A Representation of Limiting Efficiencies for Thermochemical Cycles

B C R Ewan, R W K Allen
Department of Chemical & Process Engineering, University of Sheffield,
Mappin St, Sheffield S1 3JD, UK.

Introduction

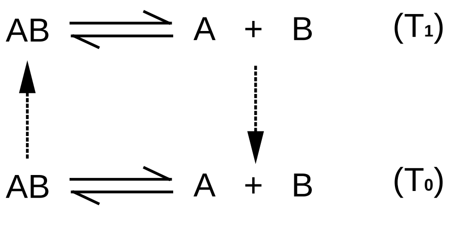
The present revival in interest in thermochemical cycles as a means of producing hydrogen has generated a number of publications which present new flowsheet variations for existing processes as well as additional cycles for consideration. In all of these, the overall process efficiency is a key parameter, although there remains some variability in the way in which this parameter is defined. Variations in process flowsheets and a lack of consistency in the way in which process efficiency is used can lead to significant uncertainties over the relative values of different cycles and suggests the adoption of a more consistent approach.

The value of a Carnot efficiency for determining the limiting efficiency of a thermal process producing work is taken for granted in power engineering and a similar approach for thermochemical cycles would aid in the assessment of the maximum efficiencies available, irrespective of the means of implementation and any subsequent flowsheet variations. The work sets out a basis for representing such a maximum possible efficiency, based on a step by step examination of each stage of the cycle in terms of its free energy change and heat requirements. The maximum thermodynamically allowed internal heat transfer is used to minimise external heat input and an overall efficiency is calculated based on the residual free energies and heat requirements, including the recombination of hydrogen and oxygen.

In this way, the thermochemical cycle is viewed as a mechanism for converting heat into work, as represented by the combination of stored chemical free energy and any additional work which the intermediate reactions can produce. The examination of the maximum theoretical efficiency of cycles in this way provides a useful starting point for any comparison between cycles and also allows identification of the strengths and weaknesses within cycles.

Carnot efficiency equivalence

For the simplest cycle, this consists of an endothermic thermal decomposition at high temperature (T_1) combined with a work recovery step at low temperature (T_0).



For the reactions from left to right, assuming to a first approximation that enthalpy and entropy changes are independent of temperature, the overall Gibbs free energy change for reactants and products at their reference condition, is

$$\Delta G_{overall} = (\Delta G_1 - \Delta G_0) = (T_0 - T_1)\,\Delta S \qquad (1)$$

i.e. the cycle will provide work output ($\Delta G_{overall}$ = -ve) if ΔS for the decomposition is a +ve quantity. In this case ΔG at the higher temperature is numerically lower, becoming zero at the decomposition temperature.

The heat balance for a simple AB decomposition can be usefully represented on a pinch diagram as shown in Figure 1. Here it assumed that the specific heats for AB heating and A + B cooling are independent of temperature.

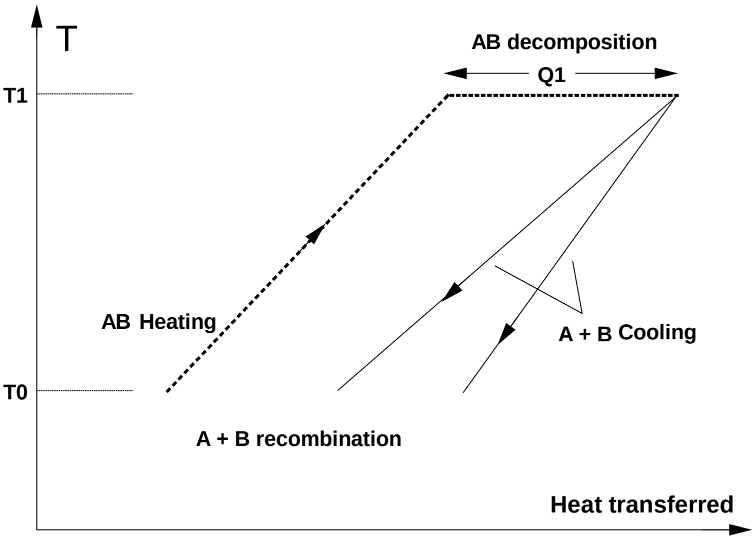


Figure 1. Heating and cooling behaviour for simple AB decomposition.

The possibility for internal heat balancing is represented by two possible product cooling lines, showing both a shortfall in cooling heat with respect to the heating line and an excess of cooling heat leading to heat rejection. When standard conditions are used to represent the free energy and enthalpy changes, the work efficiency for the cycle is given by :

$$\eta \quad = \quad -\frac{\Delta G_{overall}}{Q} \quad = \quad \frac{\Delta G^o_o - \Delta G^o_1}{Q1 + \text{heat mismatch}} \qquad (2)$$

where Q1 is the heat input at decomposition and 'heat mismatch' represents the heat transfer shortfall between A + B cooling and AB heating.

In the special case where the specific heat functions of products and reactants are identical, i.e. $C_p(A+B,T) = C_p(AB,T)$, then both the entropy changes and enthalpy changes are independent of temperature and exact heat matching results.

In this case, $\Delta H^o_0 = \Delta H^o_1$ and $\Delta S^o_0 = \Delta S^o_1$ and the efficiency then becomes :

$$\eta \quad = \quad \frac{\Delta G^o_o - \Delta G^o_1}{\Delta H^o_1 - \Delta G^o_1} \quad = \quad \frac{\Delta H^o_o - T_o \Delta S^o_o - \Delta H^o_1 + T_1 \Delta S^o_1}{T_1 \Delta S^o_1} = 1 - \frac{T_o}{T_1} \qquad (3)$$

For this special case heat is added only at the upper temperature T_1, and such simple cycles can provide the Carnot efficiency for converting heat into work.

