

A photograph of a large, multi-story brick building with a central tower and a weather vane on top. The building is surrounded by bare trees. A large red diagonal overlay covers the left side of the image, containing text.

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**Optimizing Work and Heat Flows
in Sustainable Chemical Processes
Using Attainable Regions**

Diane Hildebrandt



Introduction

- There is a growing pressure to reduce global CO₂ emissions
 - Chemical conversion of fossil fuels for the production of energy and chemicals are the major source of anthropogenic CO₂ emissions
 - This means that there is a need to:
 - Develop processes with reduced CO₂ emissions
 - Incorporate renewable energy into processes
 - Utilize new feeds such as CO₂
 - How do we design and optimize these processes?
 - Can we develop simple methods to analyze these processes to understand the relationship between material, energy and work flows?
- Image from: https://cdn.pixabay.com/photo/2017/06/04/04/16/warming-2370285_1280.jpg

Examples of Opportunities: Mature Technologies

Conversion of Methane to Methanol

Significant potential exists for improving process performance even for this mature technology.

	Tons of CH ₄ Consumed/ Ton of Methanol produced	Tons of CO ₂ Emitted/ Ton of Methanol produced
Current Processes	0.53	0.09
Target (without incorporating renewable energy)	0.43	-0.19

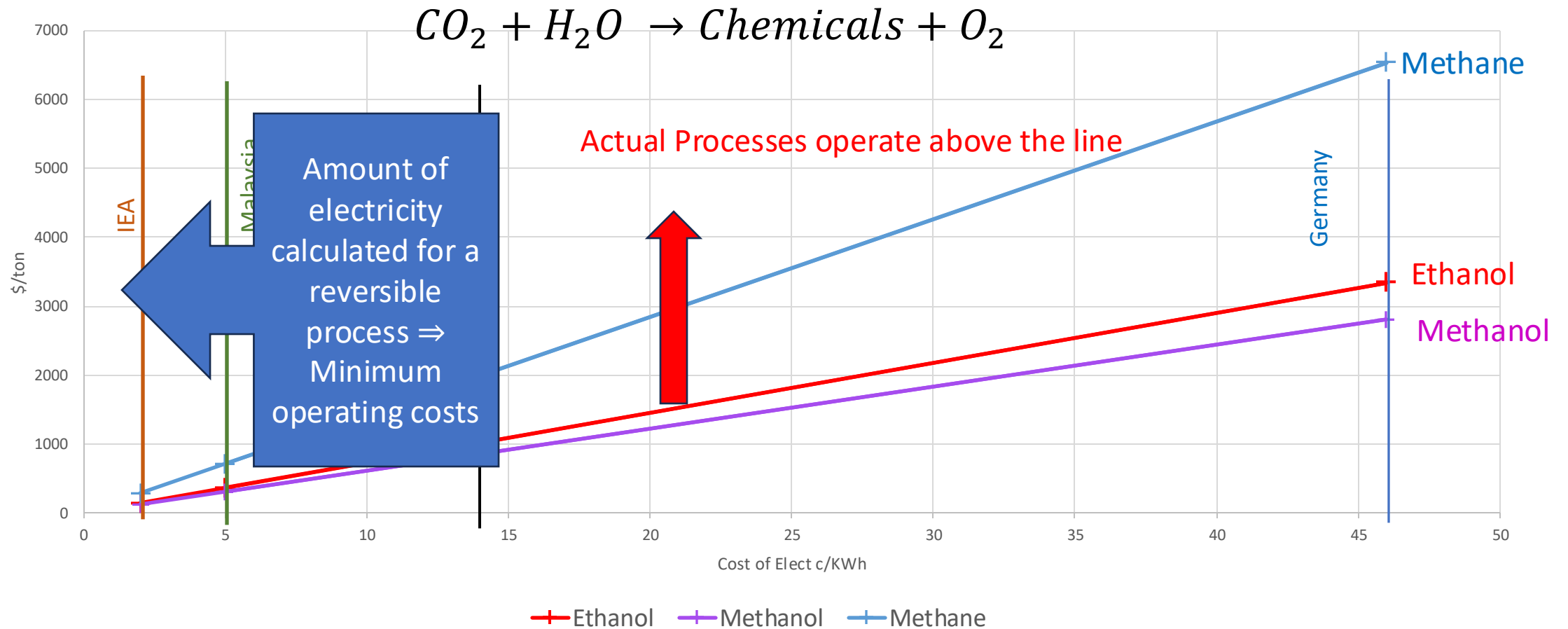
Examples of Opportunities: Emerging Technologies. Conversion of Cellulosic Biomass to Ethanol

- For every mole of C in the feed:
 - 0.35 is converted to ethanol
 - 0.65 is emitted as CO₂
- Can we do better than a 35 % carbon conversion efficiency?



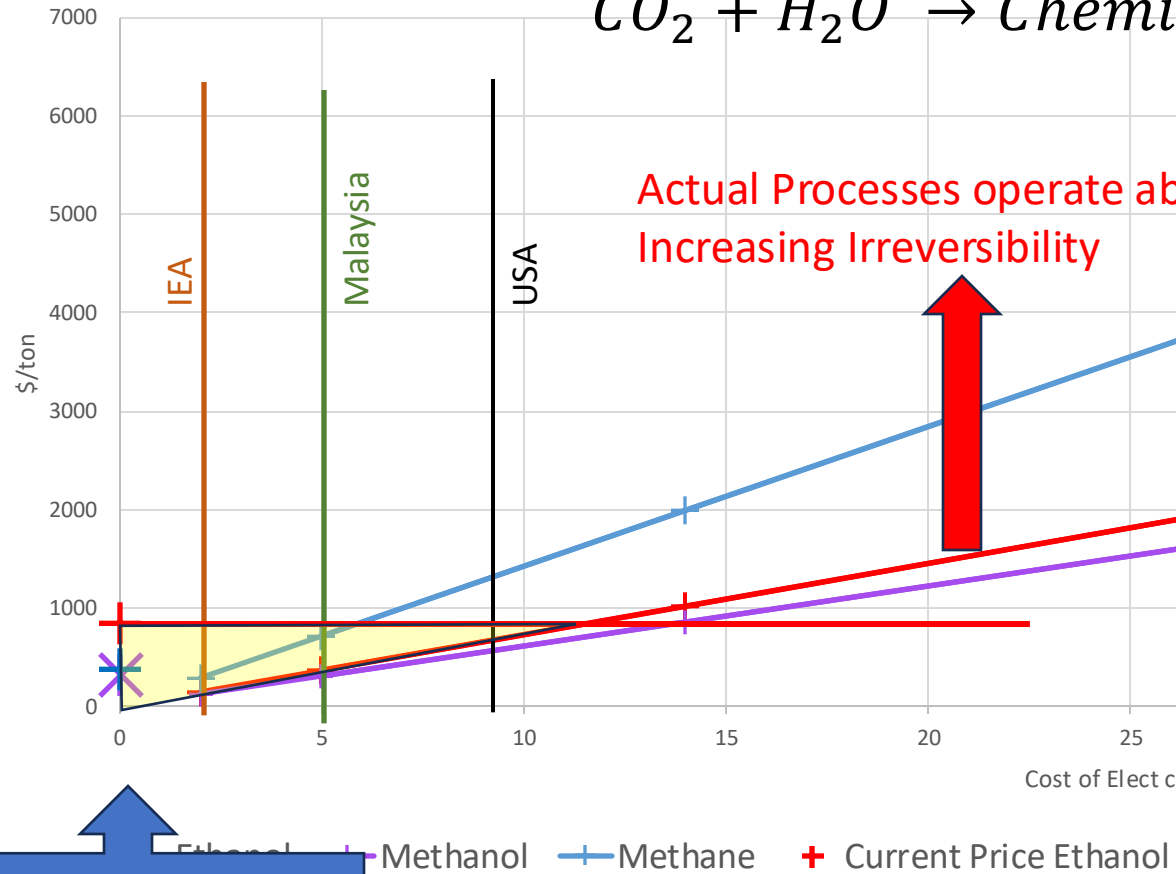
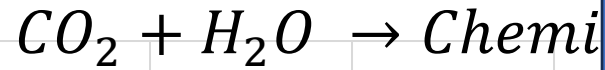
Examples of Opportunities: New Technologies

Conversion of CO₂ to chemicals



Examples of Opportunities:

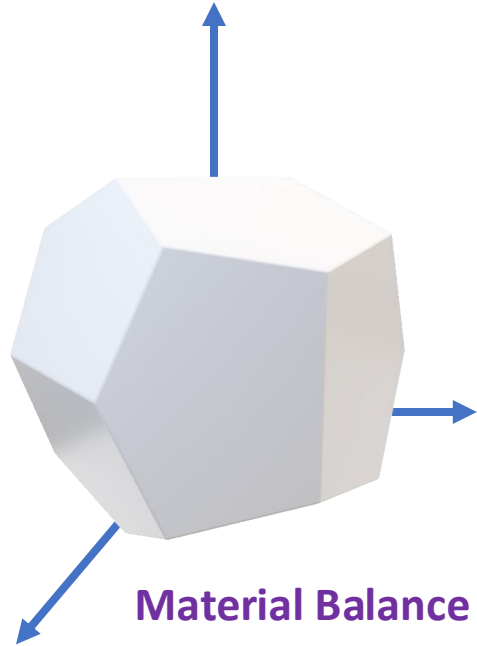
Conversion of CO₂ to chemicals



Current Selling prices

- Any inefficiency in process design or operation further increases electricity consumption.
- We may need to reconsider our design paradigms and methods to enhance process efficiency and thereby more closely approach process reversibility (minimum electricity consumption)
- This talk is based on the premiss that the choice of reaction pathways and operating conditions contributes to major process irreversibility

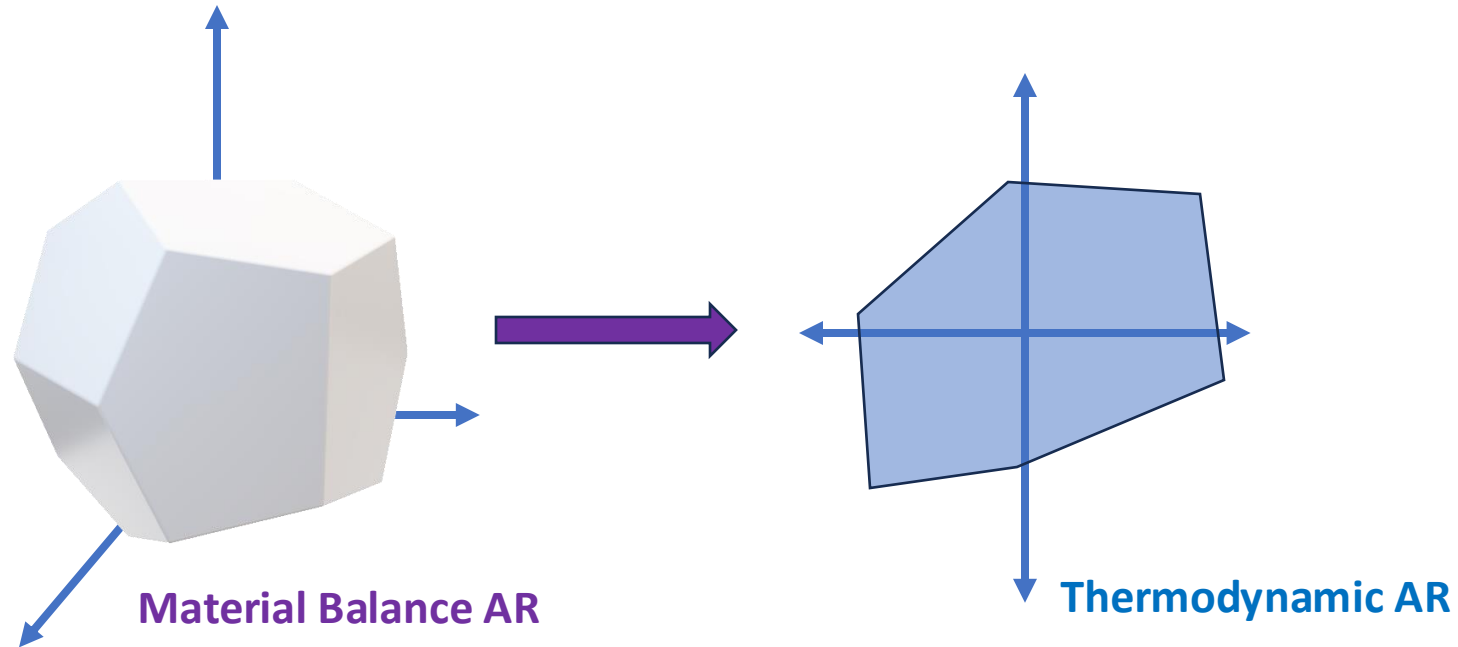
Approach Used in this Research



Material Balance Limited Attainable Region

- Start by finding the **Material Balance Limited Attainable Region**
 - Region of all concentrations stoichiometrically compatible with a given feed
 - We will discuss some of the important properties of this region

