The University Of Sheffield.

Chemical &
Process
Engineering

Assessing the Efficiency Limits for Hydrogen Production by Thermochemical Cycles

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‘Engineering from Molecules’

Objectives

To assess the maximum efficiency of specific thermochemical cycles based on their reactions as given

To enable efficiency comparison between TCs and other heat - work processes

Role of TCs

Conversion of heat into work

- in the form of chemical free energy

Characteristics of TCs	Energy demands
Species heating and cooling	± heat
Isothermal phase changes	± heat
Isothermal reactions	± heat, ± work
Species separations	± heat, ± work

Some efficiency definitions :

$$\eta = \frac{\Delta H\ (hhv)}{Q\ (per\ mol\ H_2)}$$

$$\eta = \frac{\Delta H\ (lhv)}{Q\ (per\ mol\ H_2)}$$

$$\eta = \frac{\Delta H\ (hhv)}{Q\ (per\ mol\ H_2) + Elect.\ work/\eta_{el}}$$

Work based definitions :

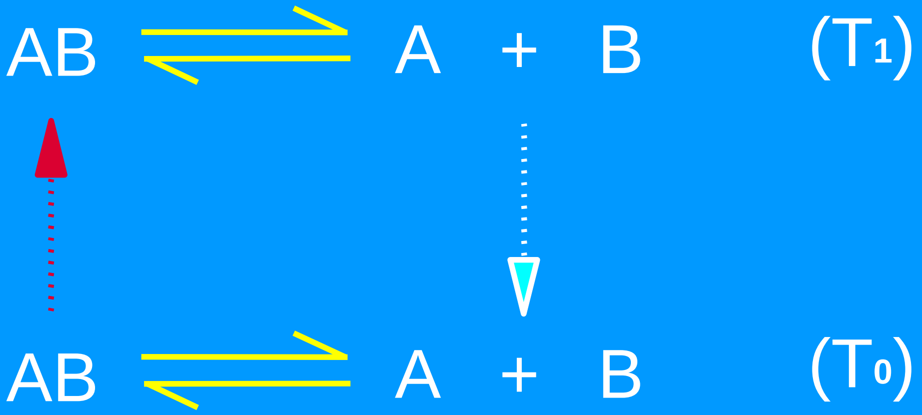
Consistent with maximum efficiency $\eta_{\text{Carnot}} = 1 - \frac{T_{\text{low}}}{T_{\text{high}}}$

$$\eta = \frac{\text{Nett work}}{Q\,(\text{per mol } H_2)} \longrightarrow \eta = \frac{\sum \Delta G^{o}}{Q\,(\text{per mol } H_2)}$$

Definition used here

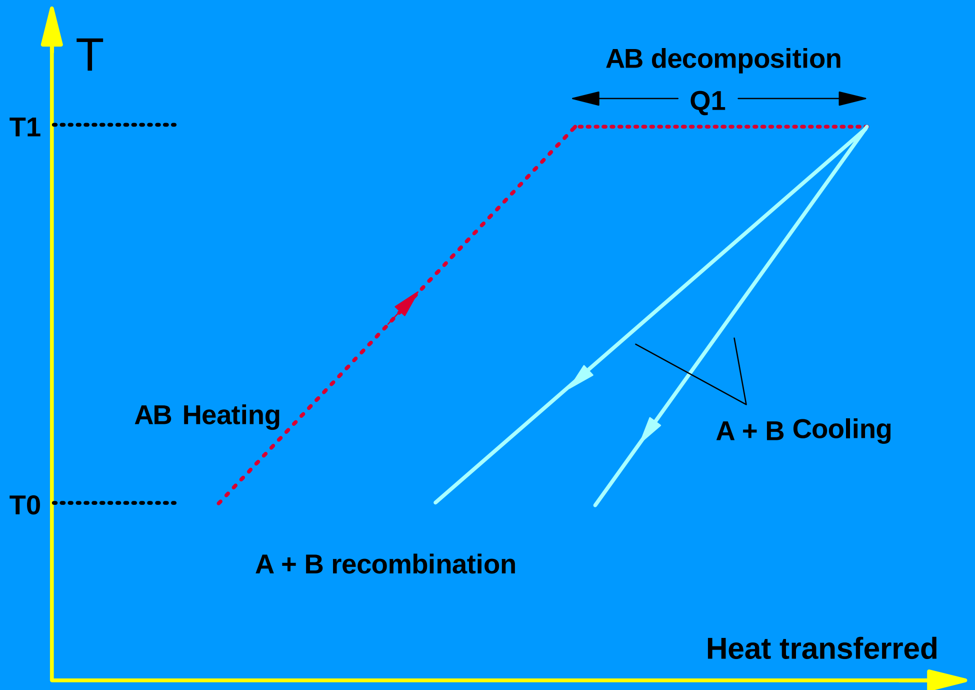
$$\eta = -\frac{\Delta G^{o}_{298}(H_2/O_2) + \sum \Delta G^{o}(-) + \sum \Delta G^{o}(+) + \sum \Delta G_{\text{sep}}}{Q\,(\text{per mol } H_2)}$$

Simplest thermochemical cycle



$$\begin{tikzcd}
AB \arrow[r, shift left, harpoon] & A + B \arrow[l, shift left, harpoon] \arrow[d, dotted] & (T_1) \\
AB \arrow[u, dotted] \arrow[r, shift left, harpoon] & A + B \arrow[l, shift left, harpoon] & (T_0)
\end{tikzcd}$$

$$\eta = -\frac{\Delta G^{o}_{o} + \Delta G^{o}_{1}}{Q_1 + \text{heat mismatch}}$$



