An Algorithm for Systematic Generation of Thermochemical Cycles for Water Splitting

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Motivation

- So far, about 280 thermochemical cycles have been proposed. S. Abanades, P. Charvin, G. Flamant, P. Neveu. Energy 31 (2006) 2805–2822.
- The best thermochemical cycles are yet to be discovered
- There is a direct analogy between thermochemical cycles and reaction routes
- Theory and enumeration of reaction routes is well developed
- Based on this analogy, a computer code may be developed to automatically enumerate thermodynamically feasible thermochemical cycles

Examples of Thermochemical Cycles

$$2Cu + 2HCl = 2CuCl + H_2$$

Examples of Reaction Routes

Heterogen

The Algorithm

- **Input: Ideally, a list of species and their Gibbs free energies of formation**
- **Reaction generation using reaction generators**
- **Enumeration of RRs – thermochemical cycles**
- **Thermodynamic feasibility check**
- **Additional screening**
- **Network Approach**

Reaction Routes – Definition (Horiuti-Temkin)

$$s_1: \quad \sum_{k=1}^{q}\alpha_{1k}\mathrm{I}_k + \sum_{i=1}^{n}\beta_{1i}\mathrm{T}_i = 0 \qquad \sigma_1$$

$$s_2: \quad \sum_{k=1}^{q}\alpha_{2k}\mathrm{I}_k + \sum_{i=1}^{n}\beta_{2i}\mathrm{T}_i = 0 \qquad \sigma_2$$

$$\ldots$$

$$s_p: \quad \sum_{k=1}^{q}\alpha_{pk}\mathrm{I}_k + \sum_{i=1}^{n}\beta_{1p}\mathrm{T}_i = 0 \qquad \sigma_\mathrm{p}$$

$$OR: \quad \sum_{i=1}^{n}\nu_i\mathrm{T}_i = 0$$

$$FR: \quad \sum_{j=1}^{p}\sigma_j s_j = OR$$

$$rank\,\boldsymbol{\alpha} = rank\begin{bmatrix}\alpha_{11} & \alpha_{12} & \ldots & \alpha_{1q}\\ \alpha_{21} & \alpha_{22} & \ldots & \alpha_{2q}\\ \ldots & \ldots & \ldots & \ldots\\ \alpha_{p1} & \alpha_{p2} & \ldots & \alpha_{pq}\end{bmatrix} = q$$

$$s_1: \quad \sum_{k=1}^{q}\alpha_{1k}\mathrm{I}_k + \sum_{i=1}^{n}\beta_{1i}\mathrm{T}_i = 0 \qquad \sigma_1$$

$$s_2: \quad \sum_{k=1}^{q}\alpha_{2k}\mathrm{I}_k + \sum_{i=1}^{n}\beta_{12}\mathrm{T}_i = 0 \qquad \sigma_2$$

$$\ldots$$

$$s_p: \quad \sum_{k=1}^{q}\alpha_{pk}\mathrm{I}_k + \sum_{i=1}^{n}\beta_{pi}\mathrm{T}_i = 0 \qquad \sigma_p$$

$$OR: \quad 0 = 0$$

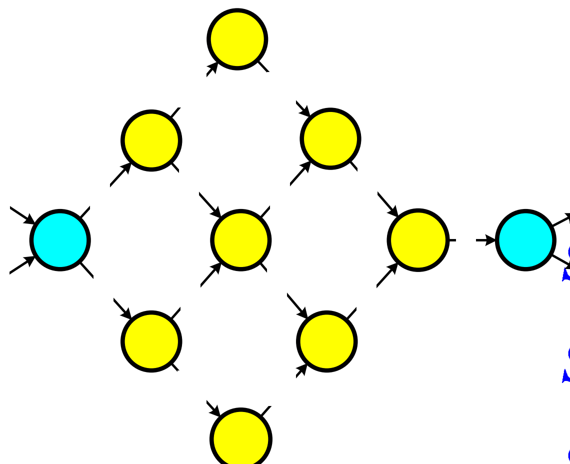
$$ER: \quad \sum_{j=1}^{p}\sigma_j s_j = 0$$

$$\begin{bmatrix}\alpha_{11} & \alpha_{21} & \ldots & \alpha_{p1}\\ \alpha_{12} & \alpha_{22} & \ldots & \alpha_{p2}\\ \ldots & \ldots & \ldots & \ldots\\ \alpha_{1q} & \alpha_{2q} & \ldots & \alpha_{pq}\end{bmatrix}\begin{pmatrix}\sigma_1\\ \sigma_2\\ \ldots\\ \sigma_p\end{pmatrix} = 0$$