Figure 2 shows the variation of the parameters of equation 3 with temperature for the hypothetical case of a system with ΔH = 100 kJ/mol and ΔS = 100 J/mol K.

As a result of the entropy and enthalpy independence with temperature, the cycle will provide the Carnot efficiency throughout the temperature range. At the decomposition temperature (1000 K), $\Delta G_1 = 0$ and only heat is required to effect the conversion of 1 mole of reactants to products under standard conditions.

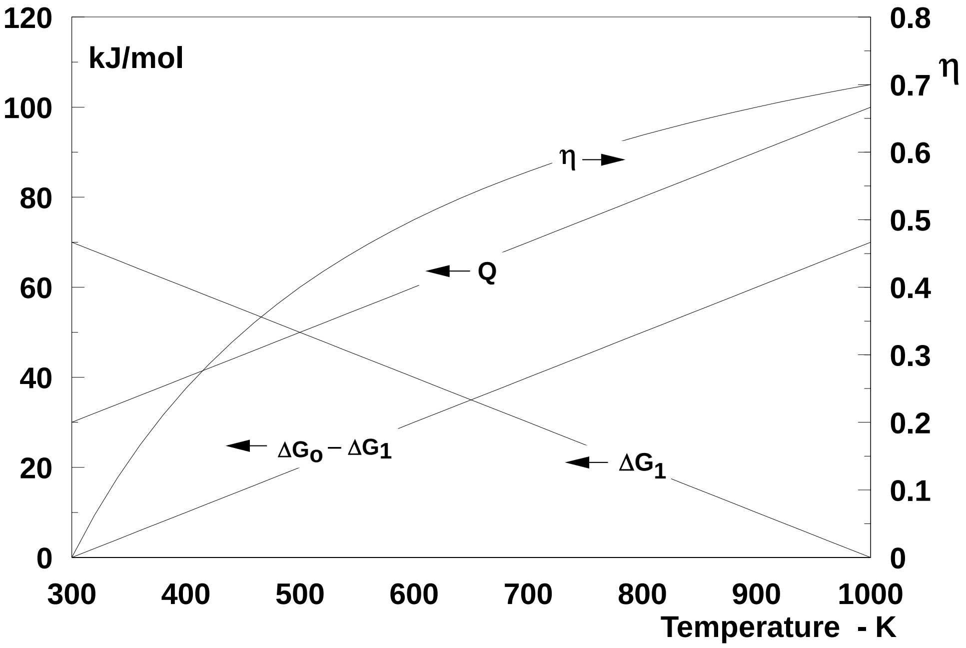


Figure 2. Variation of heat, work and efficiency with temperature for cycle with matched heating and cooling load.

Several decompositions of simple molecules approximate quite closely to this condition as shown for some examples in Table 1. In these cases, T_0 = 298 K and Q is the greater of ΔH_0^0 and ΔH_1^0.

Table 1.

Decomposition species	ΔH_1^0	ΔH_0^0	ΔG_0^0	T_1	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	0.9311	0.909
$CO_2 \rightarrow CO + 0.5\,O_2$	271.0	282.9	257.29	3340	0.911	0.908
$CaCO_3 \rightarrow CaO + CO_2$	165.8	178.2	130.5	1160	0.743	0.732

Limiting efficiency methodology

Since thermochemical reactions form a closed set, comparison of the work efficiency for different cycles can usefully be assessed using the standard condition of 1 atm pressure for each of the steps in each cycle. For the simple cycle depicted above, the operation of the decomposition at a temperature where $\Delta G_1^0 = 0$, is particularly useful since no external work is required to take the reactants to products under the standard conditions defined. As part of the objective of comparing the ability of a number of thermochemical cycles to convert heat into work, an initial approach has been taken to establish the limiting efficiency possible for these. Free energy changes for the chemical reactions are evaluated under standard conditions of 1 atm pressure for reactants and products. Since the underlying interest is in the use of heat to effect chemical changes, for reactions involving +ve values for both ΔH and ΔS, an operating temperature is chosen which results in $\Delta G^o = 0$, thus limiting any additional work required to bring the products to standard pressure. In some cases, the reaction temperature chosen in this way would exceed those of practical process conditions, and therefore an upper limit operating temperature of

1700 K has been imposed for all cycles. For those endothermic reactions with -ve values for ΔS, the quoted literature value for the operating temperature has been chosen. Literature values for the operating temperature have also been chosen for any exothermic reactions in a cycle.

The main features of the analysis are described as follows :

1. The input to each cycle is water and the outputs are H_2 and O_2, in all cases at standard conditions (1 atm, 298 K)
2. Reactions involving only heat inputs are carried out under equilibrium conditions and temperatures are chosen to satisfy $\Delta G^o = 0$, when possible, subject to a limit temperature of 1700 K.
3. Heat balancing is carried out between all of the heating and cooling branches of the process, with the constraint that the heat transfer temperature difference ΔT is greater than or equal to zero.
4. Enthalpy changes are calculated using the HSC 5.1 chemistry package (1). Enthalpy and entropy values for some species have been updated in the database where necessary from published sources.
5. Efficiency is calculated through a combination of the work terms arising within the cycle and the total heat added.

   The work components of the cycle are the Gibbs free energy changes for each of the fundamental steps required to complete the cycle, and are taken as :

   (a) Free energy work available from recombination, under standard conditions, of $H_2/½O_2$ produced by the cycle ($\mathbf{\Delta G^o_{298}}$ (H_2/O_2). This is taken as -237 kJ/mol H_2.