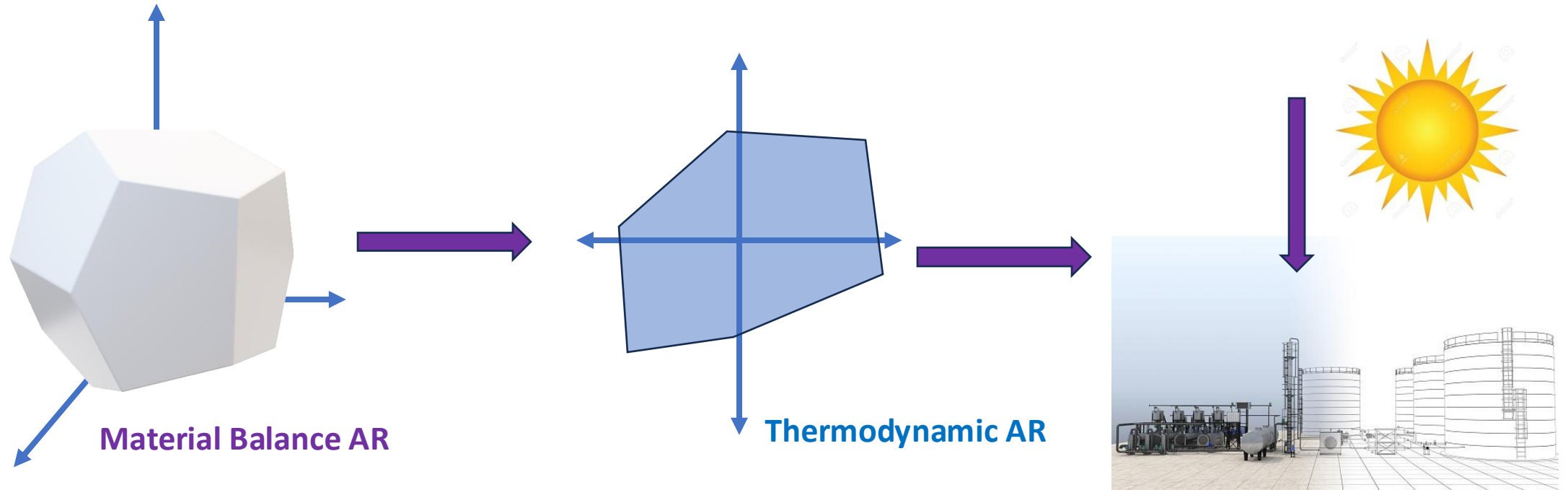
Approach Used in this Research



We will then use the *Material Balance Limited Attainable Region* to calculate the *Thermodynamic Attainable Region*

- A point in the **Thermodynamic Attainable Region** represents the quantity of heat and work flow between the process and the environment
 - We will discuss some of the important properties of this region

Approach Used in this Research

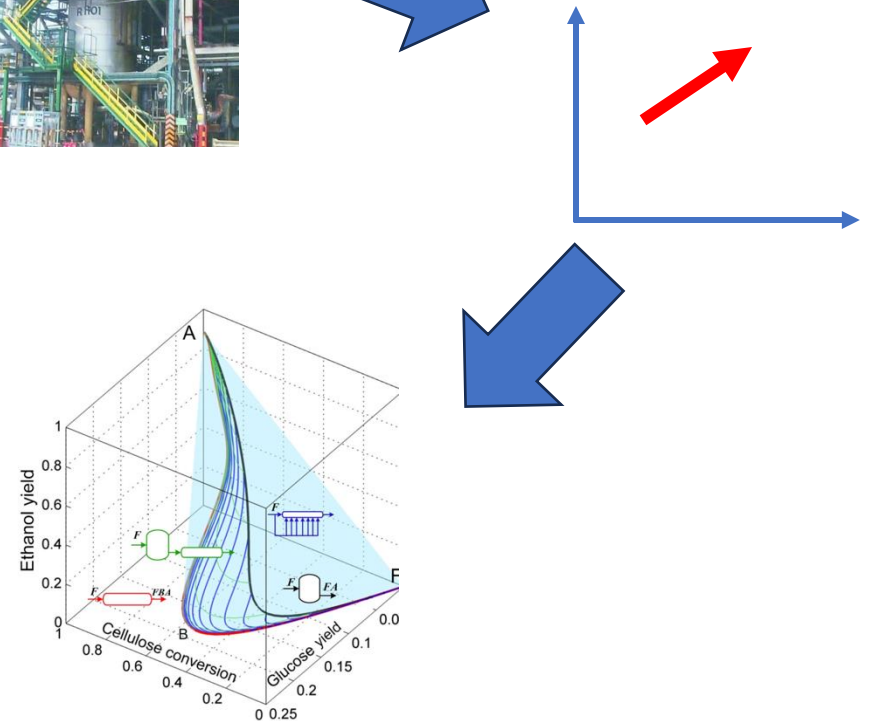


- We will then discuss the implication of the heat and workflows on process
- Will finally consider the addition of work and heat using renewable energy
- We will use a geometric approach based on vectors

What is an Attainable Region (AR)?

Fritz Horn (1964) addressed the problem of finding an optimal reactor

- He proposed finding the set of all possible outputs for all possible reactors, for a given feed and reaction kinetics.
- He called this set of outputs the **Attainable Region (AR)**
 - If one could find the AR, one could search the region for a given objective function and find the point corresponding to the optimal value of the objective function;
 - This point would correspond to the output of the optimal reactor.
- He was unable to develop a method to find the AR
- Glasser and Hildebrandt (1987) developed a geometrical-based approach to determine the AR for reaction and mixing
 - Other researchers have since used this approach and developed it further



Scott, F., Conejeros, R. & Aroca, G. Attainable region analysis for continuous production of second generation bioethanol. *Biotechnol Biofuels* 6, 171 (2013).
<https://doi.org/10.1186/1754-6834-6-171>

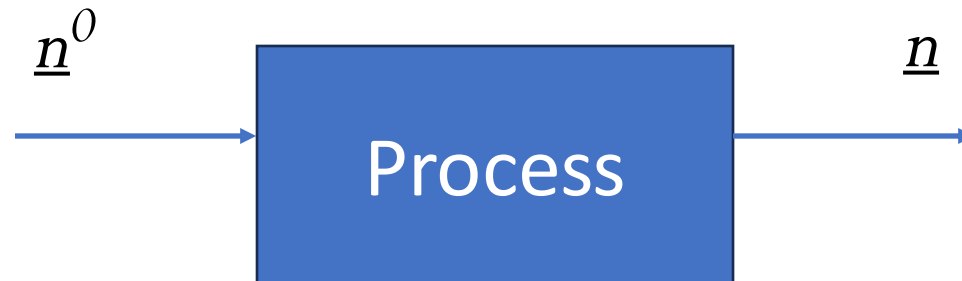


Extension of the AR to other situations

- We can extend the concept of the Attainable Region (AR) to other situations
- In general, we can consider an **AR** to be the set of all possible outputs (sets of values of the choice variables) of a problem that satisfy the problem's constraints.
- The dimensionality of the region is \mathcal{R}^m , where m is related to the number of variables.

Definition:
Material
Balance
Limited
Attainable
Region AR^{MB}

- The Material Balance Limited Attainable Region (AR^{MB}) is the set of all possible outputs \underline{n} for a given feed \underline{n}^0 that is consistent with the material balance constraints, where \underline{n} is the molar flowrate
 - The AR^{MB} does not take other constraints such as kinetics, equilibrium, energy, etc. into account



Previous work on the AR^{MB}

- The AR^{MB} has previously been referred to as the stoichiometric compatibility class or reaction hyperplane.
- Methods exist for finding the AR^{MB}
- In this talk, we will discuss some of the properties of the AR^{MB} that are useful for process synthesis
 - Use an example to demonstrate this

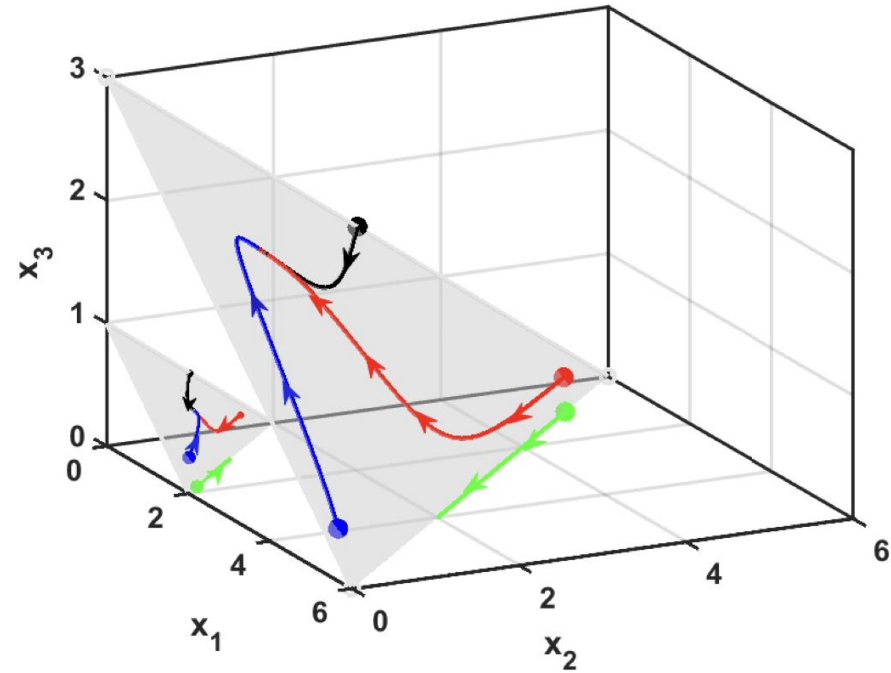
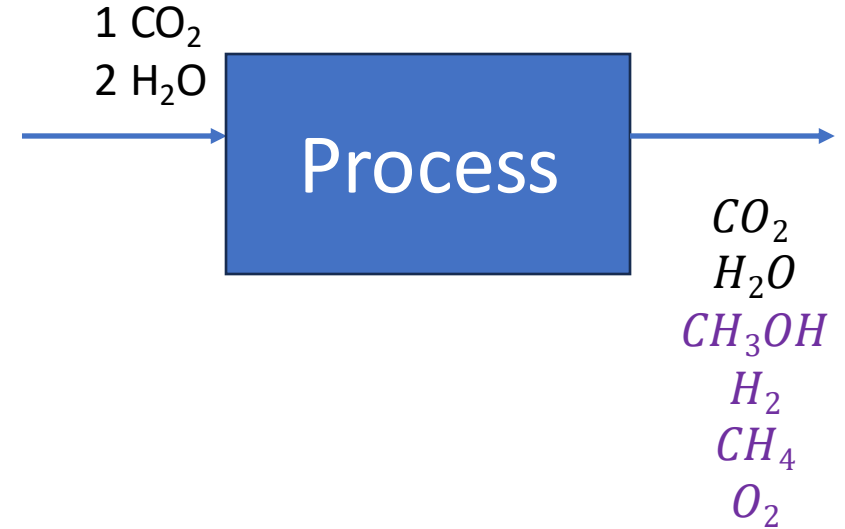


Fig. 1. Chemical stoichiometric compatibility classes and trajectories of the system in Example 3.