When

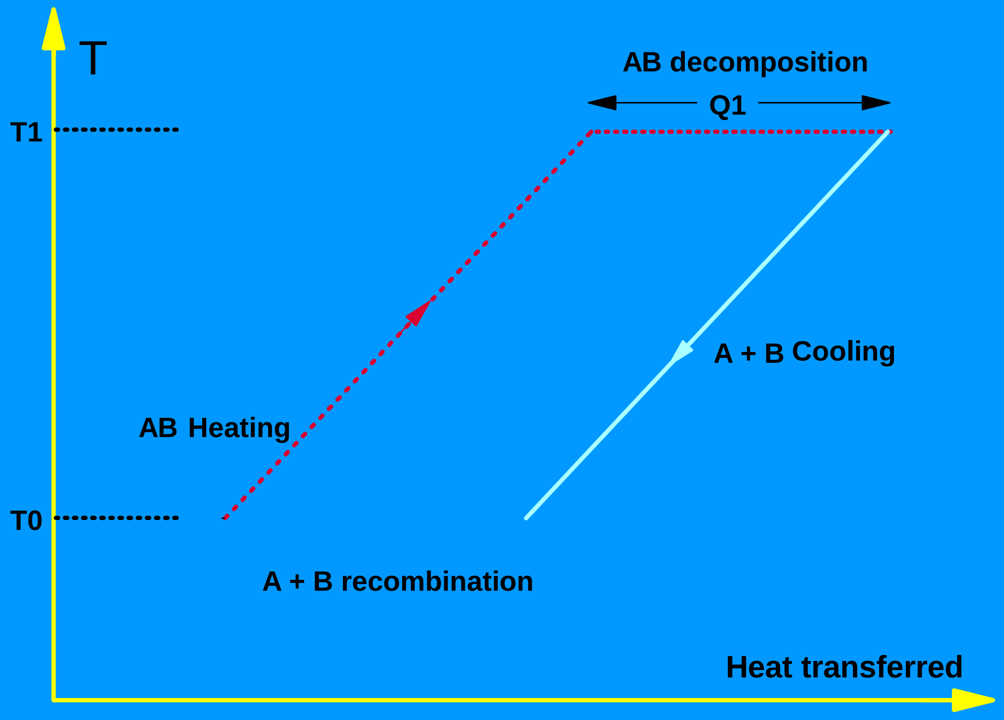
Cp(A+B,T) = Cp(AB,T)