   (b) Free energy work available from certain reactions within the set under standard conditions, characterised by -ve ΔG^o values, $\Delta G^o(-)$

   (c) Free energy work consumed by certain reactions within the set under standard conditions, characterised by +ve ΔG^o values, $\Delta G^o(+)$

   (d) Free energy work associated with the separation of reaction products. This is calculated as the negative of the mixing free energy

   $$\mathbf{\Delta G_{sep} = -R\,T \sum_i n_i \ln(x_i)} \qquad (5)$$

   where n_i and x_i are the number of moles and mole fraction of species **i** in the mixture respectively. This is a +ve quantity, consistent with the sign of the other work terms.

In representing an efficiency (η) for the cycle, all free energy components providing output work, $\Delta G^o(-)$ and $\mathbf{\Delta G^o_{298}}$ (H_2/O_2), and consuming input work, $\Delta G^o(+)$ and ΔG_{sep}, are considered equivalent.

The efficiency thus becomes defined by :

$$\boldsymbol{\eta} = -\frac{\left\lfloor \mathbf{\Delta G_{298}(H_2/O_2) + \sum \Delta G^o(-) + \sum \Delta G^o(+) + \sum \Delta G_{sep}} \right\rfloor}{\textbf{heat input}} \qquad (6)$$

It is noted that the above definition of efficiency differs from those often used in the thermochemical cycle literature where the HHV of hydrogen is frequently used in the numerator and any work capability of some reactions ($\Delta G^o(-)$) is ignored. In some cases this may be a less generous definition, although it is believed that it provides some consistency with the normal calculation of a Carnot efficiency.

The representation of a cycle by a series of elementary steps is demonstrated for the case of the US Chlorine cycle (2), which involves the following three reactions :

(1) $Cl_2(g) + H_2O(g) \longrightarrow 2HCl(g) + 0.5O_2(g)$
$T = 850$ K
$\Delta H^o = 58.8$ kJ/mol
$\Delta G^o = 0$ kJ/mol

(2) $2CuCl(s) + 2HCl(g) \longrightarrow 2CuCl_2(s) + H_2(g)$
$T = 473$ K
$\Delta H^o = 24.9$ kJ/mol
$\Delta G^o = 118.1$ kJ/mol

(3) $2CuCl_2(s) \longrightarrow 2CuCl(l) + Cl_2(g)$
$T = 850$ K
$\Delta H^o = 185.5$ kJ/mol
$\Delta G^o = 0$

The elementary steps required to evaluate a limiting efficiency are shown in Figure 2. Reaction (2) has a negative value for ΔS and therefore does not provide the possibility of equilibrium under standard conditions for reactant and products, resulting in a positive ΔG value in the temperature range of interest.

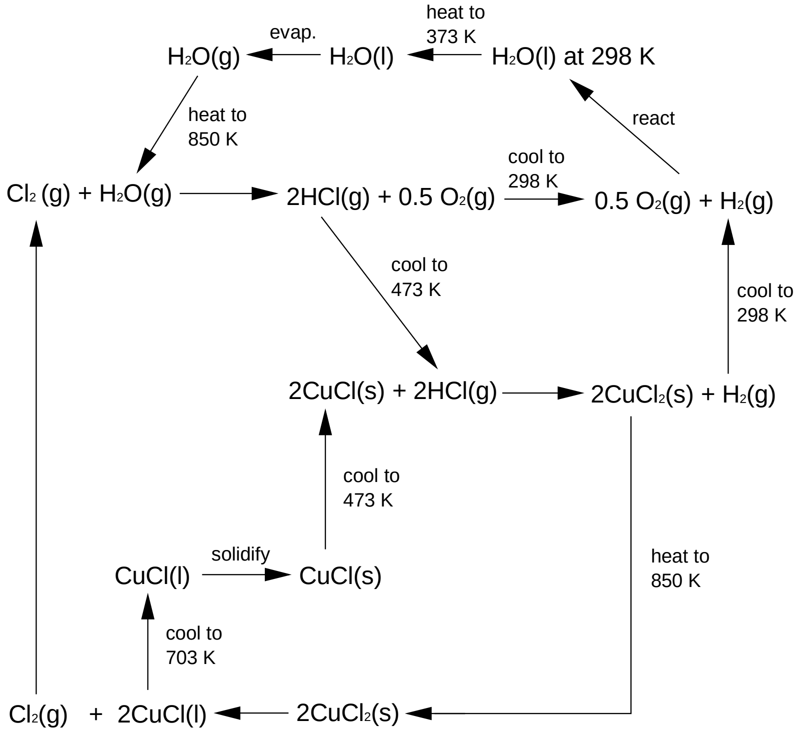


Figure 2. US Chlorine cycle for hydrogen production.

Table 2. summarises the individual steps representing the operation of the cycle. T_o and T_1 define the starting and finishing temperatures of each step, ΔG^o represents the standard Gibbs free energy change for the reactions and any work required to separate components for a further reaction step and Q± is the heat change involved with the step (+ve when heat is added). Separation work terms are not included when reaction products exist in different phases. All of the thermochemical cycles considered are dealt with in the same way, i.e. heating, reaction, phase change and cooling.

Table 2. Steps required to complete US Chlorine cycle.

