C(l))} dT + \Delta H_{v(C)} + a\int_{T_{m(C)}}^{Tflame} C_{P(C(g))} dT \right] = c(H_{Tflame} - H_{298})_{C(g)}$$

$$\Delta H_5 = d\int_{298}^{T_{Tflame}} C_{P(D(g))} dT = d(H_{Tflame} - H_{298})_{D(g)}$$