Milner (1964) – Direct Reaction Routes
Happell – Sellers (1983) - Direct Overall Reactions

Fishtik and Datta (2000) – Directness from Chemical Thermodynamics

Reaction Route Analysis



s_1: E + B = E

s_2: EB + A =

s_3: E + A = E

s_4: EA+ B =

s_5: EAB = E

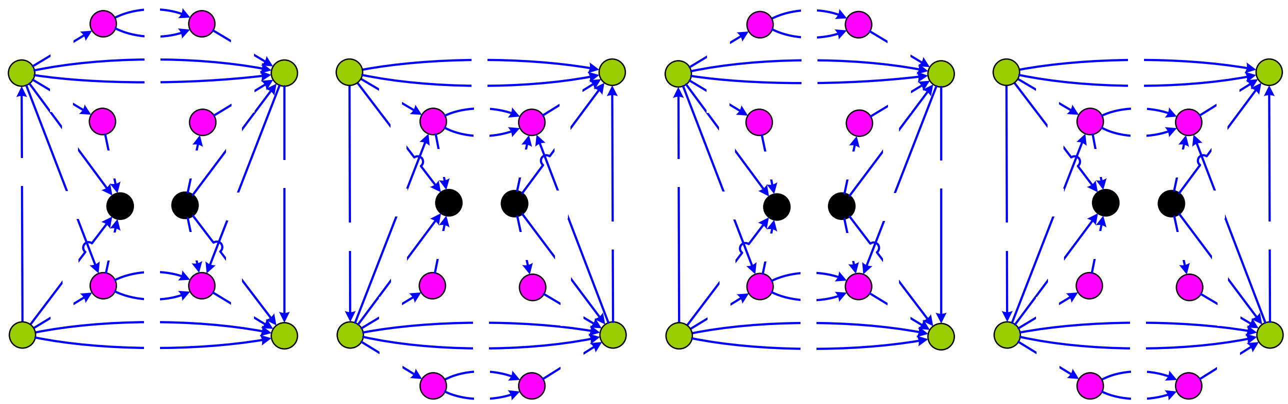
Example - 1

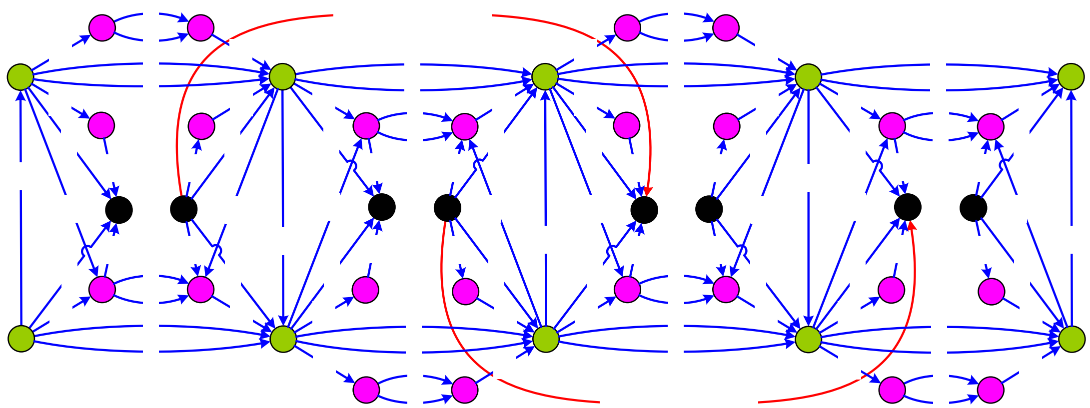
Example-1

s_1: $H_2O + M = MO + H_2$
s_2: $2HX = X_2 + H_2$
s_3: $M + 2HX = MX_2 + H_2$
s_4: $2HY = Y_2 + H_2$
s_5: $2MO = 2M + O_2$
s_6: $2MO + 2X_2 = 2MX_2 + O_2$
s_7: $2H_2O + 2X_2 = 4HX + O_2$
s_8: $2NO = 2N + O_2$
s_9: $MX_2 = M + X_2$
s_{10}: $H_2O + MX_2 = MO + 2HX$
s_{11}: $M + X_2 + H_2O = MO + 2HX$
s_{12}: $2HX + Y_2 = 2HY + X_2$
s_{13}: $MO + N = M + NO$