Step No.	US Chlorine Cycle	To	T1	ΔG^o	Q±
		K	K	kJ	kJ
1	$Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + 0.5O_2(g)$	850	850	0	58.8
	2HCl and $0.5O_2$ separation at 473 K			4.92	
2	$2CuCl_2 \rightarrow 2CuCl(l) + Cl_2(g)$	850	850	0	185.5
3	$2CuCl_2(s) \rightarrow 2CuCl_2(s)$	473	850		62.46
4	$H_2O(l) \rightarrow H_2O(l)$	298	373		7.5
5	$H_2O(l) \rightarrow H_2O(g)$	373	373		40.9
6	$H_2O(g) \rightarrow H_2O(g)$	373	850		17.5
7	$2CuCl(l) \rightarrow 2CuCl(l)$	850	703		-17.8
8	$2HCl(g) \rightarrow 2HCl(g)$	850	473		-22.54
9	$2CuCl(l) \rightarrow 2CuCl(s)$	703	703		-14.2
10	$2CuCl(s) \rightarrow 2CuCl(s)$	703	473		-55.7
11	$\frac{1}{2} O_2(g) \rightarrow \frac{1}{2} O_2(g)$	850	298		-17.5
12	$2CuCl + 2HCl(g) \rightarrow 2CuCl_2 + H_2(g)$	473	473	118.1	-93.2
13	$H_2(g) \rightarrow H_2(g)$	473	298		-5.0

For each cycle it is confirmed that an overall energy balance is satisfied, i.e.,

$$\sum_i \Delta G_i^0(\text{reactions}) = \sum_i Q_i$$

This also includes the additional heat rejected at 298 K when the hydrogen and oxygen are recombined (-48.6 kJ/mol). For an efficiency calculation, it is necessary to know the overall heat input requirement and this is evaluated on the basis of the maximum possible heat transfer from the cooling side to the heating side of the process. This is most easily calculated using a pinch diagram for each of the cycles. These are constructed for the limiting case of a heat transfer temperature difference $\Delta T = 0$ degrees, and refer to the production of 1 mol of H_2. The pinch diagram for US Chlorine cycle corresponding to Table 2 is shown in Figure 3.

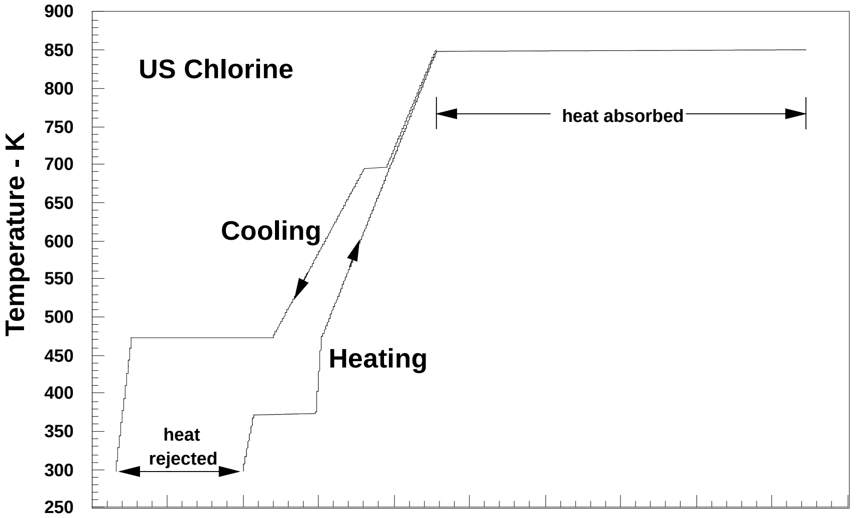


Figure 3. Pinch diagram for US Chlorine cycle.

Examination of 10 Cycles

A selection of the preferred cycles originally proposed by Brown et al (3) have been examined in the same way and the operating conditions and thermodynamic parameters for these under standard conditions are collected together in Table 3.

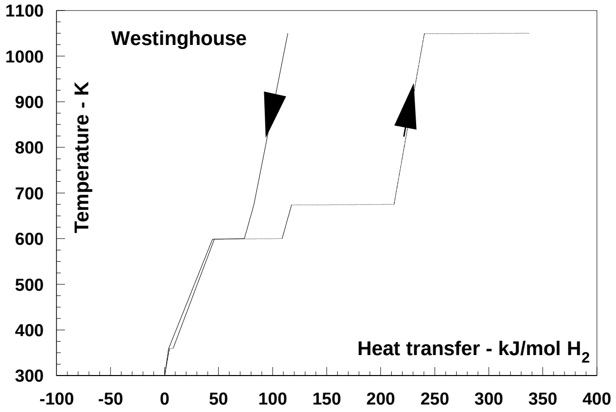
Table 3.