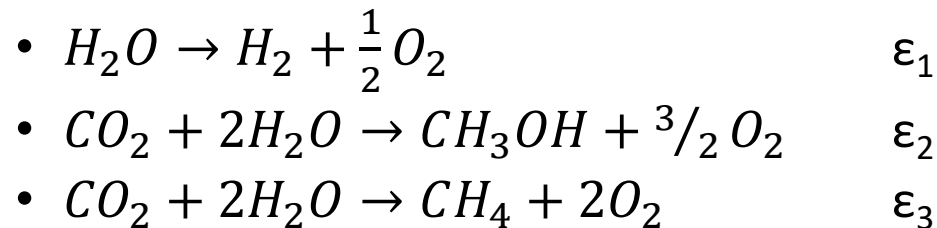
Taken from: Zhang, X., Fang, Z., Gao, C., & Dochain, D. (2023). On the relation between ω -limit set and boundaries of mass-action chemical reaction networks. *Automatica*, 149, 110828

Example: Production of Chemicals from CO₂ and H₂O



- Consider:
 - a feed of CO₂ and H₂O, in the ratio 1:2
 - possible products: CH₃OH, H₂ and CH₄ and O₂

- There are 3 Independent Material Balances:



Use linear programming to find the AR^{MB}

$$N_{CO_2} = 1 - \epsilon_2 - \epsilon_3 \geq 0$$

$$N_{H_2O} = 2 - \epsilon_1 - 2\epsilon_2 - 2\epsilon_3 \geq 0$$

$$N_{CH_3OH} = \epsilon_2 \geq 0$$

$$N_{H_2} = \epsilon_1 \geq 0$$

$$N_{CH_4} = \epsilon_3 \geq 0$$

$$N_{O_2} = \frac{1}{2}\epsilon_1 + \frac{3}{2}\epsilon_2 + 2\epsilon_3 \geq 0$$

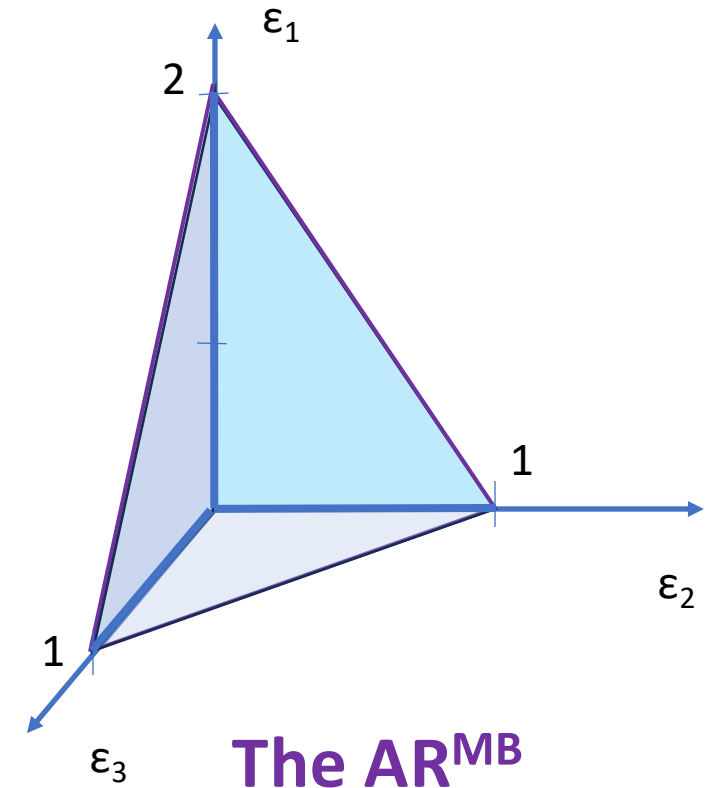
The AR^{MB}: Production of Chemicals from CO₂ and H₂O

- $H_2O \rightarrow H_2 + \frac{1}{2} O_2$
- $CO_2 + 2H_2O \rightarrow CH_3OH + \frac{3}{2} O_2$
- $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$

ϵ_1

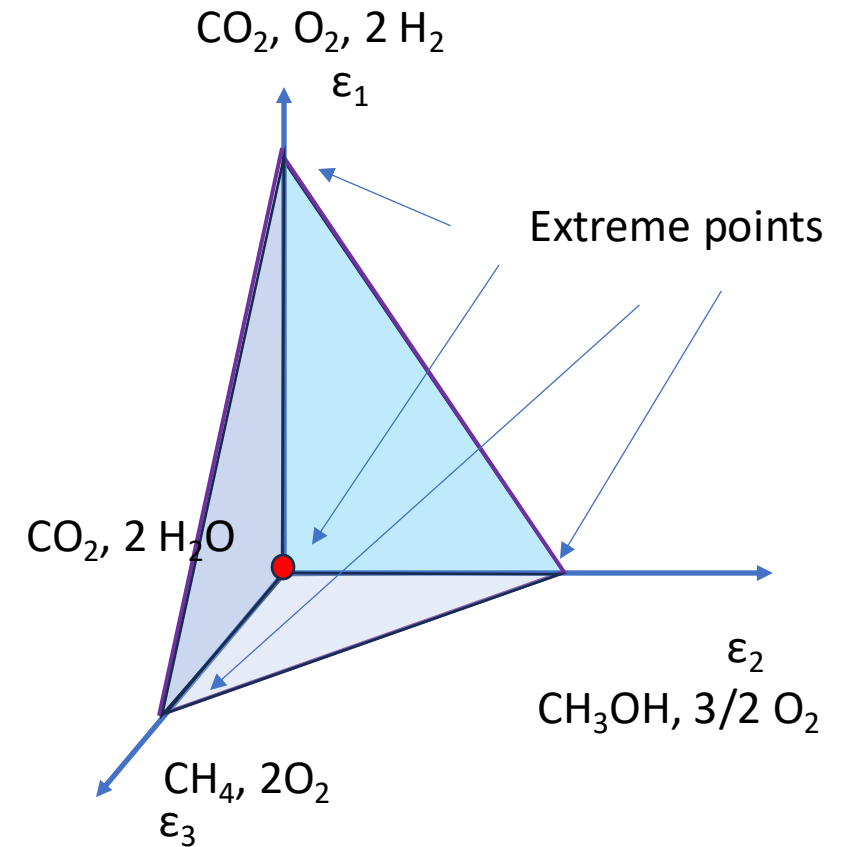
ϵ_2

ϵ_3



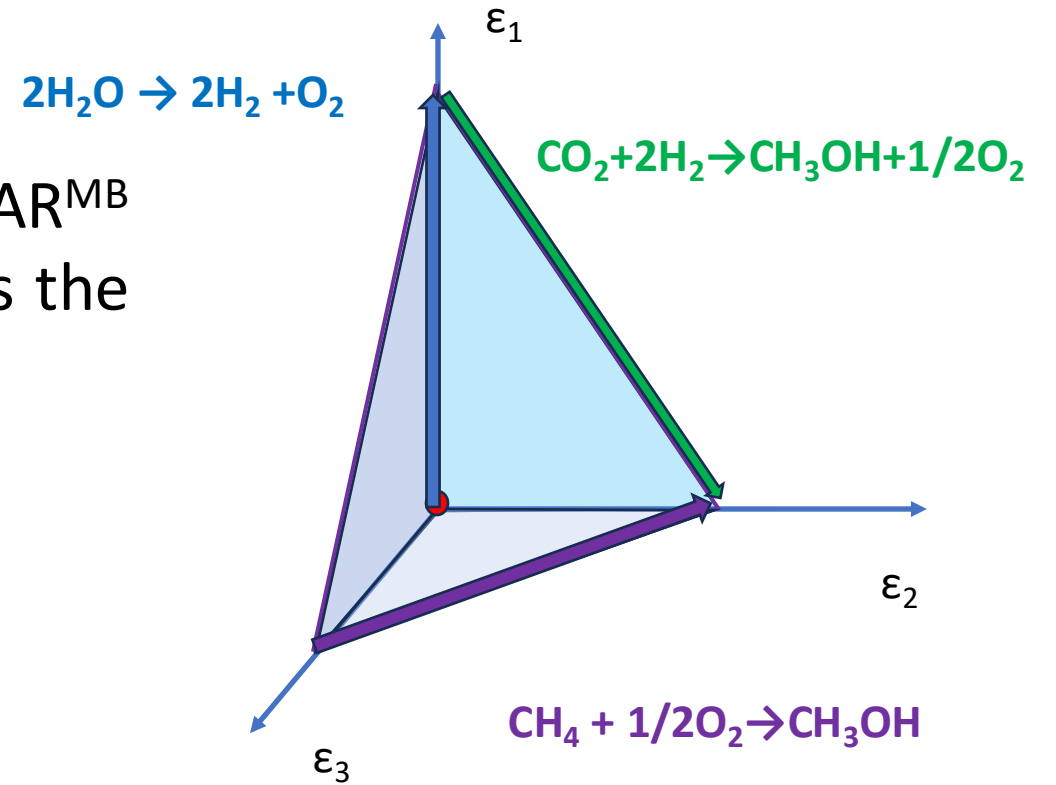
Properties of the AR^{MB}

- At extreme points, the moles of one or more species is zero.
- The AR^{MB} is the convex hull of the extreme points of the region
 - it follows that AR^{MB} is a convex, connected set.
 - the AR^{MB} contains the feed point



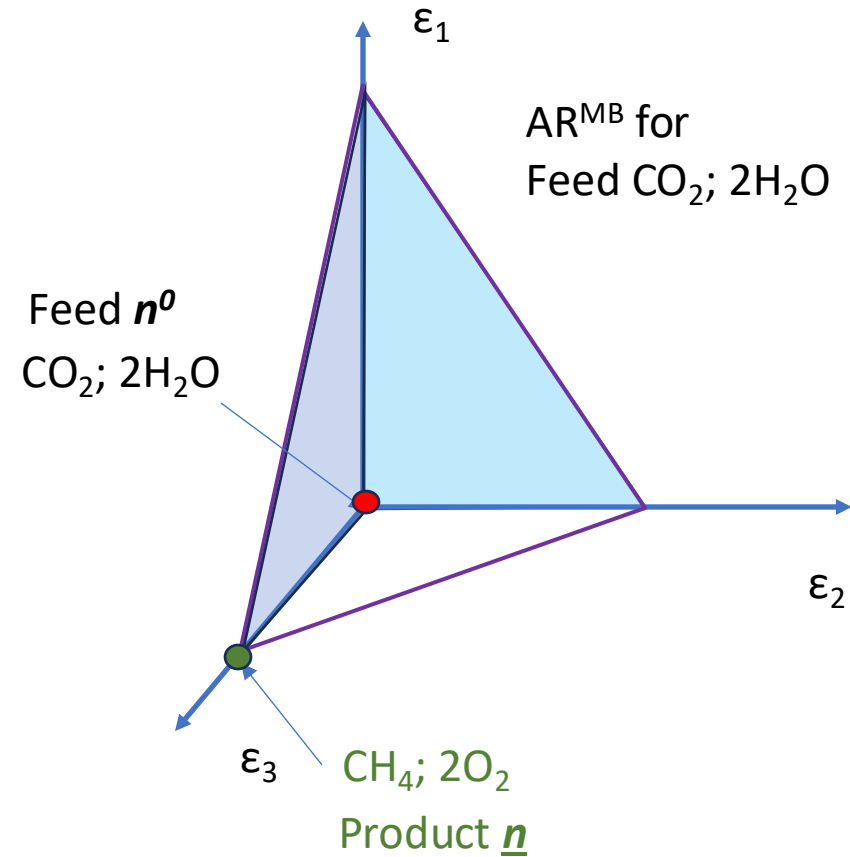
Properties of the AR^{MB}

- The vector between 2 points in the AR^{MB} corresponds to a material balance across the process