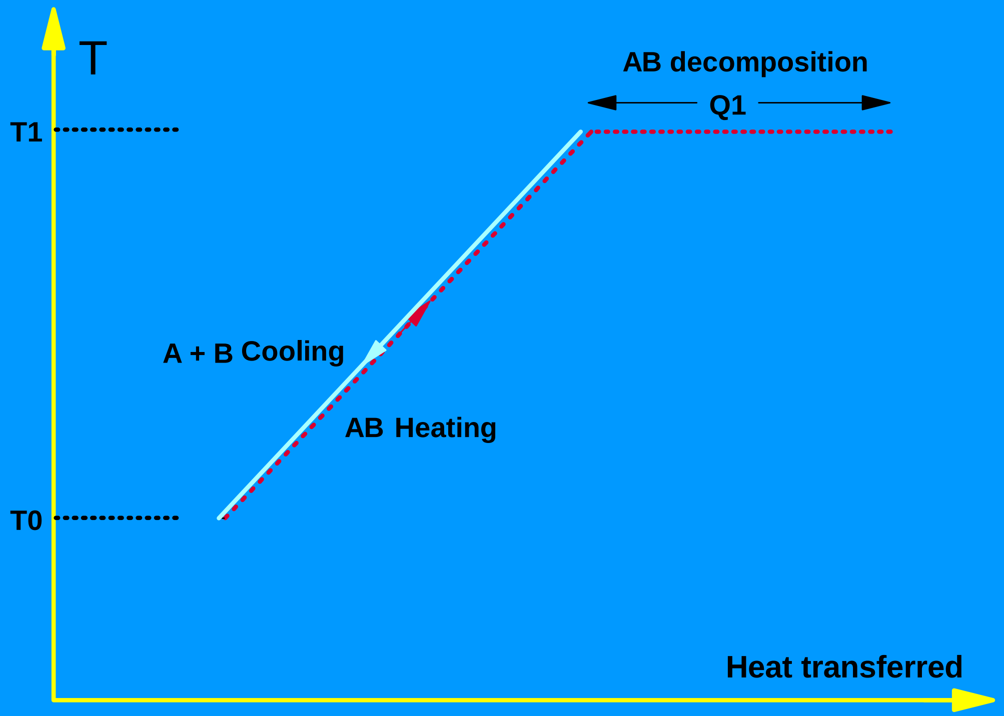
↓

perfect heat matching

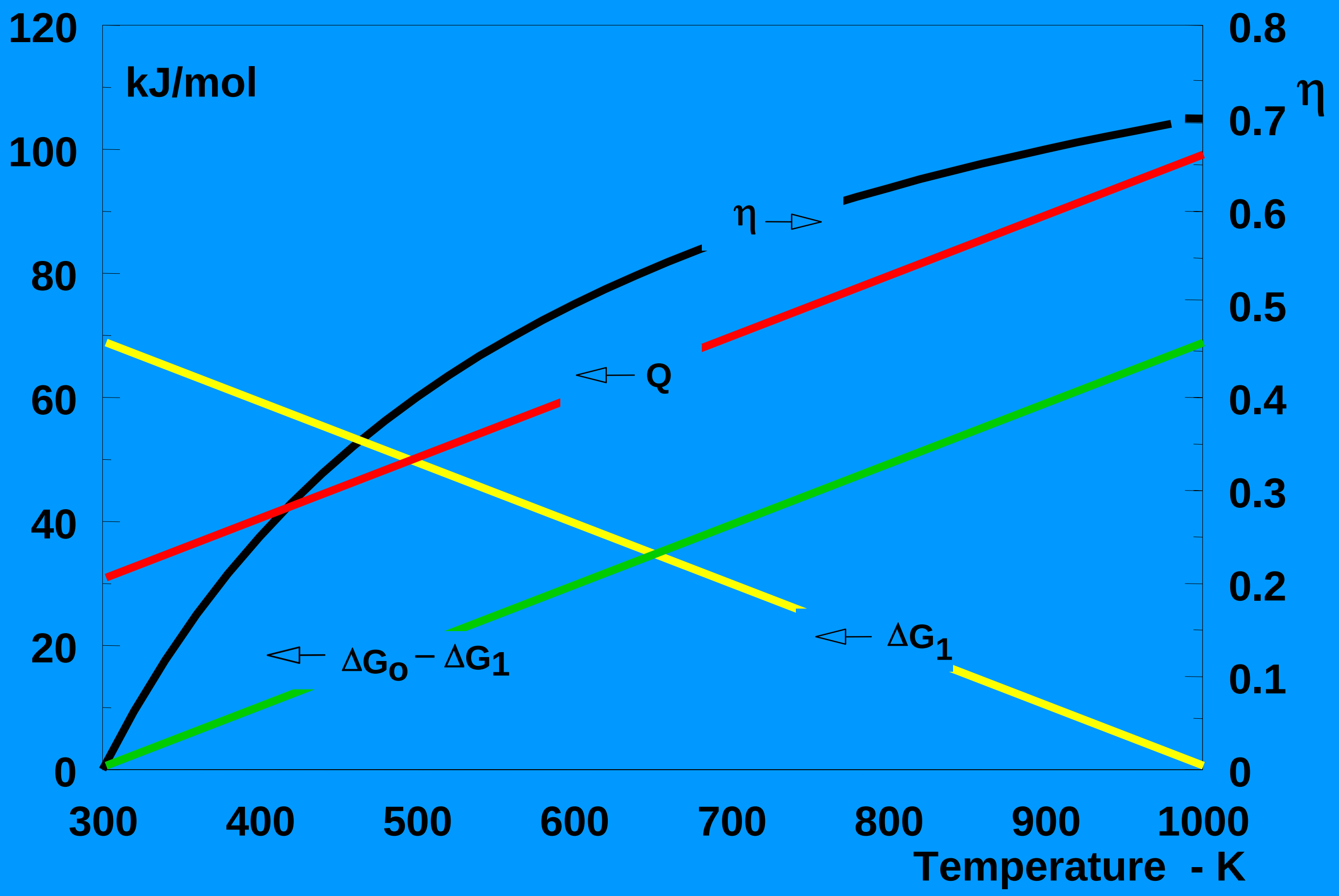
$$\Delta H^{o}_{o} = \Delta H^{o}_{1}$$

$$\Delta S^{o}_{0} = \Delta S^{o}_{1}$$


T
T1
T0
AB decomposition
Q1
AB Heating
A + B Cooling
A + B recombination
Heat transferred



$$\eta = \frac{\Delta G_o^o - \Delta G_1^o}{\Delta H_1^o - \Delta G_1^o} = \frac{\Delta H_o^o - T_o \Delta S_o^o - \Delta H_1^o + T_1 \Delta S_1^o}{T_1 \Delta S_1^o} = 1 - \frac{T_o}{T_1}$$



Variation of heat, work and efficiency terms for simple cycle with ΔH = 100 kJ/mol, ΔS = 100 J/Mol K

Limiting efficiencies of some simple cycles

Decomposition species	ΔH_1^o kJ	ΔH_0^0 kJ	ΔG_0^0 kJ	T_1 (K)	ηCarnot	$\Delta G_0^0 / Q$
$SO_3 \rightarrow SO_2 + 0.5\ O_2$	97.3	98.9	70.9	1055	0.717	0.716
$H_2O \rightarrow H_2 + 0.5\ O_2$	251.2	241.8	228.5	4346	0.931	0.909
$CO_2 \rightarrow CO + 0.5\ O_2$	271.0	282.9	257.3	3340	0.911	0.908
$CaCO_3 \rightarrow CaO + CO_2$	165.8	178.2	130.5	1160	0.743	0.732

Efficiency methodology