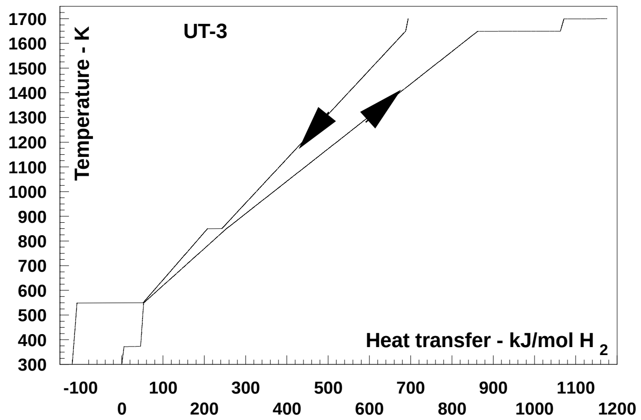
	Reaction set	ΔG^o (kJ)	ΔH^o (kJ)	E/T *	T (K)
Westinghouse (4)	$SO_2(g) + 2H_2O(l) \rightarrow H_2SO_4(l) + H_2(g)$	75.7	78.9	E	360
	$H_2SO_4(g) \rightarrow H_2O(g) + SO_3(g)$	0	94.6	T	675
	$SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$	0	97.3	T	1050
Sulphur - Iodine (3)	$SO_2(g) + 16H_2O(l) + 9I_2(l) \rightarrow H_2SO_4(aq) + 2HI.10H_2O.8I_2(l)$	-60.8	-133.3	T	398
	$H_2SO_4(aq) + [2HI.10H_2O.8I_2](l) \rightarrow [H_2SO_4 + 4H_2O](l) + 2HI(g) + [10H_2O + 8I_2(l)$	156.5	232	T	398
	$H_2SO_4(g) \rightarrow H_2O(g) + SO_3(g)$	0	94.6	T	675
	$SO_3(g) \rightarrow SO_2(g) + \frac{1}{2} O_2(g)$	0	97.3	T	1050
	$2HI(g) \rightarrow H_2(g) + I_2(g)$	22.7	12.1	T	650
US Chlorine (2)	$Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + \frac{1}{2}O_2(g)$	0	58.8	T	850
	$2CuCl(s) + 2HCl(g) \rightarrow 2CuCl_2(s) + H_2(g)$	118.1	24.9	T	473
	$2CuCl_2(s) \rightarrow 2CuCl(l) + Cl_2(g)$	0	185.5	T	850
Zinc oxide (5)	$ZnO(s) \rightarrow Zn(g) + \frac{1}{2} O_2(g)$	122.9	461.8	T	1700
	$Zn(s) + H_2O(l) \rightarrow ZnO(s) + H_2(g)$	-89.1	-67.7	T	400
UT - 3 (6)	$CaBr_2(s) + H_2O(g) \rightarrow CaO(s) + 2HBr(g)$	61.77	165.57	T	1700
	$CaO(s) + Br_2(g) \rightarrow CaBr_2(s) + 0.5 O_2(g)$	-39.69	-74.15	T	850
	$Fe_3O_4(s) + 8HBr(g) \rightarrow 3FeBr_2(s) + Br_2(g) + 4H_2O(g)$	-99.7	-259.4	T	550
	$3FeBr_2 + 4H_2O(g) \rightarrow Fe_2O_3 + H_2(g) + 6HBr(g)$	0	199.7	T	1650
Gaz de France (2)	$2K(l) + 2KOH(l) \rightarrow 2K_2O(s) + H_2(g)$	260.9	71.9	T	1000
	$2K_2O(s) \rightarrow 2K(g) + K_2O_2(l)$	210.1	390.7	T	1100
	$K_2O_2(s) + H_2O(l) \rightarrow 2KOH(s) + 0.5O_2(g)$	-151.4	-121.5	T	400
Ispra Mark 4 (7)	$Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + 0.5O_2(g)$	0	58.8	T	850
	$2FeCl_2(s) + 2HCl(g) + S(s) \rightarrow 2FeCl_3(s) + H_2S(g)$	107.2	54.5	T	373
	$H_2S(g) \rightarrow S(g) + H_2(g)$	189.5	306.3	T	1073
	$2FeCl_3(g) \rightarrow Cl_2(g) + 2FeCl_2(s)$	-29.3	-166.0	T	693
Ispra Mark 7B (7)	$1.5Fe_2O_3(s) + 3Cl_2(g) \rightarrow 3FeCl_2(l) + 2.25O_2(g)$	0	382.4	T	1000
	$3FeCl_2(l) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 6HCl(g) + H_2(g)$	0	195.0	T	1175
	$Fe_3O_4(s) + 0.25O_2(g) \rightarrow 1.5Fe_2O_3(s)$	-73.8	-117.6	T	623
	$6HCl(g) + 1.5O_2(g) \rightarrow 3Cl_2(g) + 3H_2O(g)$	-39.5	-175.3	T	673
Ispra Mark 9 (7)	$3FeCl_3(g) \rightarrow 1.5Cl_2(g) + 3FeCl_2(s)$	-41.9	-248.5	T	693
	$1.5Cl_2(g) + Fe_3O_4 + 6HCl(g) \rightarrow 3FeCl_3(s) + 3H_2O(g) + 0.5O_2(g)$	-34.8	-237.2	T	423
	$3FeCl_2(s) + 4H_2O(g) \rightarrow Fe_3O_4 + 6HCl + H_2(g)$	48.3	334.6	T	923
Nickel Ferrite (8)	$0.5NiMnFe_4O_8 \rightarrow 0.5NiMnFe_4O_6 + 0.5O_2(g)$	0	228.0	T	1650
	$0.5NiMnFe_4O_6 + H_2O(g) \rightarrow 0.5NiMnFe_4O_8 + H_2(g)$	97.7	32.0	T	900

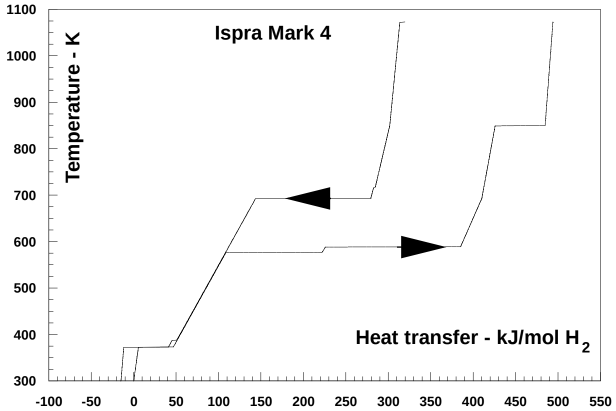
* Refers to thermal or electrochemical step

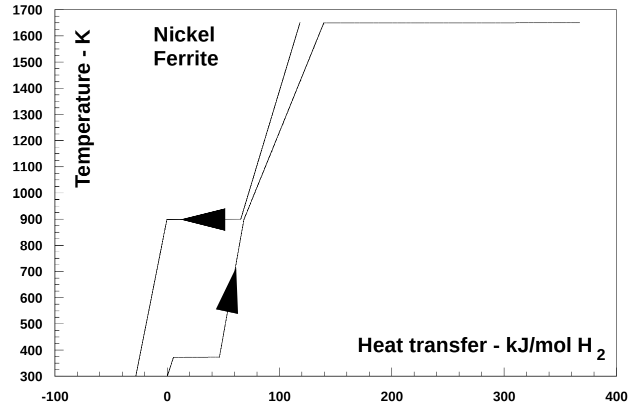
In the same way as described for the US Chlorine cycle above, a detailed heating and cooling scheme for the cycles of Table 3 has been derived, based on the needs of individual species involved transforming from products of one reaction to reactants of another.