Properties of the AR^{MB}

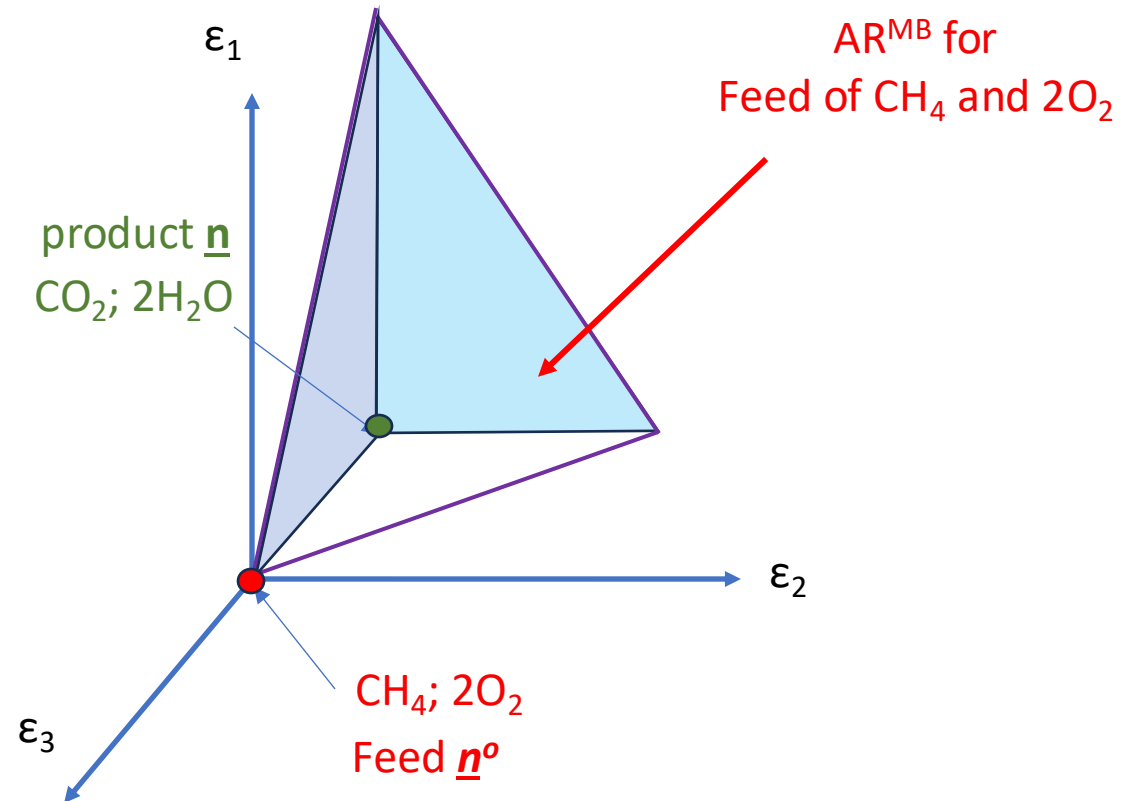
- Consider a product represented by a point \underline{n} that lies in the AR^{MB} for feed \underline{n}^0 .



Properties of the AR^{MB}

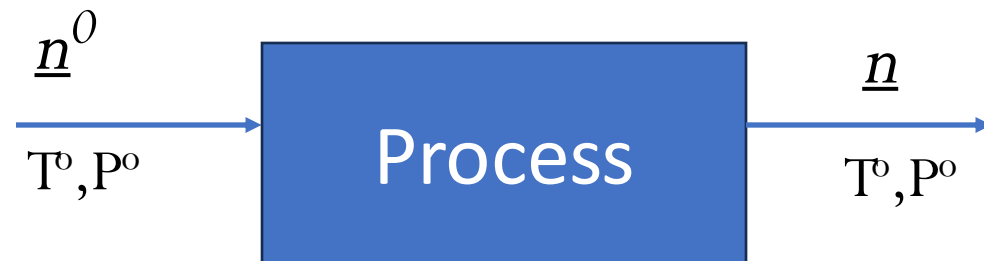
It follows that:

- If we find the AR^{MB} for feed \underline{n} , then \underline{n}^o will lie in this AR^{MB} .



Definition: Enthalpy and Gibbs Free Energy Vectors

- We define
- $\underline{\hat{H}}_f(T^0, P^0) = (\hat{H}_{f1}, \hat{H}_{f2}, \dots, \hat{H}_{fn})^T$
 - where \hat{H}_{fi} = enthalpy of formation of component i at temperature T^0 and pressure P^0
- and
- $\underline{\hat{G}}_f(T^0, P^0) = (\hat{G}_{f1}, \hat{G}_{f2}, \dots, \hat{G}_{fn})^T$
 - where \hat{G}_{fi} = Gibbs Free Energy of formation of component i at temperature T^0 and pressure P^0



Definition:
Change in
Enthalpy and
Gibbs Free
Energy across a
process

Consider a process where the feed \underline{n}^0 and the product \underline{n} enter and leave at temperature T^0 and pressure P^0

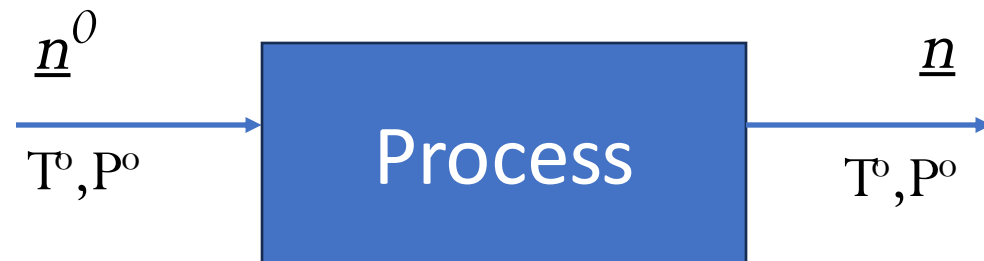
- We define

Change in enthalpy across the process =

$$\Delta H(T^0, P^0) = (\underline{n} - \underline{n}^0)^T \cdot \underline{\hat{H}}_f(T^0, P^0)$$

Change in Gibbs Free Energy across the process =

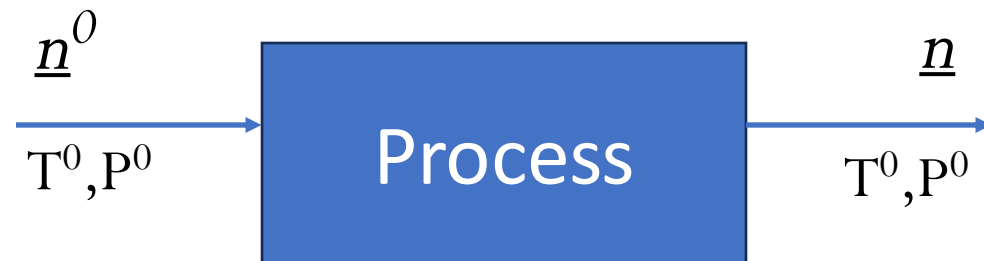
$$\Delta G(T^0, P^0) = (\underline{n} - \underline{n}^0)^T \cdot \underline{\hat{G}}_f(T^0, P^0)$$



Definition:
Thermodynamic
Attainable
Region AR^T

We define:

The **Thermodynamic Attainable Region AR^T** as the set of all $\{\Delta H(T^o, P^o), \Delta G(T^o, P^o)\}$ for all products \underline{n} that lie in the AR^{MB} corresponding to a feed \underline{n}^o



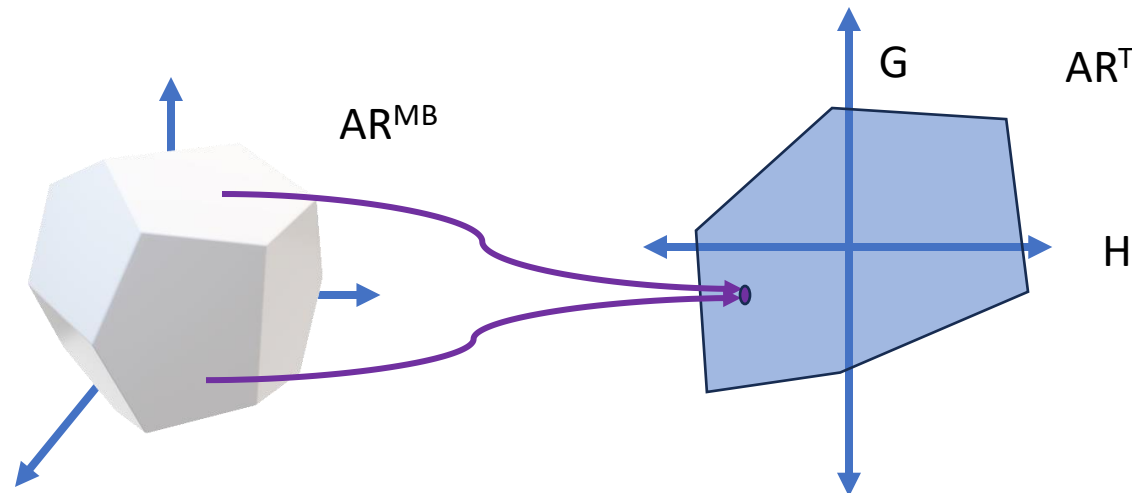
Relationship
between the:

Material Balance
 AR^{MB}

and the

Thermodynamic
Attainable Region
 AR^T

- Consider the transformation $T : \mathcal{R}^N \rightarrow \mathcal{R}^2$ where: $T(\underline{n}) = \{\Delta H(T^o, P^o), \Delta G(T^o, P^o)\} = (\underline{n} - \underline{n}^o)^T \cdot [\underline{\hat{H}}_f(T^o, P^o), \underline{\hat{G}}_f(T^o, P^o)]$
- AR^T is thus a linear transformation of the elements of AR^{MB} .
- It follows that AR^T is a surjective mapping of the elements of AR^{MB} ,
 - equivalently there is a one-to-many relationship between elements of AR^{MB} and elements of AR^T .



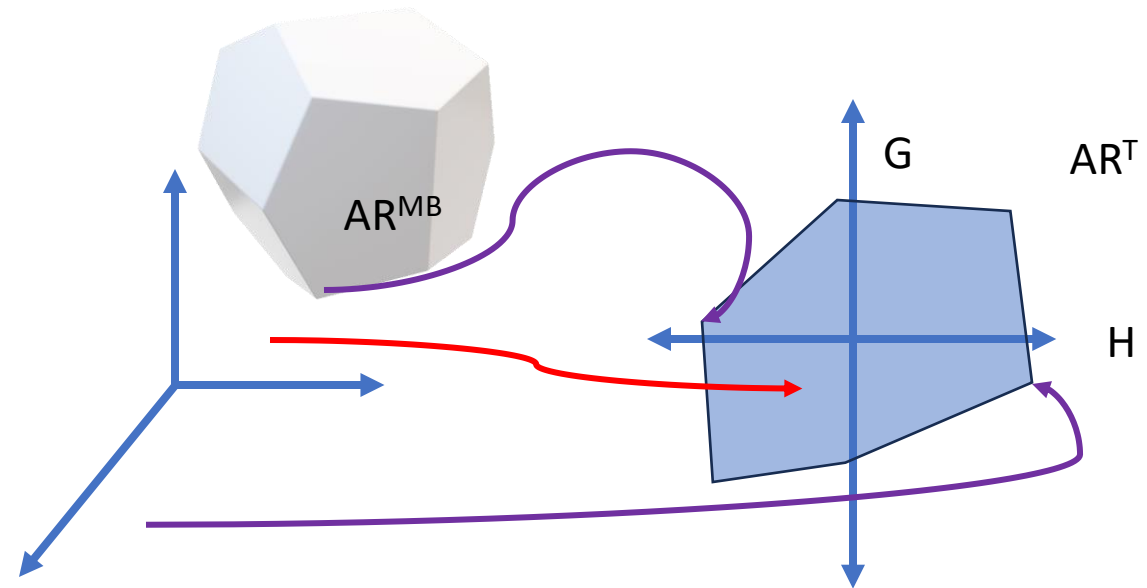
Relationship
between the:

Material Balance
 AR^{MB}

and the

Thermodynamic
Attainable Region
 AR^T

- Consequently, extreme points of the AR^{MB} are linearly transformed and are elements of AR^T but may not be extreme points of AR^T .