- starting point = liquid water
  finishing point = liquid water (both at 1atm, 298 K)
- Processes carried out at reference condition of 1 atm
- Reactions with $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$ carried out for $\Delta G^\circ = 0$ (subject to $T < 1700$ K)
- Heat balancing for heating and cooling branches ($\Delta T \geq 0$)
- ΔH°, ΔS° and ΔG° values calculated from HSC 5.1 Chemistry package

- Work components are Gibbs free energy changes at certain points of cycle
- Free energy work available from H_2/O_2 recombination at 298 K (taken as -237 kJ/mol H_2)
- Free energy available for certain reactions [$\Delta G^o(-)$]
- Free energy consumed by certain reactions [$\Delta G^o(+)$]
- Free energy consumed by any separation processes

$$\Delta G_{sep} = - RT \sum n_i \ln(x_i)$$

Methodology applied to US Chlorine cycle -

$Cl_2(g) + H_2O(g) \longrightarrow 2HCl + 0.5\ O_2(g)$

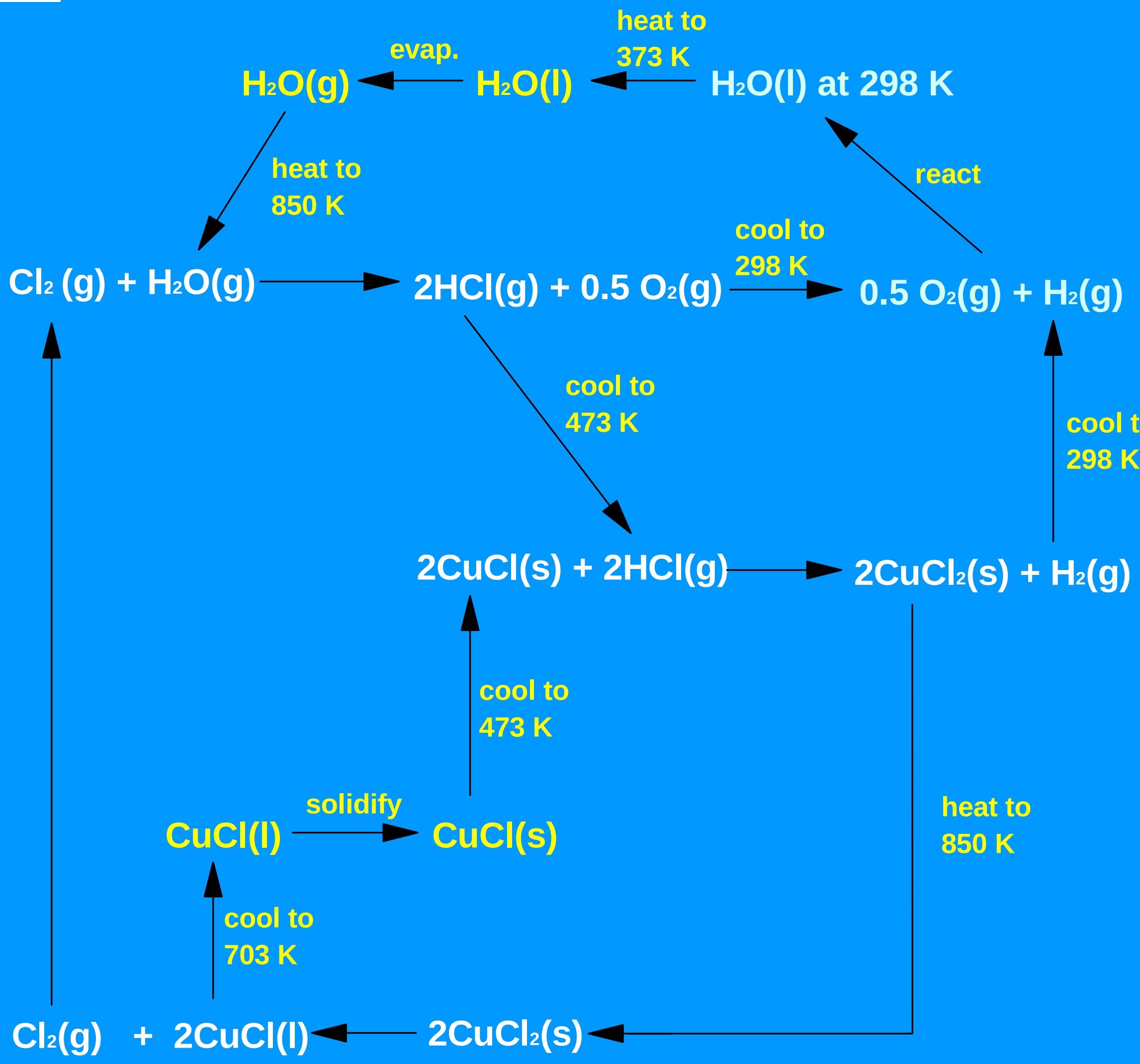
$T = 850$ K
$\Delta H^o = 58.8$ kJ/mol
$\Delta G^o = 0$