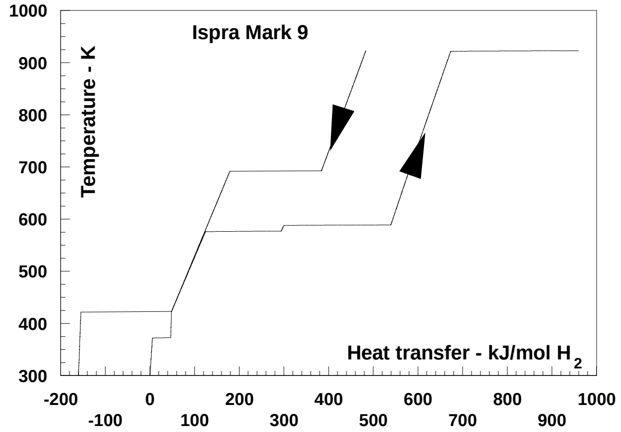
The heating and cooling needs of these have been presented in pinch diagram form as before and are shown in Figures 4.

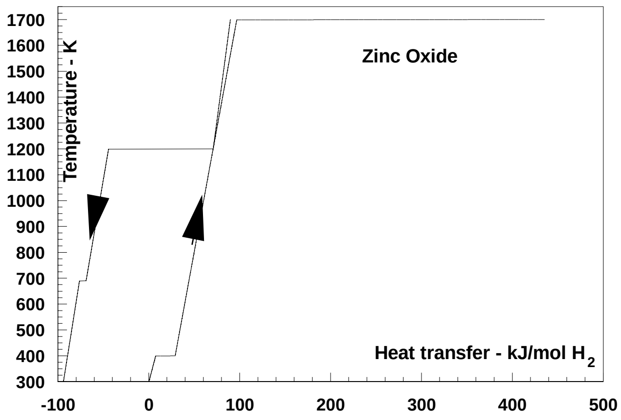

Westinghouse
Temperature - K
Heat transfer - kJ/mol H_2
1100
1000
900
800
700
600
500
400
300
-100
-50
0
50
100
150
200
250
300
350
400

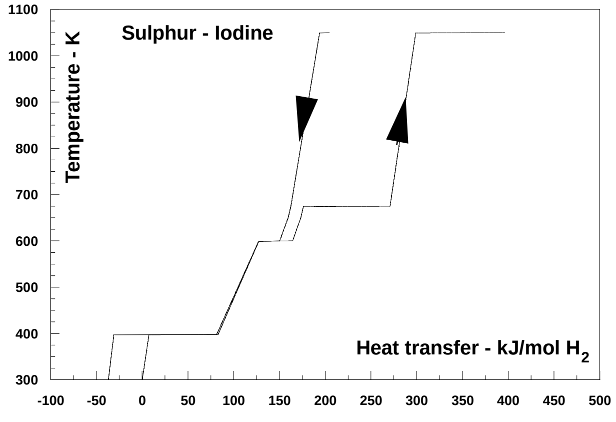

UT-3
Temperature - K
Heat transfer - kJ/mol H 2
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
-100
100
300
500
700
900
1100
0
200
400
600
800
1000
1200

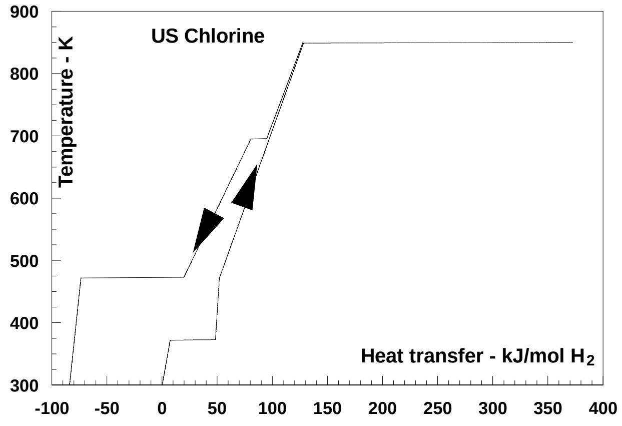

Ispra Mark 4
Temperature - K
Heat transfer - kJ/mol H_2
1100
1000
900
800
700
600
500
400
300
-100
-50
0
50
100
150
200
250
300
350
400
450
500
550


Nickel
Ferrite
Temperature - K
Heat transfer - kJ/mol H 2
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
-100
0
100
200
300
400


Ispra Mark 9
Temperature - K
Heat transfer - kJ/mol H_2
1000
900
800
700
600
500
400
300
-200
0
200
400
600
800
1000
-100
100
300
500
700
900


Zinc Oxide
Temperature - K
Heat transfer - kJ/mol H_2
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
-100
0
100
200
300
400
500


Sulphur - Iodine
Temperature - K
Heat transfer - kJ/mol H_2
1100
1000
900
800
700
600
500
400
300
-100
-50
0
50
100
150
200
250
300
350
400
450
500