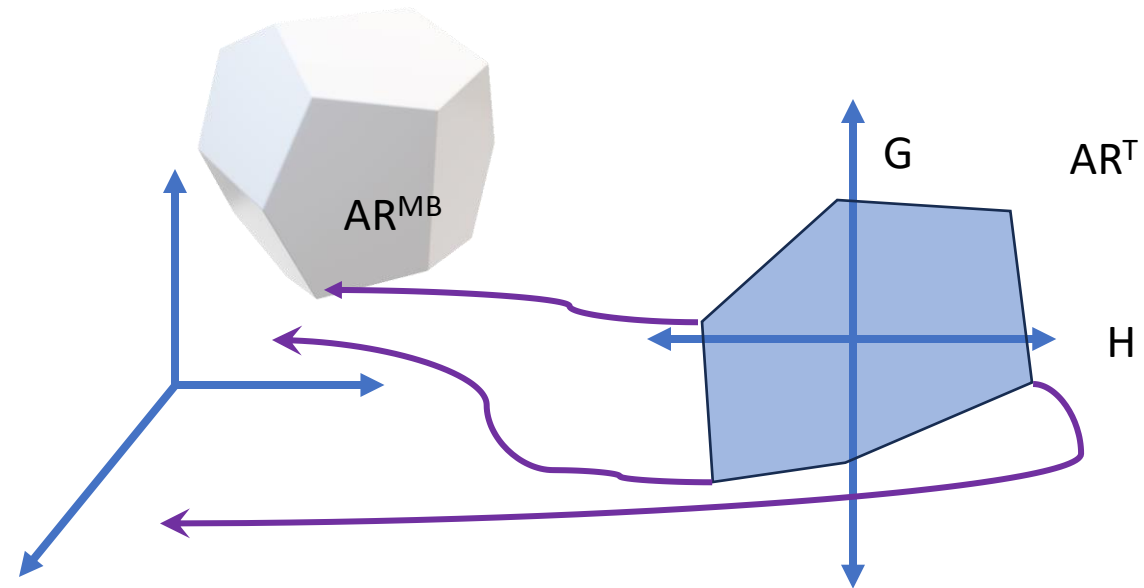
Relationship
between the:

Material Balance
 AR^{MB}

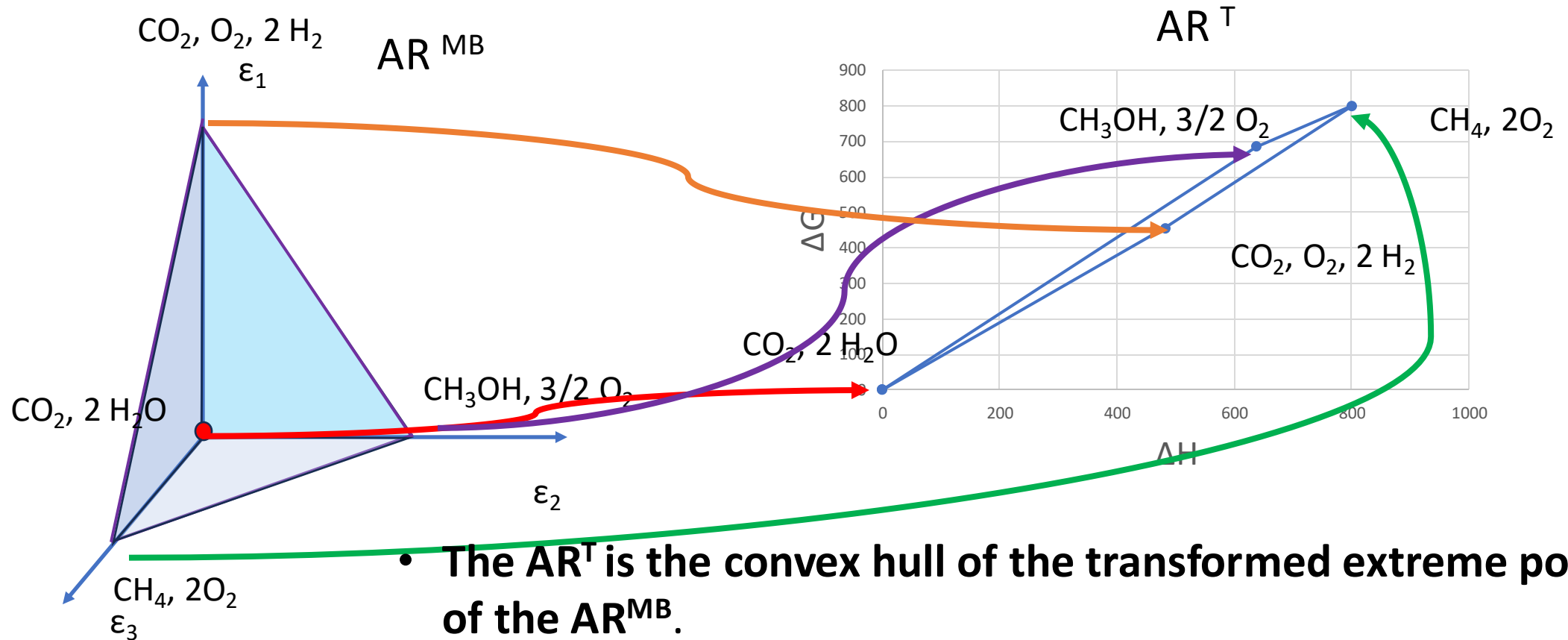
and the

Thermodynamic
Attainable Region
 AR^T

- Consequently, extreme points of the AR^{MB} are linearly transformed and are elements of AR^T but may not be extreme points of AR^T .
- **However all extreme points of AR^T correspond extreme points of AR^{MB} .**



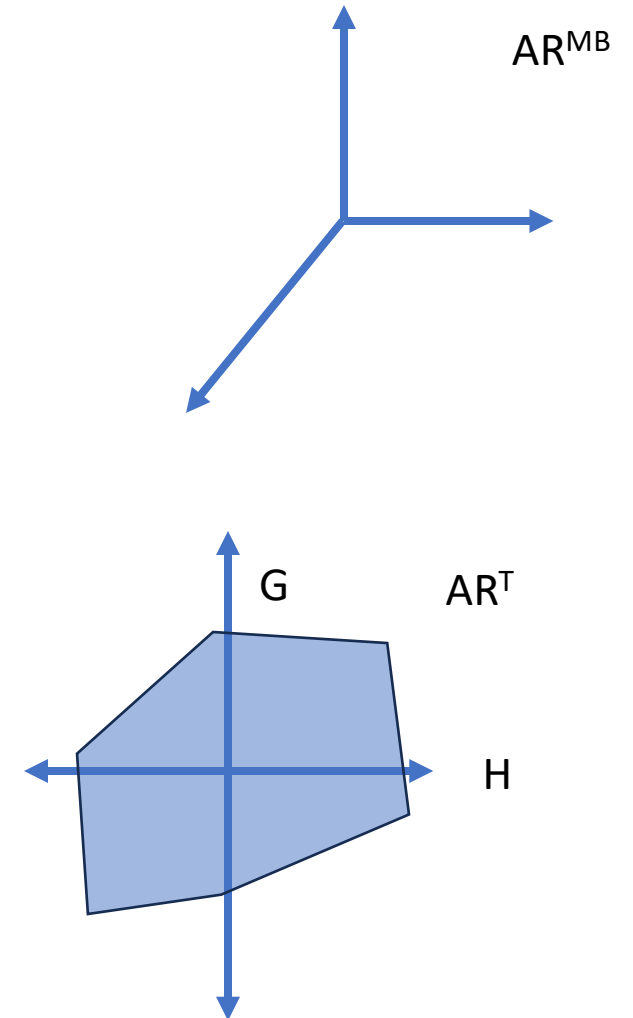
Example of AR^T : Finding the AR^T

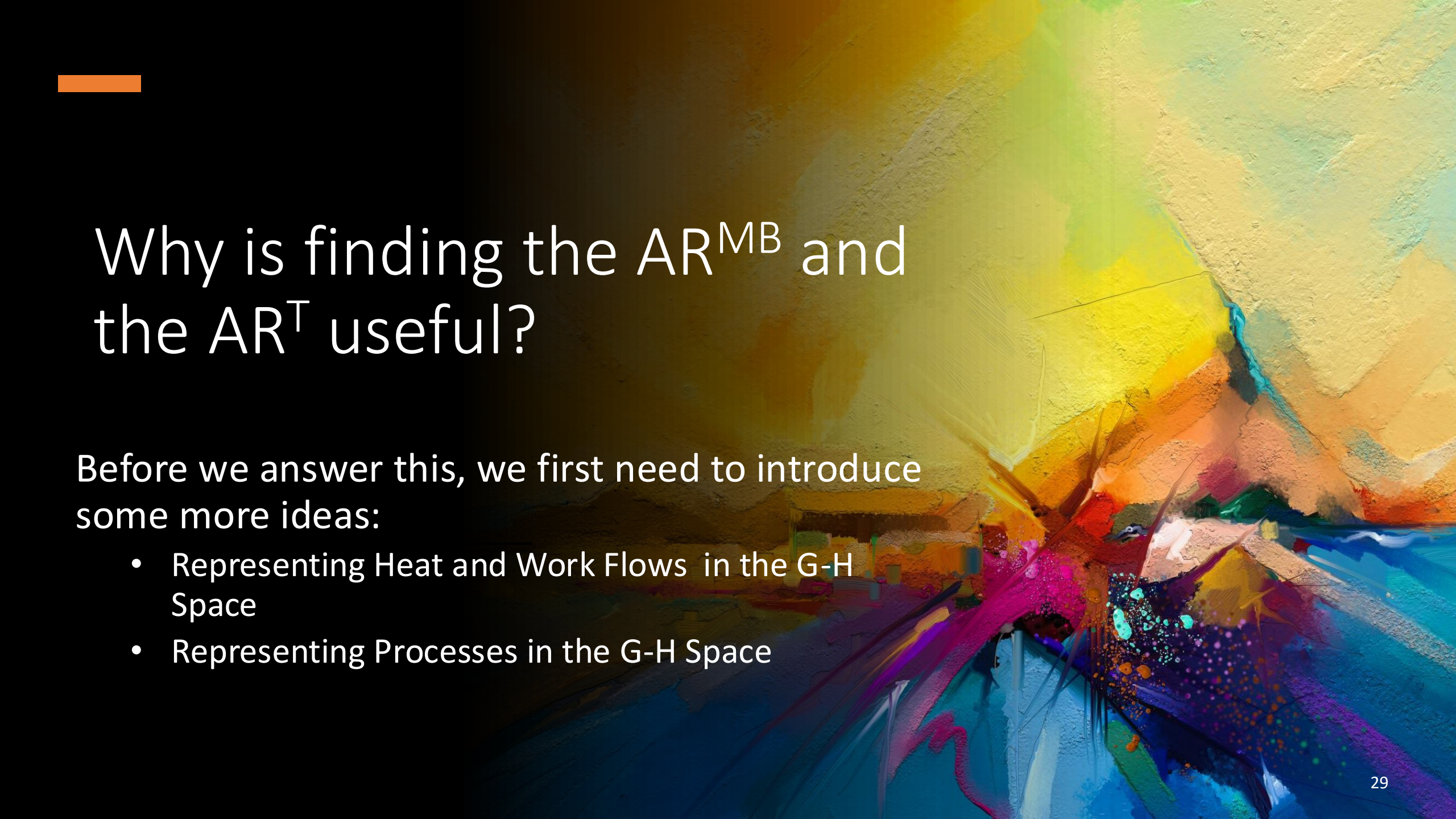


- The AR^T is the convex hull of the transformed extreme points of the AR^{MB} .
- It follows that AR^T is a convex, connected set that contains the feed point.