$2CuCl(s) + 2HCl(g) \longrightarrow 2CuCl_2(s) + H_2(g)$

$T = 473$ K
$\Delta H^o = 24.9$ kJ/mol
$\Delta G^o = 118.1$ kJ/mol

$2CuCl_2(s) \longrightarrow 2CuCl(s) + Cl_2(g)$

$T = 850$ K
$\Delta H^o = 185.5$ kJ/mol
$\Delta G^o = 0$



$H_2O(g)$ evap. $H_2O(l)$ heat to 373 K $H_2O(l)$ at 298 K

heat to 850 K

react

$Cl_2(g) + H_2O(g)$

$2HCl(g) + 0.5\ O_2(g)$

cool to 298 K

$0.5\ O_2(g) + H_2(g)$

cool to 473 K

cool to 298 K

$2CuCl(s) + 2HCl(g)$

$2CuCl_2(s) + H_2(g)$

cool to 473 K

heat to 850 K

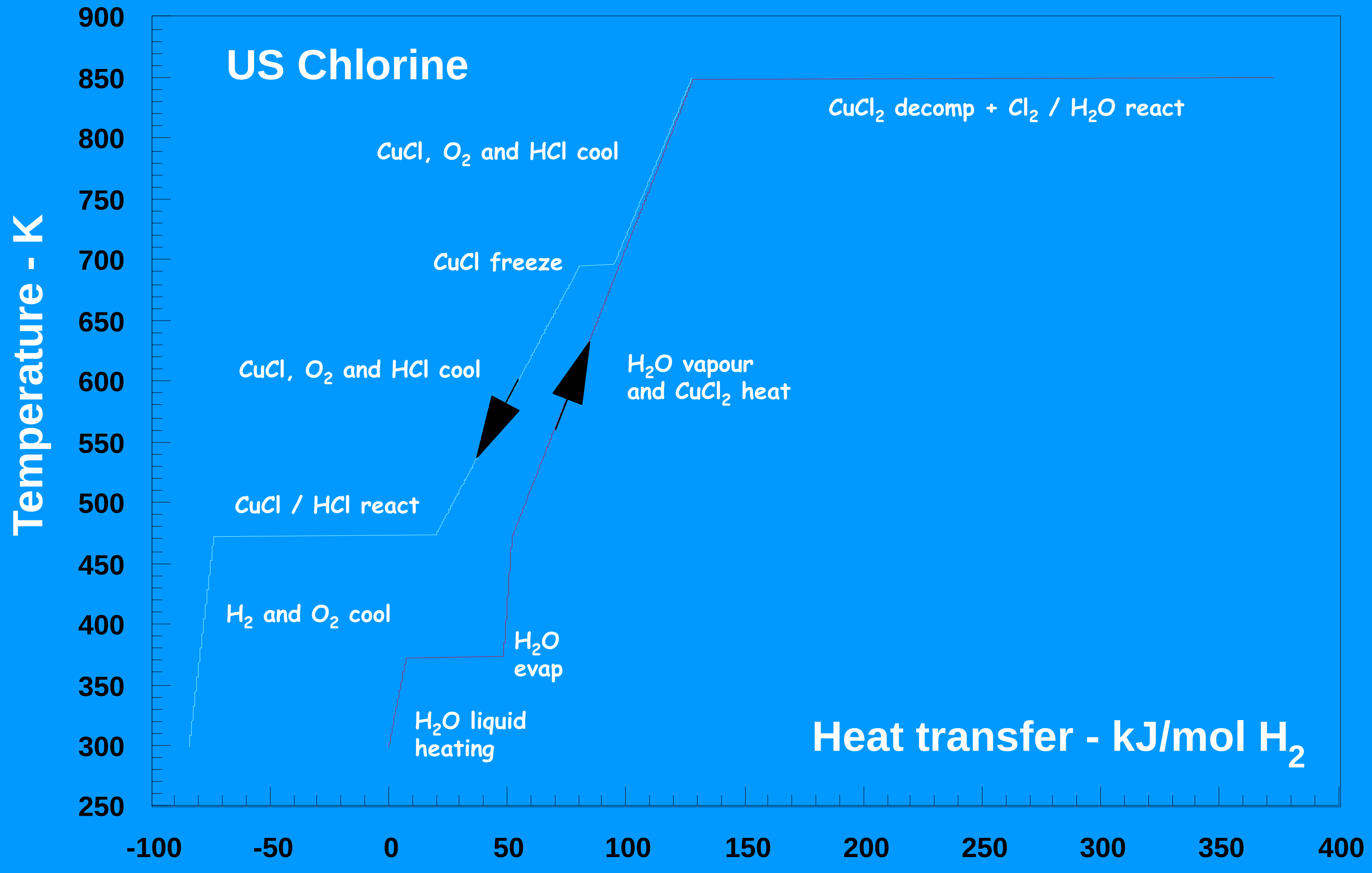
$CuCl(l)$ solidify $CuCl(s)$

cool to 703 K

$Cl_2(g) + 2CuCl(l)$

$2CuCl_2(s)$

US Chlorine Cycle	To	T1	ΔG°	Q±
	K	K	kJ	kJ
$Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + 0.5O_2(g)$	850	850	0	58.8
2HCl and $0.5O_2$ separation at 473 K			4.92	
$2CuCl_2(s) \rightarrow 2CuCl(l) + Cl_2(g)$	850	850	0	185.5
$2CuCl_2(s) \rightarrow 2CuCl_2(s)$	473	850		62.46
$H_2O(l) \rightarrow H_2O(l)$	298	373		7.5
$H_2O(l) \rightarrow H_2O(g)$	373	373		40.9
$H_2O(g) \rightarrow H_2O(g)$	373	850		17.5
$2CuCl(l) \rightarrow 2CuCl(l)$	850	703		-17.8
$2HCl(g) \rightarrow 2HCl(g)$	850	473		-22.54
$2CuCl(l) \rightarrow 2CuCl(s)$	703	703		-14.2
$2CuCl(s) \rightarrow 2CuCl(s)$	703	473		-55.7
$\frac{1}{2} O_2(g) \rightarrow \frac{1}{2} O_2(g)$	850	298		-17.5
$2CuCl(s) + 2HCl(g) \rightarrow 2CuCl_2(s) + H_2(g)$	473	473	118.1	-93.2
$H_2(g) \rightarrow H_2(g)$	473	298		-5.0


US Chlorine
Temperature - K
Heat transfer - kJ/mol H_2
900
850
800
750
700
650
600
550
500
450
400
350
300
250
-100
-50
0
50
100
150
200
250
300
350
400
$CuCl_2$ decomp + Cl_2 / H_2O react
CuCl, O_2 and HCl cool
CuCl freeze
CuCl, O_2 and HCl cool
H_2O vapour and $CuCl_2$ heat
CuCl / HCl react
H_2 and O_2 cool
H_2O evap
H_2O liquid heating

Westinghouse

$SO_2(g) + 2H_2O(l) \rightarrow H_2SO_4(l) + H_2(g)$

$H_2SO_4(g) \rightarrow H_2O(g) + SO_3(g)$

$SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$

US Chlorine

$Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + \frac{1}{2}O_2(g)$

$2CuCl(s) + 2HCl(g) \rightarrow 2CuCl_2(s) + H_2(g)$

$2CuCl_2(s) \rightarrow 2CuCl(l) + Cl_2(g)$

Sulphur Iodine

$SO_2(g) + 16H_2O(l) + 9I_2(l) \rightarrow H_2SO_4(aq) + 2HI.10H_2O.8I_2(l)$

$H_2SO_4(aq) + [2HI.10H_2O.8I_2](l) \rightarrow [H_2SO_4 + 4H_2O](l) + 2HI(g) + [10H_2O + 8I_2(l)]$