US Chlorine
Temperature - K
Heat transfer - kJ/mol H_2
900
800
700
600
500
400
300
-100
-50
0
50
100
150
200
250
300
350
400

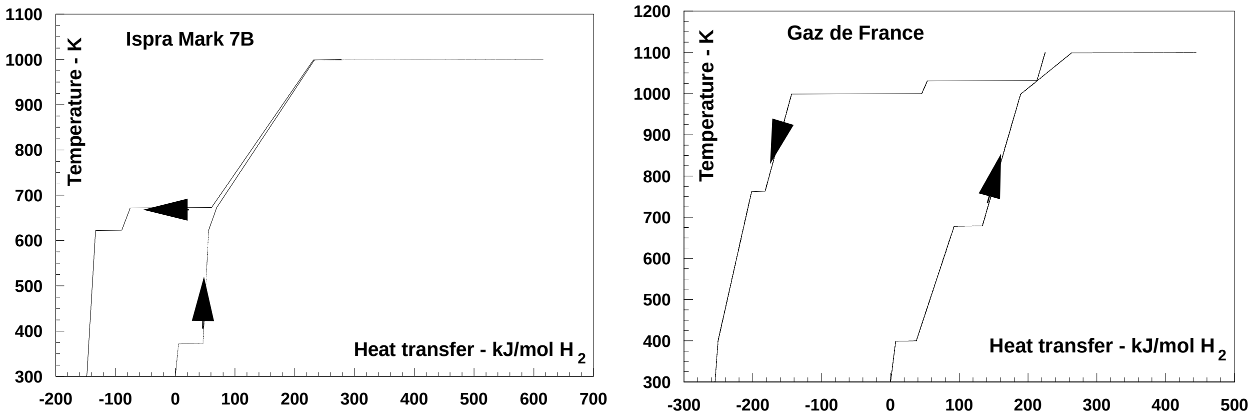


Figure 4. Pinch diagrams for thermochemical cycles of Table 3 showing heating (↑) and cooling (↓) curves.

The definition of efficiency (Eq. 6) indicates that the maximum value for this is achieved when use is made of any available work arising from the cycle reactions, in addition to that from the H_2 and O_2 produced. The efficiency information in Table 4 is therefore presented in two ways, represented by η_1 and η_2. These are defined by :

$$\eta_1 = -\frac{\lfloor \Delta G_{298}(H_2/O_2) + \sum \Delta G^{o}(-) + \sum \Delta G^{o}(+) + \sum \Delta G_{sep} \rfloor}{\textbf{heat input}} \qquad (7)$$

$$\eta_2 = -\frac{\lfloor \Delta G_{298}(H_2/O_2) + \sum \Delta G^{o}(+) + \sum \Delta G_{sep} \rfloor}{\textbf{heat input}} \qquad (8)$$

These definitions reflect the fact that additional measures need to be implemented to realise the full potential of cycles which provide additional sources of work (η_1) and without these measures the lower efficiency (η_2) will be the maximum available.
In cases where $\eta_1 = \eta_2$ in the table, no additional work $\Delta G^{o}(-)$, is available and no additional measures are required. The pinch diagrams provide the necessary information on heat demand and heat rejected, and the overall heat and work inputs and outputs for the cycles are summarised in Table 4.

Table 4.

Process	Heat input kJ/mol H_2	Heat rejection kJ/mol H_2	Work input kJ/mol H_2	η_1	η_2
Westinghouse	222.5	0	87.7	0.67	0.67
UT - 3	441.5	157.7	86.3	0.60	0.31
Ispra Mark 4	174.4	15.2	155.1	0.62	0.45
Nickel ferrite	249.3	28.0	97.7	0.56	0.56
Ispra Mark 9	393.3	183.3	76.7	0.53	0.36
Zinc oxide	341.7	94.5	136.4	0.56	0.29
Sulphur - Iodine**	192.0	37.0	179.3	0.51	0.19
US Chlorine	258.9	84.0	123.0	0.44	0.44
Ispra Mark 7B	337.7	148.0	249.1	0.30	0
Gaz de France	219.8	255.0	471.0	0	0

** Thermodynamic data for the Bunsen reaction calculated from the strong acid model (9)

Discussion

The examples shown have been chosen as they typify the behaviour of different classes of thermochemical cycles.

Those cycles which approximate most closely with the heating and cooling curves of Figure 1 are expected to have the highest efficiencies due to good heat matching. Differences in the heating and cooling curves arise from specific heat differences, isothermal phase changes and chemical reaction heats, in particular the relative positioning of these on the temperature axis. Good heat matching behaviour is associated with similar specific heat values for reactants and products across the temperature range, or similar isothermal heat absorption and rejection behaviour, with the rejection temperature located above the absorption temperature. A number of the isothermal stages in Figure 4 are also connected with work inputs or outputs required to achieve standard conditions and these will often involve related heat changes. In some cases, work inputs appear as work outputs via the +ve enthalpy changes which result, whilst in others the work inputs appear as rejected heat due to the -ve entropy change associated with a reaction whose equilibrium lies to the left.

One can arbitrarily define high, medium and low values for efficiency, heat input, heat rejected and the secondary work, characterised by the ΔG^o(-) terms.

The ranges for these, based on the above cycles, are shown in Table 5.

Table 5.

	Efficiency	Heat input (kJ)	Heat rejected (kJ)	Secondary work (kJ)
High	≥ 0.6	350 - 450	250 - 400	> 100
Medium	0.5 - 0.6	250 - 350	150 - 250	50 - 100
Low	< 0.5	150 - 250	0 - 100	0 - 50

The behaviour of those cycles with high and medium efficiencies is observed to follow the pattern depicted in Figure 5.