What does this all imply for calculating the AR^T

- Find the AR^{MB} by solving the set of linear equations:
 - $n_i \leq 0$ for all components i in the systems
 - find all extreme points of the AR^{MB}
- Transform the extreme points of the AR^{MB} .
 - $T(\underline{n}) = \{\{\Delta H(T^o, P^o), \Delta G(T^o, P^o)\}\} = (\underline{n} - \underline{n}^o)^T \cdot [\Delta H(T^o, P^o), \Delta G(T^o, P^o)]$
 - Find the convex hull of the transformed extreme points
- This convex hull corresponds to the AR^T
 - **No matter the dimension of the AR^{MB} (ie no matter how many components in the process), the AR^T is always 2D**





Why is finding the AR^{MB} and the AR^T useful?

Before we answer this, we first need to introduce some more ideas:

- Representing Heat and Work Flows in the G-H Space
- Representing Processes in the G-H Space

Relationship between process heat and workflows and ΔH and ΔG

- The energy balance across a process gives:

$$\Delta H = Q(T) + W$$

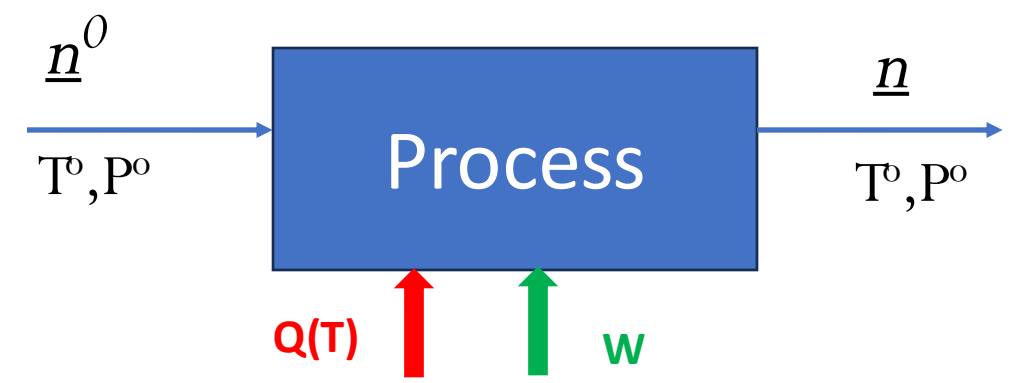
- The entropy balance across a reversible process gives:

$$\Delta S = Q(T)/T$$

- Combining these, gives for a reversible process, that:

$$\Delta G(T^0, P^0) = \Delta H(T^0, P^0) - T^0 \Delta S(T^0, P^0)$$

or $\Delta G = W + Q(T)(1 - T^0/T)$

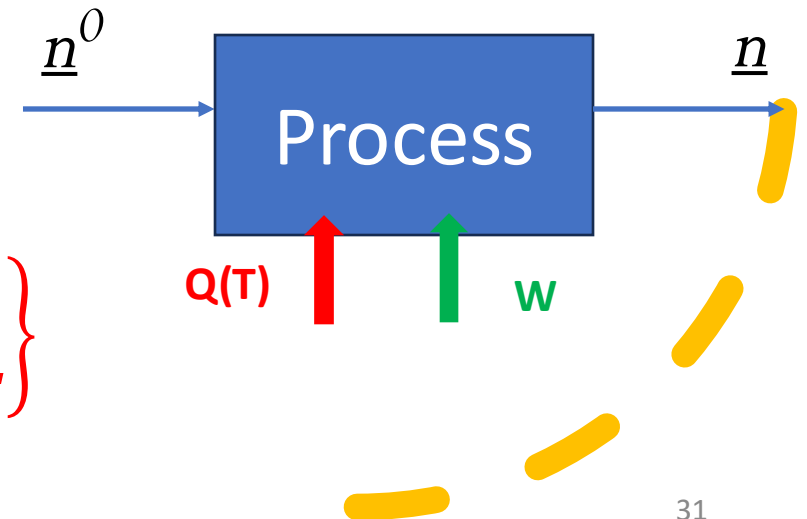


Representation of Heat and Work flows in the ART

Result: Heat and work flows can be represented as vectors in the GH plot

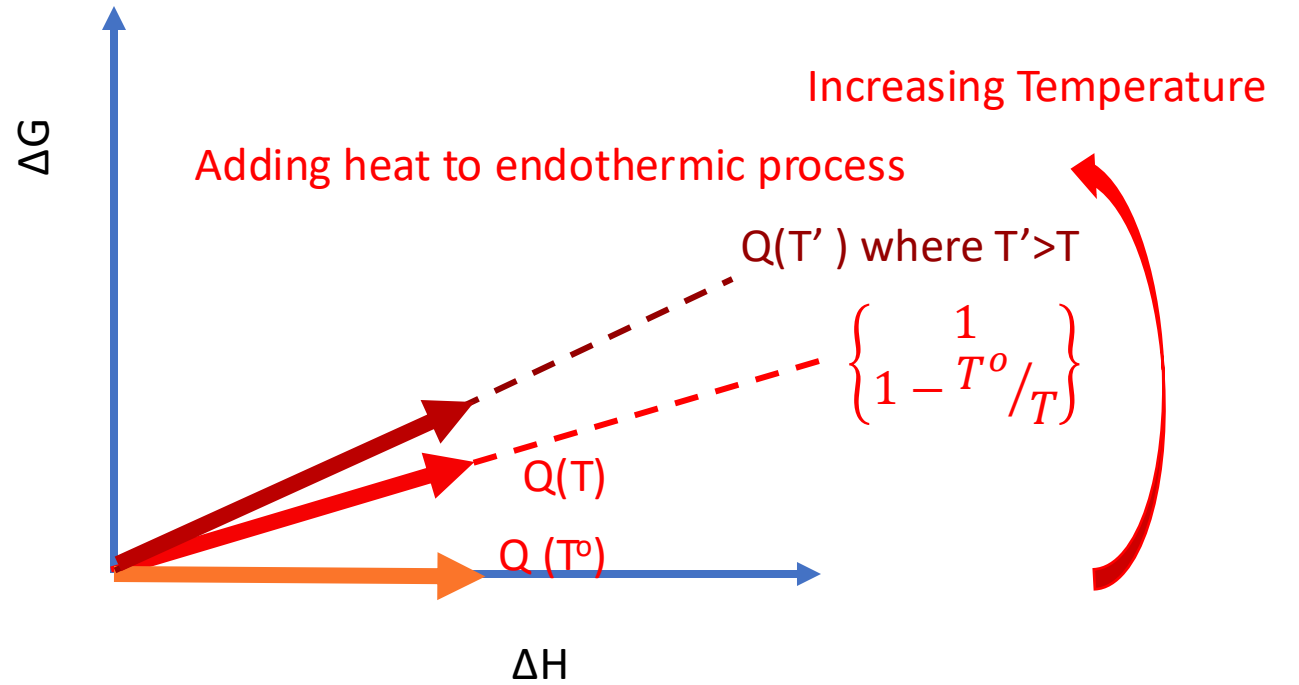
The *reversible* addition of work W and heat $Q(T)$ at temperature T is described by:

$$\begin{Bmatrix} \Delta H \\ \Delta G \end{Bmatrix} = W \begin{Bmatrix} 1 \\ 1 \end{Bmatrix} + Q \begin{Bmatrix} 1 \\ 1 - T^o/T \end{Bmatrix}$$



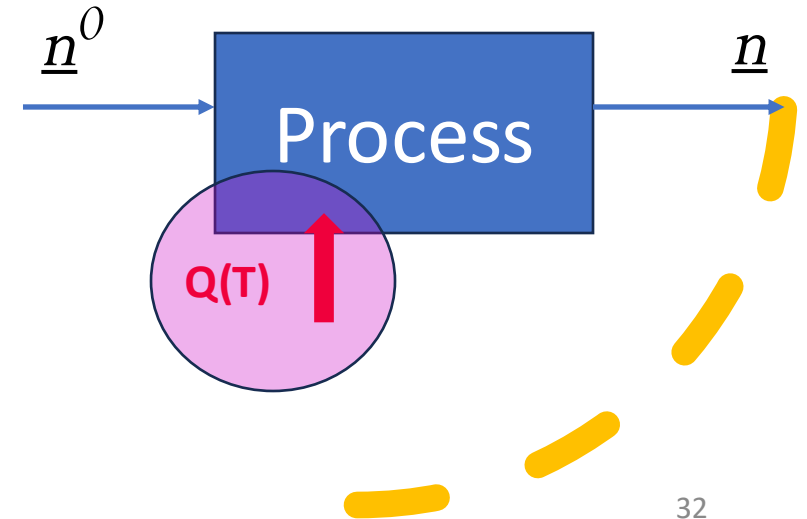
Interpretation of the AR^T

Vector representation of Heat addition



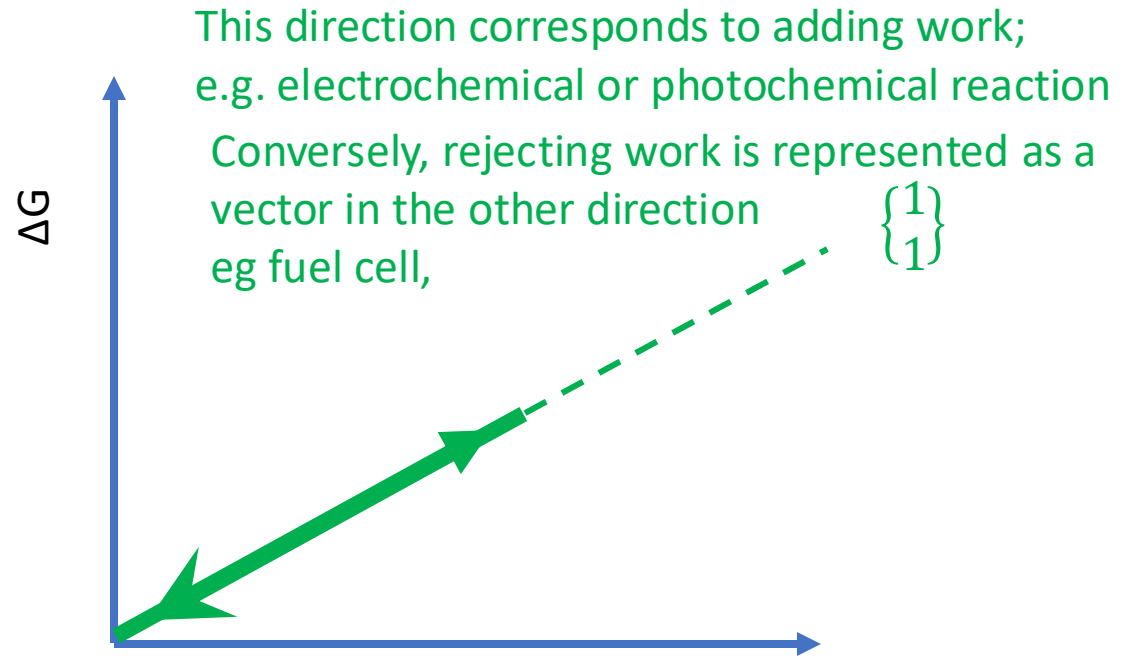
Consider a process where only **heat** $Q(T)$ at temperature T is added

$$\begin{Bmatrix} \Delta H \\ \Delta G \end{Bmatrix} = Q \begin{Bmatrix} 1 \\ 1 - T^{\circ}/T \end{Bmatrix}$$