$H_2SO_4(g) \rightarrow H_2O(g) + SO_3(g)$

$SO_3(g) \rightarrow SO_2(g) + \frac{1}{2} O_2(g)$

$2HI(g) \rightarrow H_2(g) + I_2(g)$

Zinc oxide

$ZnO(s) \rightarrow Zn(g) + \frac{1}{2} O_2(g)$

$Zn(s) + H_2O(l) \rightarrow ZnO(s) + H_2(g)$

Nickel Ferrite

$0.5NiMnFe_4O_8 \rightarrow 0.5NiMnFe_4O_6 + 0.5O_2(g)$

$0.5NiMnFe_4O_6 + H_2O(g) \rightarrow 0.5NiMnFe_4O_8 + H_2(g)$

UT- 3

$CaBr_2(s) + H_2O(g) \rightarrow CaO(s) + 2HBr(g)$

$CaO(s) + Br_2(g) \rightarrow CaBr_2(s) + 0.5\ O_2(g)$

$Fe_3O_4(s) + 8HBr(g) \rightarrow 3FeBr_2(s) + Br_2(g) + 4H_2O(g)$

$3FeBr_2 + 4H_2O(g) \rightarrow Fe_2O_3 + H_2(g) + 6HBr(g)$

Ispra Mark 4

$Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + 0.5O_2(g)$

$2FeCl_2(s) + 2HCl(g) + S(s) \rightarrow 2FeCl_3(s) + H_2S(g)$

$H_2S(g) \rightarrow S(g) + H_2(g)$

$2FeCl_3(g) \rightarrow Cl_2(g) + 2FeCl_2(s)$

Ispra Mark 9

$3FeCl_3(g) \rightarrow 1.5Cl_2(g) + 3FeCl_2(s)$

$1.5Cl_2(g) + Fe_3O_4 + 6HCl(g) \rightarrow 3FeCl_3\ (s) + 3H_2O(g) + 0.5O_2(g)$

$3FeCl_2(s) + 4H_2O(g) \rightarrow Fe_3O_4 + 6HCl + H_2(g)$

Gaz de France

$2K(l) + 2KOH(l) \rightarrow 2K_2O(s) + H_2(g)$

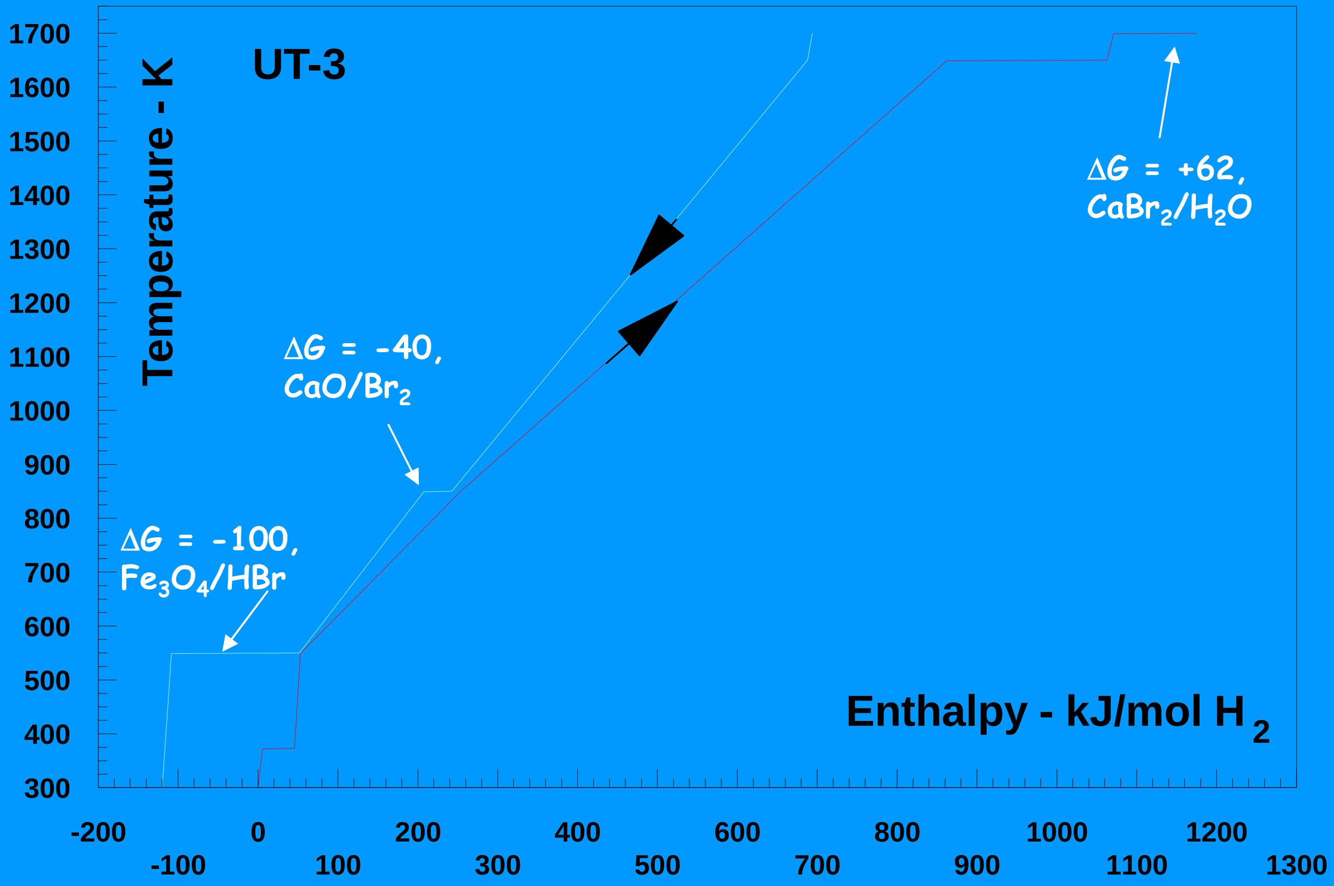
$2K_2O(s) \rightarrow 2K(g) + K_2O_2(l)$

$K_2O_2(s) + H_2O(l) \rightarrow 2KOH(s) + 0.5O_2(g)$

Pinch diagram features -

- Heat outputs need to be positioned beneficially with respect to heat inputs - if not then heat balancing will be poor
- Isothermal heat changes at reaction points influential in determining extent of matching
- Heat changes often associated with work inputs and outputs
  - direct effect on efficiency
- Heat inputs ==> +ve entropy changes
  - for ΔG +ve, both heat and work contribute to ΔH increase
  - work input has relatively neutral effect on efficiency
  - for ΔG -ve can reduce temperature

- Heat outputs ==> -ve entropy changes
  - for ΔG +ve, work converted to heat and rejected
  - need work input to achieve reference condition
  - work input has adverse effect on efficiency
  - if ΔH -ve, some or all enthalpy goes to balance rejected heat