OR: $2H_2O = 2H_2 + O_2$

Example -1
Reaction Route Network Approach





S_8

S_8

S_{13} S_5 S_{13}

S_5

S_{12} S_{12}

Example -2
System Cu-Cl

Cu	Cl	H	O	
1	0	0	0	Cu
2	0	0	1	Cu_2O
1	0	0	1	CuO
1	1	0	0	$CuCl$
1	2	0	0	$CuCl_2$
0	1	1	0	HCl
0	2	0	0	Cl_2
0	0	2	1	H_2O
0	0	2	0	H_2
0	0	0	2	O_2

Example -2
Reaction Generation

s_1: $Cu + CuO = Cu_2O$

s_2: $2Cu_2O = 4Cu + O_2$

s_3: $2CuO = 2Cu + O_2$

s_4: $4CuO = 2Cu_2O + O_2$

Example -2
Reaction Screening

s_1: 2Cu

s_2: 2Cu

Example - 2
RR Enumeration

$$RR_1: \quad 2s_2 + s_5$$

$$RR_2: \quad 2s_4 + s_6$$

Example - 2
Cycle Screening

RR_4: $2s_2 + s_6 + 2s_{11}$ US-Chlorine

$2s_2$:	$4CuCl + 4HCl = 4CuCl_2 + 2H_2$	+	(electrochem)
s_6:	$2Cl_2 + 2H_2O = 4HCl + O_2$	+/-	600^0C
$2s_{11}$:	$4CuCl_2 = 4CuCl + 2Cl_2$	+/-	500^0C
OR:	$2H_2O = 2H_2 + O_2$		

RR_7: $2s_4 + s_9 + 2s_{12}$

$2s_4$:	$4HCl = 2Cl_2 + 2H_2$	+	(electrochem)
s_9:	$2CuO + 2Cl_2 = 2CuCl_2 + O_2$	-	
$2s_{12}$:	$2CuCl_2 + 2H_2O = 2CuO + 4HCl$	+/-	700^0C
OR:	2H2O = $2H_2 + O_2$		

RR_5: $2s_2 + 2s_{12} + s_{13}$

$2s_2$:	$4CuCl + 4HCl = 4CuCl_2 + 2H_2$	+	electrochem
$2s_{12}$:	$2CuCl_2 + 2H_2O = 2CuO + 4HCl$	+/-	700^0C
s_{13}:	$2CuO + 2CuCl_2 = 4CuCl + O_2$	+/-	300^0C
OR:	$2H_2O = 2H_2 + O_2$		

RR_1: $2s_2 + s_5$

$2s_2$:	$4CuCl + 4HCl = 4CuCl_2 + 2H_2$	+
s_5:	$4CuCl_2 + 2H_2O = 4CuCl + 4HCl + O_2$	+/-

Example - 2
Cycle Screening

RR_{14}: $4s_4 + s_7 + s_8 + 4s_{12}$

$4s_4$:	$8HCl = 4Cl_2 + 4H_2$	+	(electrochem)
s_7:	$4CuO = 2Cu_2O + O_2$	+/-	1200^0C
s_8:	$2Cu_2O + 4Cl_2 = 4CuCl_2 + O_2$	-	
$4s_{12}$:	$4CuCl_2 + 4H_2O = 4CuO + 8HCl$	+/-	700^0C

OR: $4H_2O = 4H_2 + 2O_2$

Conclusions

- The concept of direct reaction routes may be used to generate thermochemical cycles in a systematic way
- The success depends on our ability to generate, select and screen reactions that proceed quantitatively as written
- The network approach may be a useful tool to analyze the effectiveness of the cycles
- A database of reactions producing hydrogen and oxygen that have been studied experimentally can dramatically improve the computer search for new thermochemical cycles