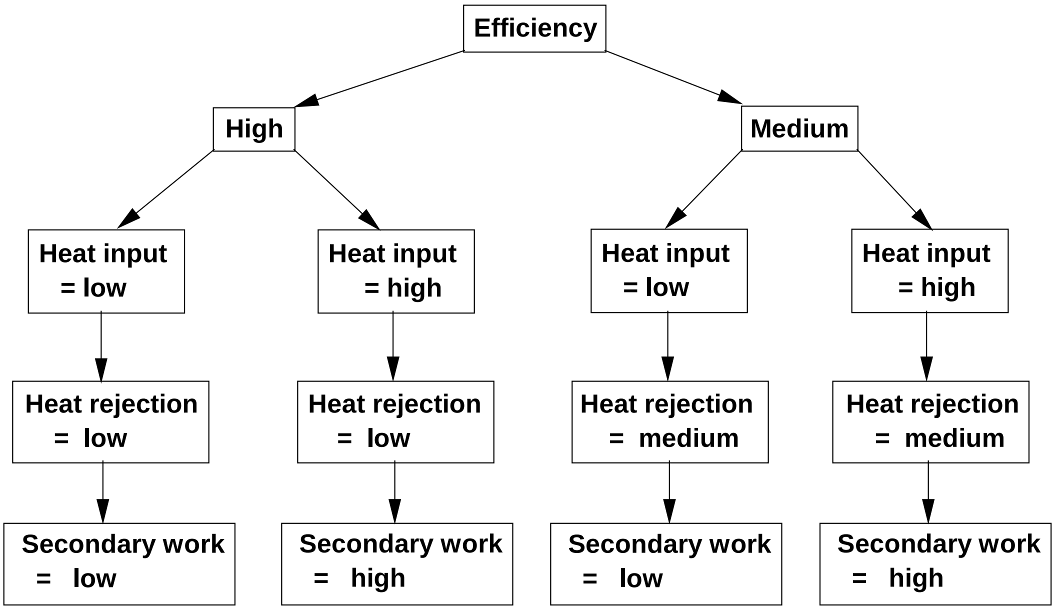


Figure 5.

This shows that high or medium efficiency is particularly associated with low or medium levels of heat rejection respectively. In both cases the level of heat input can be high or low. When this is high, the level of secondary work tends to be high, i.e. the additional heat input can be transformed into productive work terms without loss of overall efficiency. This normally means that work input arises from an enthalpy demand from a reaction rather than a -ve entropy change. The UT3 and Zinc oxide cycles are an example of such behaviour, which also show significant differences between η_1 and η_2 due to the conversion of input work, arising from an enthalpy demand, into output work.

Low efficiencies are generally characterised by medium levels of heat input, relatively high levels of heat rejection and work input, and medium - low levels of secondary work. In these cases, high levels of work input tend to give rise to high levels of heat rejection, i.e. the processes act to convert input work into heat. Such behaviour can often be traced to two dominant causes, (i) reactions with large +ve ΔG values arising from large -ve entropy changes, which require significant work input to achieve standard conditions, giving rise to large isothermal heat rejection and (ii) serious mis-matches between the heating and cooling sides of the process due to poorly aligned phase changes. Figure 4 reveals a number of these features, the Gaz de France cycle showing both adverse features. In this particular case, for two of the reactions (K_2O decomposition and K/KOH reaction), the equilibrium lies strongly to the left requiring significant input work to meet standard conditions, with result that overall, no nett work is produced on H_2/O_2 recombination.

The above approach has a number of features which are useful in making comparisons between thermochemical cycles and with other heat - work processes. Some of these include :

- an evaluation, without the use of process flowsheeting, of the maximum thermal efficiency which a cycle can provide
- identification of the sources of work produced by the cycle and the feasibility of making use of all $\Delta G^o(-)$ contributions to the overall work output
- the provision of a starting point for process optimisation, identifying the main geometrical needs for heat transfer
- 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

References

1. HSC Chemistry v 5.1, Outokumpu Research, Finland, 2002
2. L O Williams, Hydrogen Power, Pergamon (1980)
3. J H Norman, G E Besenbruch, L C Brown, D R O'Keefe, L C Allen, 'Thermo-chemical Water-Splitting Cycle, Bench Scale Investigations and Process Engineering', Final Report GA-A16713, may 1982, General Atomics.
4. L E Brecher, S Spewock, C J Warde, 'The Westinghouse Sulfur Cycle for the Thermochemical Decomposition of Water', *Int J Hydrogen Energy*, 2, 7 - 15, (1977)
5. A Steinfeld, 'Solar hydrogen production via a two-step water-splitting thermochemical cycle based on Zn/ZnO redox reactions', *Int J Hydrogen Energy* 27(6), 611 - 619 (2002)
6. J K Funk, R M Reinstorm, 'Energy requirements in the production of hydrogen from water', *Ind Eng Chem Proc Des Develop* 5, 336 - 342 (1966)
7. G E Beghi, 'A decade of research on thermochemical hydrogen at the joint research center, Ispra', *Int. J Hydrogen Energy* 11, 761 - 771 (1986)

8. Y Tamaura, Ainfeld, P Kuhn, K Ehrensberger, 'Production of solar hydrogen by a novel, 2-step, water-splitting thermochemical cycle', *Energy* 20(4), 325 -330, (1995)
9. H Engels, K F Knoche, 'Vapor pressures of the system HI/H_2O/I_2 and H_2, *Int J Hydrogen Energy* 12 (11), 703 - 707 1986