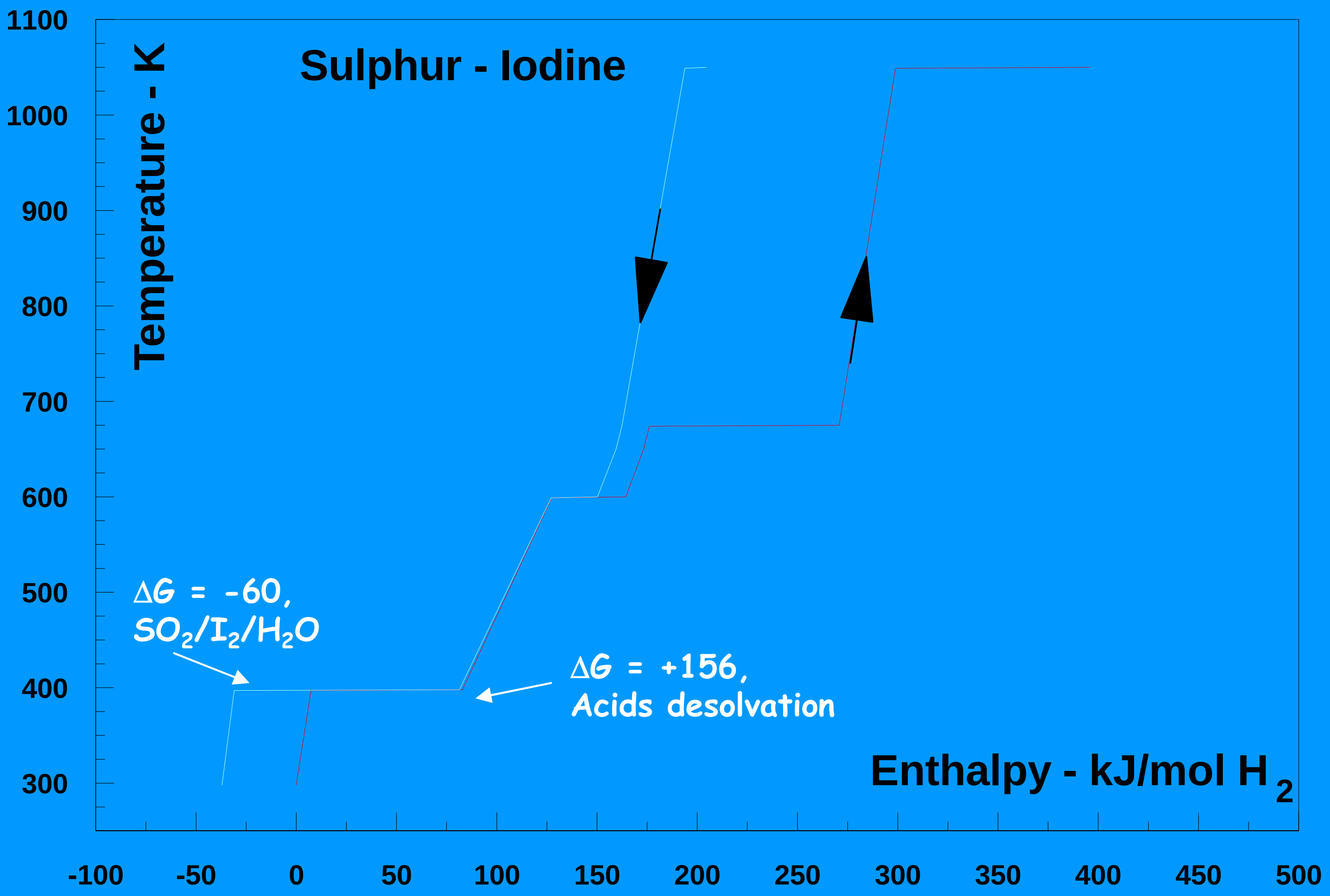


$CaBr_2(s) + H_2O(g) \rightarrow CaO(s) + 2HBr(g)$

$CaO(s) + Br_2(g) \rightarrow CaBr_2(s) + 0.5\ O_2(g)$

$Fe_3O_4(s) + 8HBr(g) \rightarrow 3FeBr_2(s) + Br_2(g) + 4H_2O(g)$

$3FeBr_2 + 4H_2O(g) \rightarrow Fe_2O_3 + H_2(g) + 6HBr(g)$



ΔG = -60, $SO_2/I_2/H_2O$

ΔG = +156, Acids desolvation

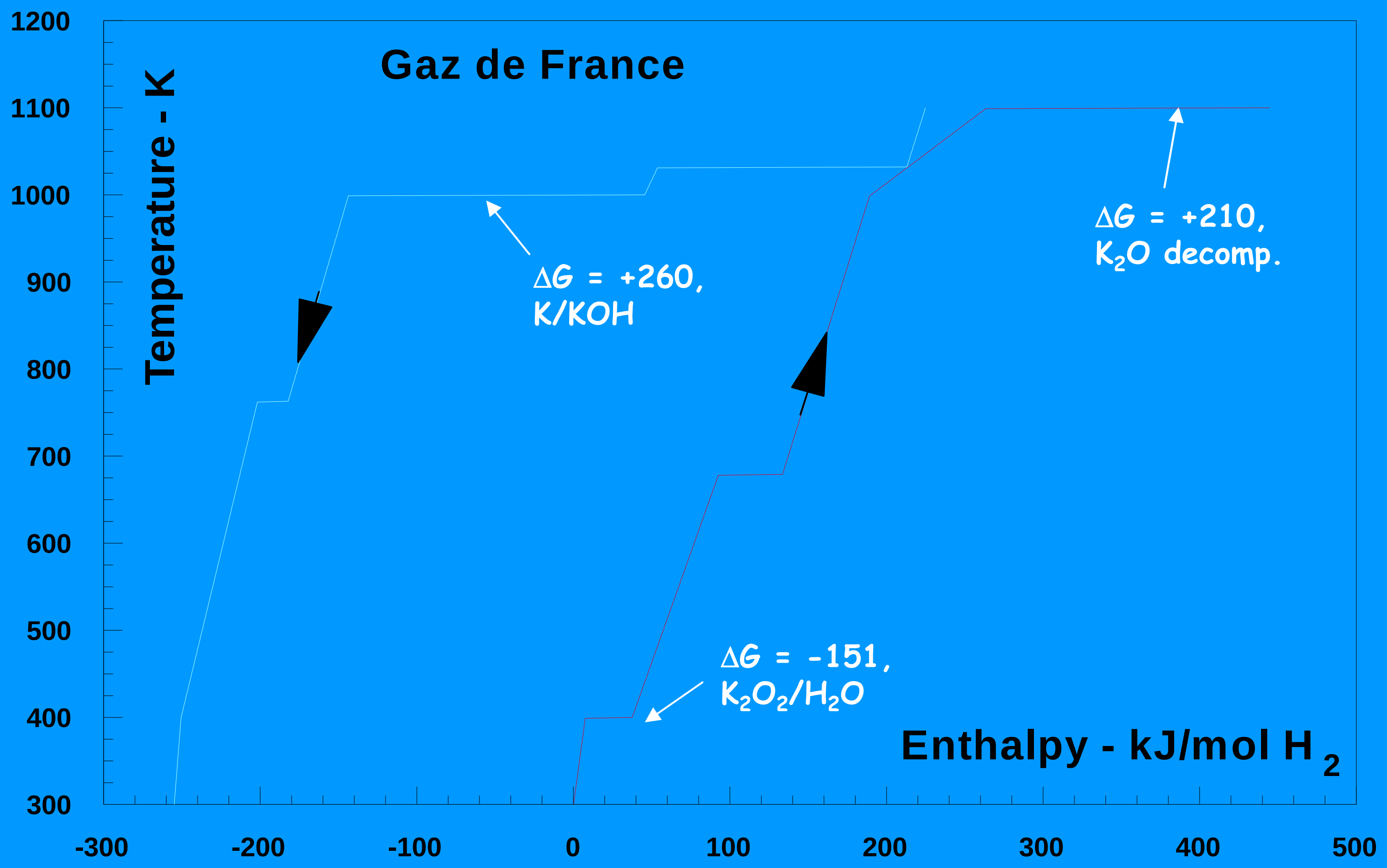
$SO_2(g) + 16H_2O(l) + 9I_2(l) \rightarrow H_2SO_4(aq) + 2HI.10H_2O.8I_2(l)$

$H_2SO_4(aq) + [2HI.10H_2O.8I_2](l) \rightarrow [H_2SO_4 + 4H_2O](l) + 2HI(g) + [10H_2O + 8I_2(l)]$

$2HI(g) \rightarrow H_2(g) + I_2(g)$

$SO_3(g) \rightarrow SO_2(g) + \frac{1}{2} O_2(g)$

$H_2SO_4(g) \rightarrow H_2O(g) + SO_3(g)$

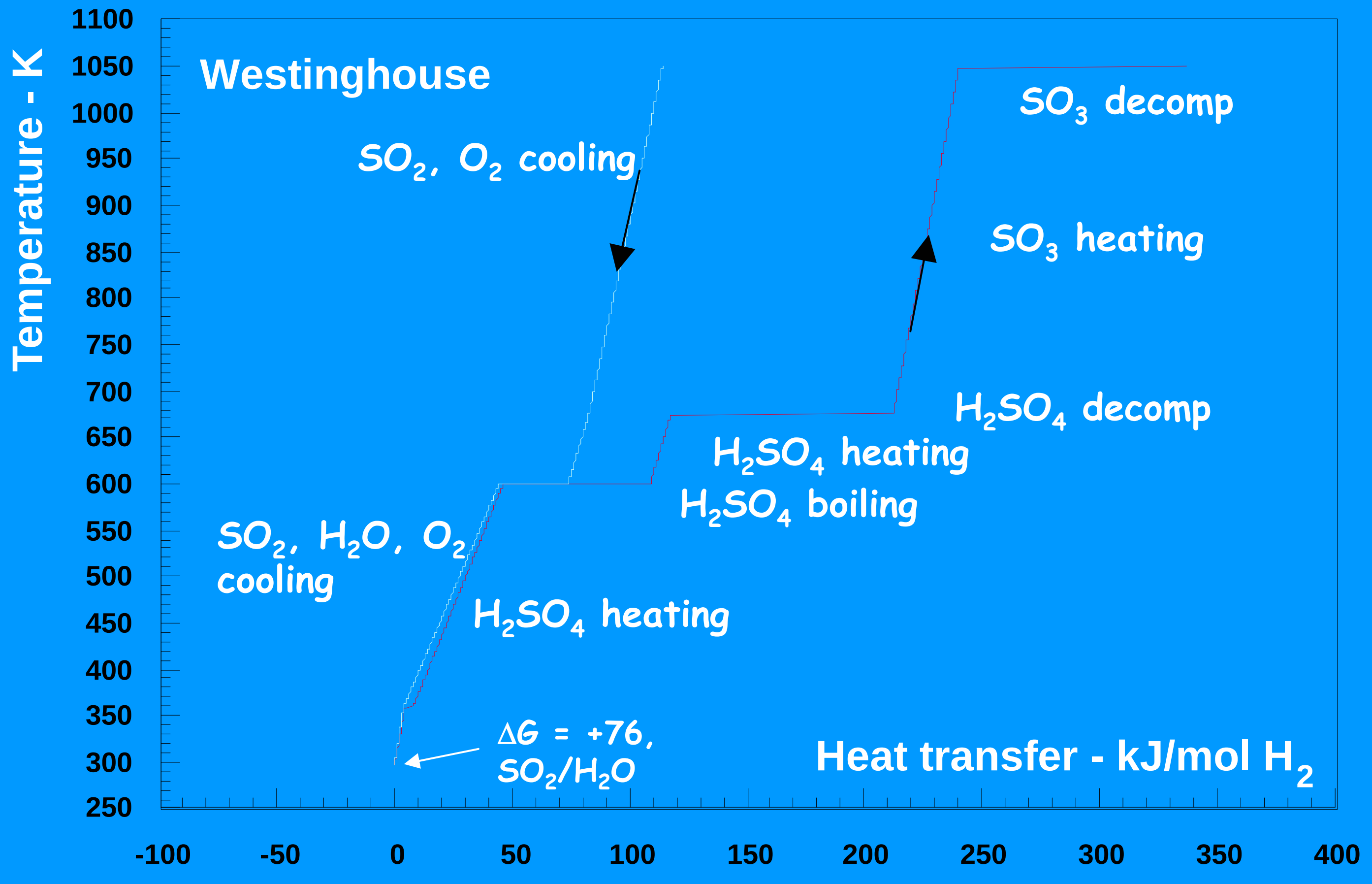


$2K(l) + 2KOH(l) \rightarrow 2K_2O(s) + H_2(g)$

$2K_2O(s) \rightarrow 2K(g) + K_2O_2(l)$

$K_2O_2(s) + H_2O(l) \rightarrow 2KOH(s) + 0.5O_2(g)$

Pinch diagram for Westinghouse cycle



$SO_2(g) + 2H_2O(l) \rightarrow H_2SO_4(l) + H_2(g)$ $H_2SO_4(g) \rightarrow H_2O(g) + SO_3(g)$

$SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$

Efficiencies calculated from pinch diagrams

1. Including all work producing terms

$$\eta_1 = -\frac{\left[\Delta G_{298}(H_2/O_2) + \sum \Delta G^{o}(-) + \sum \Delta G^{o}(+) + \sum \Delta G_{sep}\right]}{\text{heat input}}$$

2. Including only H_2/O_2 recombination work

$$\eta_2 = -\frac{\left[\Delta G_{298}(H_2/O_2) + \sum \Delta G^{o}(+) + \sum \Delta G_{sep}\right]}{\text{heat input}}$$

Summary of results for 10 cycles

Process	Heat input kJ/mol H_2	Heat rejection kJ/mol H_2	Work input kJ/mol H_2	Additional work output kJ/mol H_2	η_1	
Westinghouse	222.5	0	87.7	0	0.67	
UT - 3	481.3	120.0	86.3	-139.3	0.60	
Ispra Mark 4	174.4	15.2	155.1	-29.3	0.62	
Nickel ferrite	249.3	28.0	97.7	0	0.56	
Ispra Mark 9	476.6	160.0	63.4	-76.7	0.53	
Zinc oxide	341.7	94.5	136.4	-89.1	0.56	
Sulphur - Iodine	192.0	37.0	179.3	-60.8	0.51	
US Chlorine	258.9	84.0	123.0	0	0.44	
Ispra Mark 7B	337.7	148.0	249.1	-113.3	0.30	
Gaz de France	219.8	255.0	471.0	-151.4	0	

Summary of results for 10 cycles

Process	Heat input kJ/mol H_2	Heat rejection kJ/mol H_2	Work input kJ/mol H_2	Additional work output kJ/mol H_2	η_1	η_2
Westinghouse	222.5	0	87.7	0	0.67	0.67
UT - 3	481.3	120.0	86.3	-139.3	0.60	0.31
Ispra Mark 4	174.4	15.2	155.1	-29.3	0.62	0.45
Nickel ferrite	249.3	28.0	97.7	0	0.56	0.56
Ispra Mark 9	476.6	160.0	63.4	-76.7	0.53	0.36
Zinc oxide	341.7	94.5	136.4	-89.1	0.56	0.29
Sulphur - Iodine	192.0	37.0	179.3	-60.8	0.51	0.19
US Chlorine	258.9	84.0	123.0	0	0.44	0.44
Ispra Mark 7B	337.7	148.0	249.1	-113.3	0.30	0
Gaz de France	219.8	255.0	471.0	-151.4	0	0

Conclusions - usefulness of approach

- an evaluation, without the use of process flowsheeting, of the maximum thermal efficiencies
- identification of the sources of work produced and feasibility of making use of all ΔG^{o}(-) contributions
- the provision of a starting point for process optimisation, identifying heat transfer needs
- assessment of the relative efficiencies of heat - electricity cycles and thermochemical cycles for use with hybrid cycles
- the basis for improvement of existing cycles through chemicals selection and better positioning of isothermal heat processes