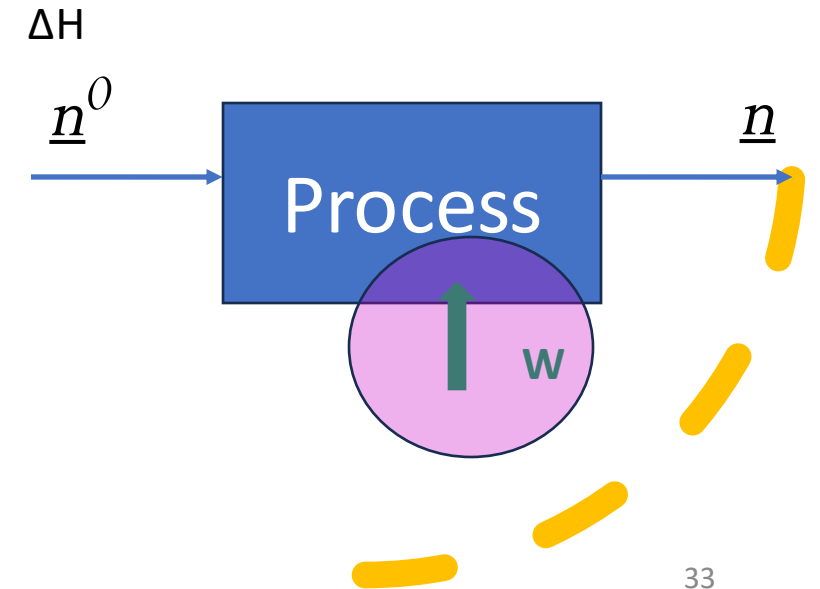
Interpretation of the AR^T

Vector representation of reversible Work flow



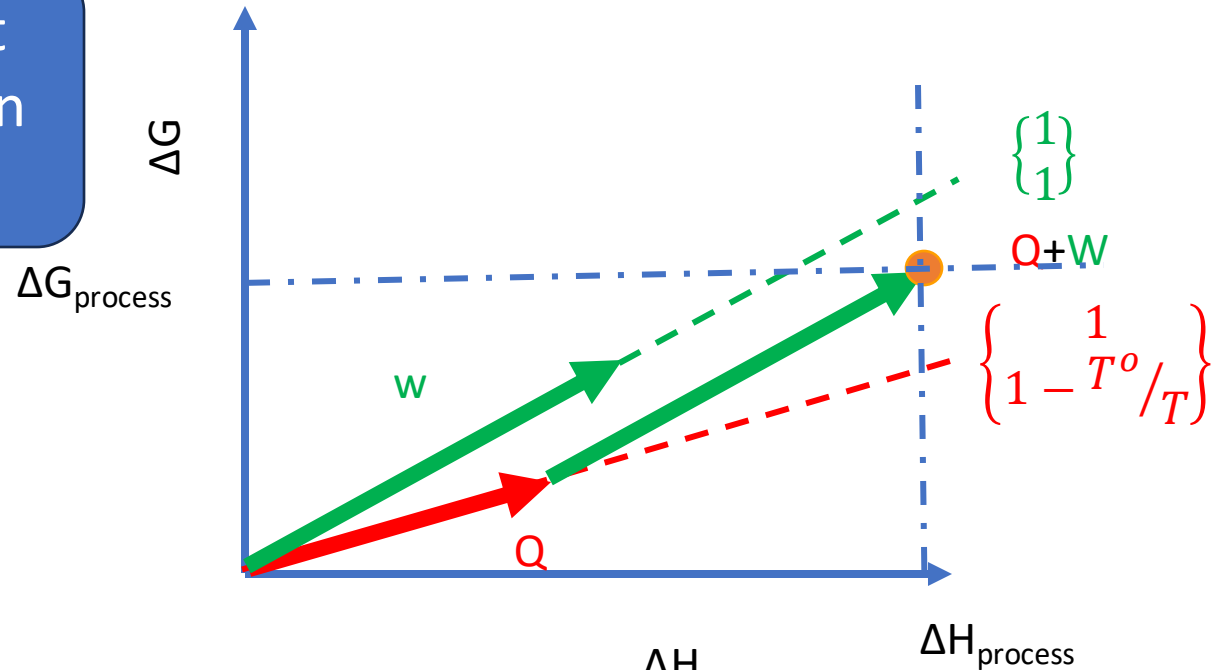
The reversible addition of work W is described by:

$$\begin{Bmatrix} \Delta H \\ \Delta G \end{Bmatrix} = W \begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$$



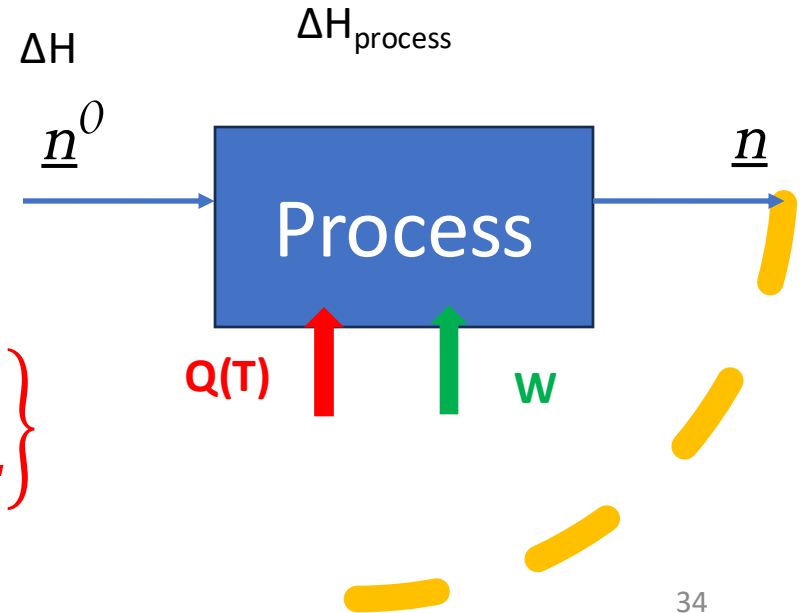
Heat and work inputs must match process ΔH and ΔG in a reversible process

Vector Representation of process heat and work flows



The addition of work W and heat $Q(T)$ can be represented as a vector sum:

$$\begin{Bmatrix} \Delta H \\ \Delta G \end{Bmatrix} = W \begin{Bmatrix} 1 \\ 1 \end{Bmatrix} + Q \begin{Bmatrix} 1 - T^0/T \\ 1 \end{Bmatrix}$$

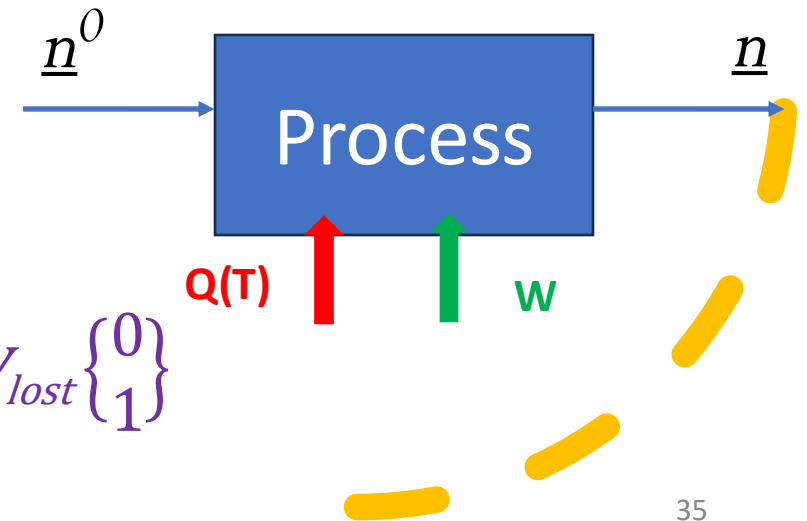


Reversible vs Irreversibility of processes

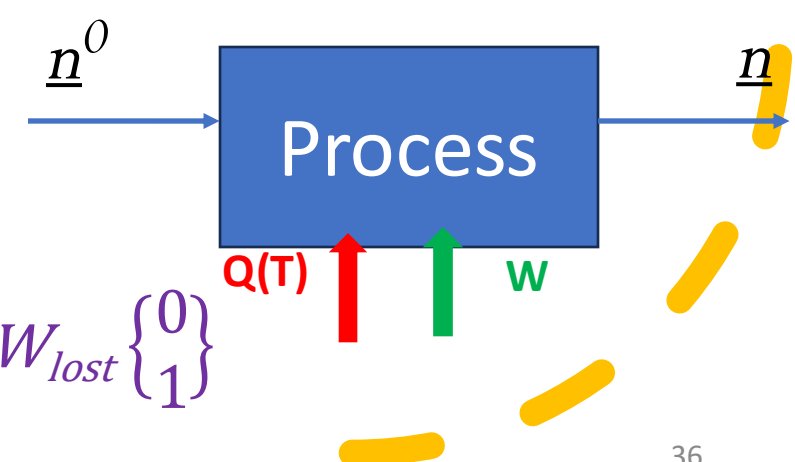
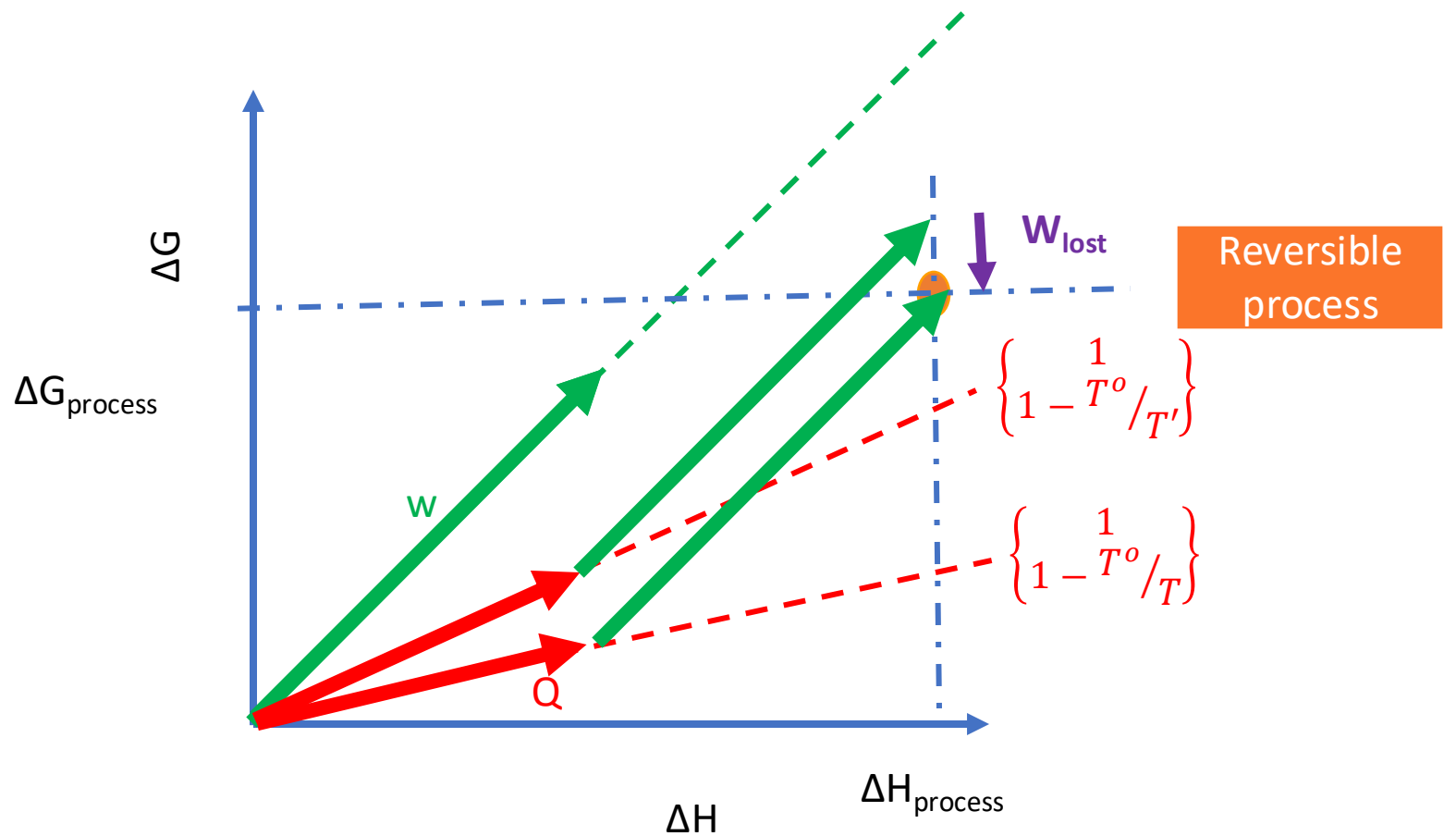
Comparing reversible and irreversible processes:

- The energy balance always balances
 - $\Delta H_{\text{process}} = W + Q$, but
- More work is added through either W or $Q(T)$ than ΔG (the reversible limit)
 - $\Delta G_{\text{process}} = W + Q (1 - T^0/T) - W_{\text{lost}}$
- This extra work adds operating costs to the process, usually resulting in increased CO₂ emissions, extra electricity consumption etc.

$$\begin{Bmatrix} \Delta H \\ \Delta G \end{Bmatrix} = W \begin{Bmatrix} 1 \\ 1 \end{Bmatrix} + Q \begin{Bmatrix} 1 \\ 1 - T^0/T \end{Bmatrix} - W_{\text{lost}} \begin{Bmatrix} 0 \\ 1 \end{Bmatrix}$$

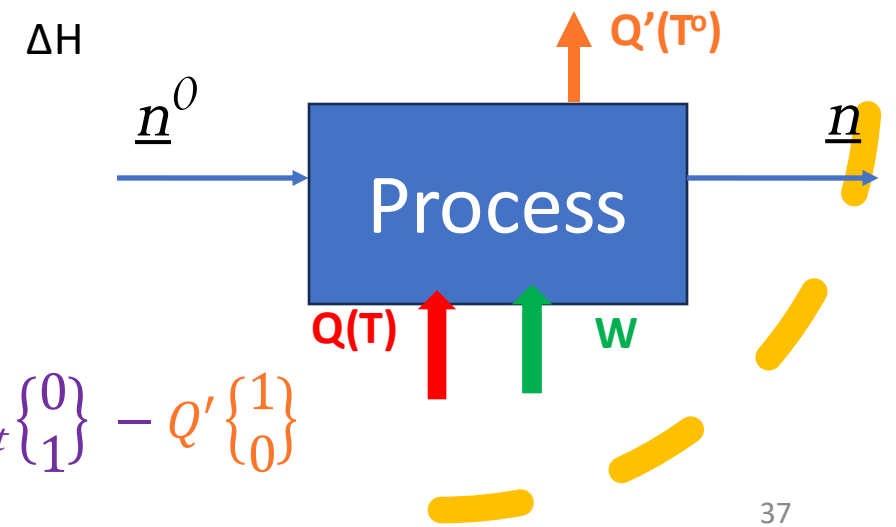
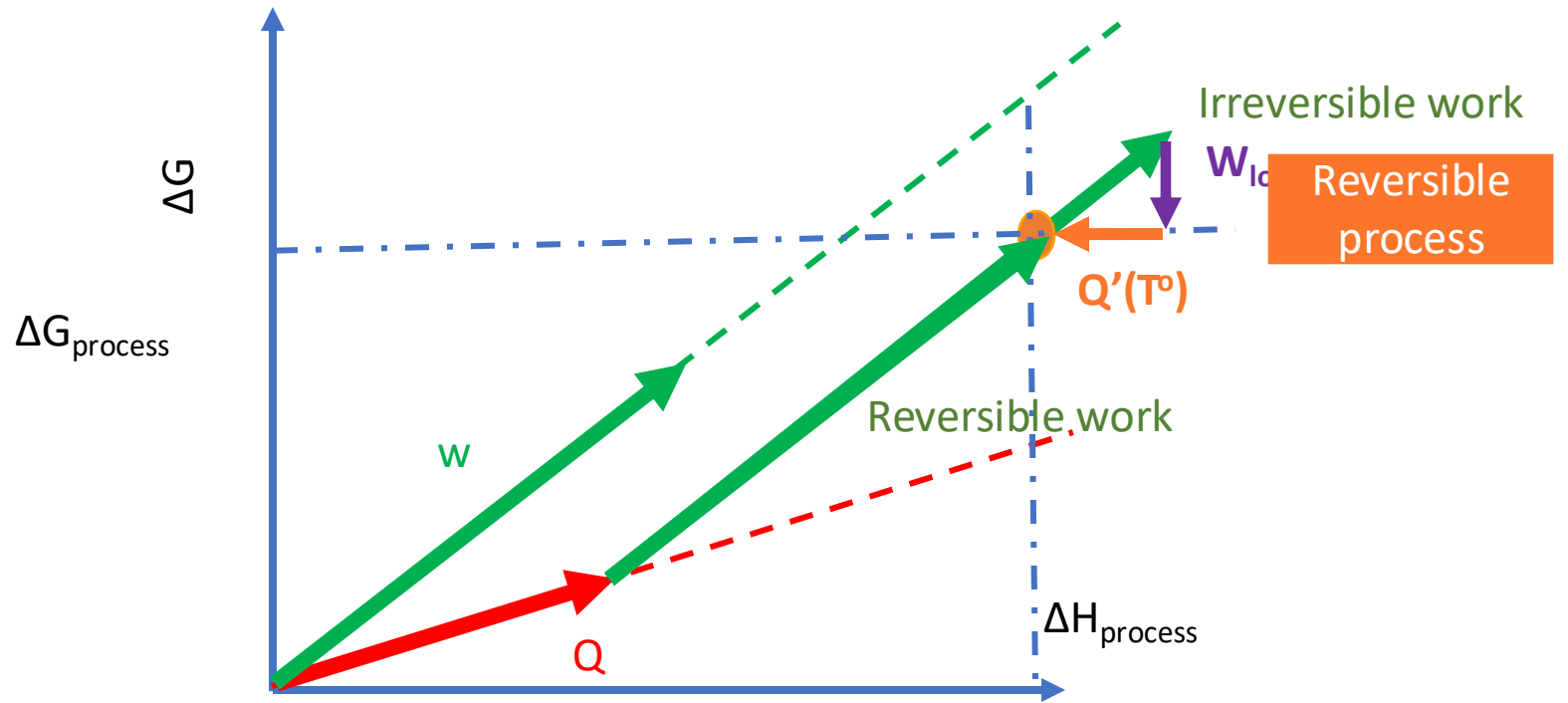


Effect of increasing the temperature of the heat added to process



$$\begin{Bmatrix} \Delta H \\ \Delta G \end{Bmatrix} = W_{irr} \begin{Bmatrix} 1 \\ 1 \end{Bmatrix} + Q \begin{Bmatrix} 1 \\ 1 - T^o/T' \end{Bmatrix} - W_{lost} \begin{Bmatrix} 0 \\ 1 \end{Bmatrix}$$

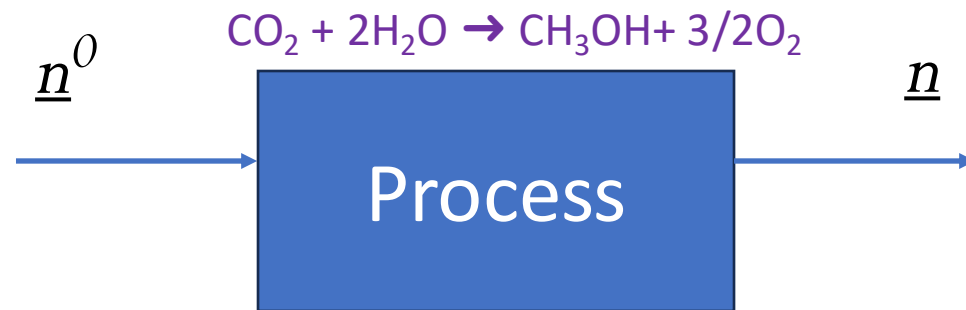
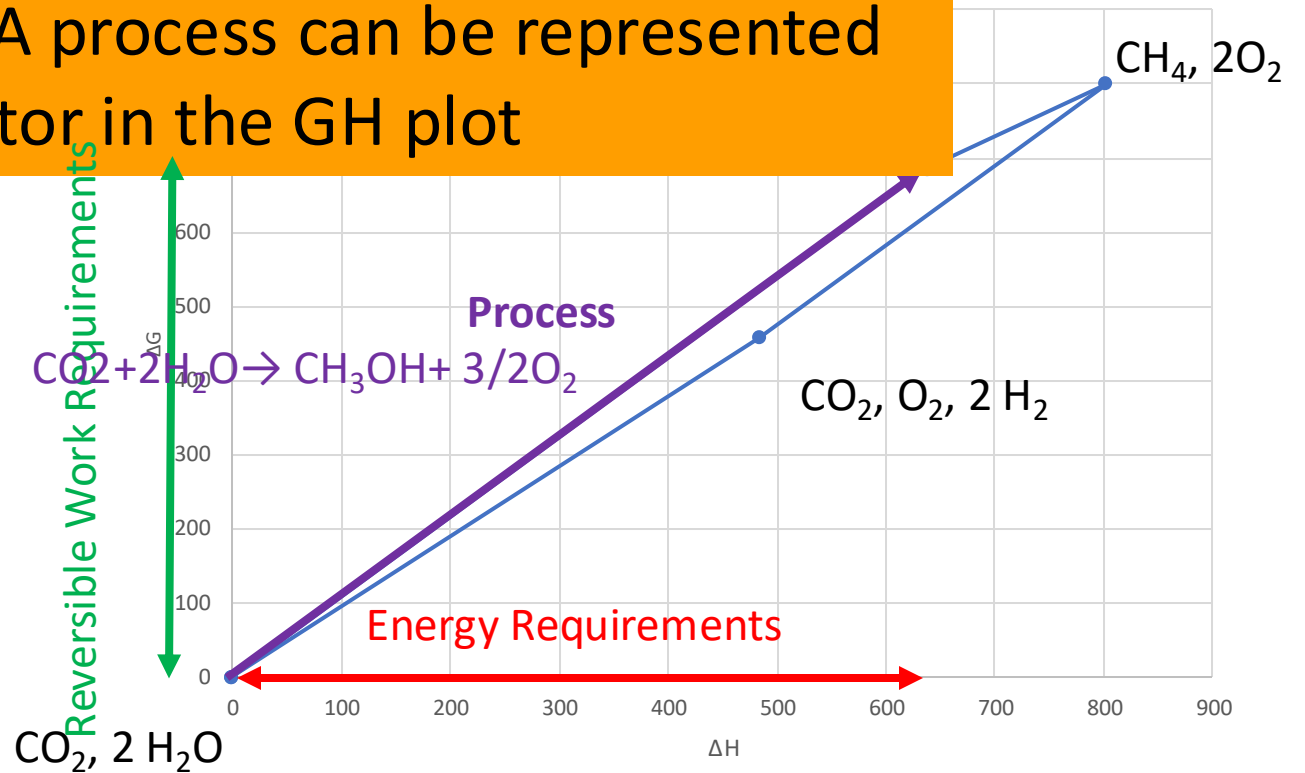
Adding work irreversibly



$$\begin{Bmatrix} \Delta H \\ \Delta G \end{Bmatrix} = W_{irr} \begin{Bmatrix} 1 \\ 1 \end{Bmatrix} + Q \begin{Bmatrix} 1 \\ 1 - T^0/T \end{Bmatrix} - W_{lost} \begin{Bmatrix} 0 \\ 1 \end{Bmatrix} - Q' \begin{Bmatrix} 1 \\ 0 \end{Bmatrix}$$

Representing
a Process as a
vector

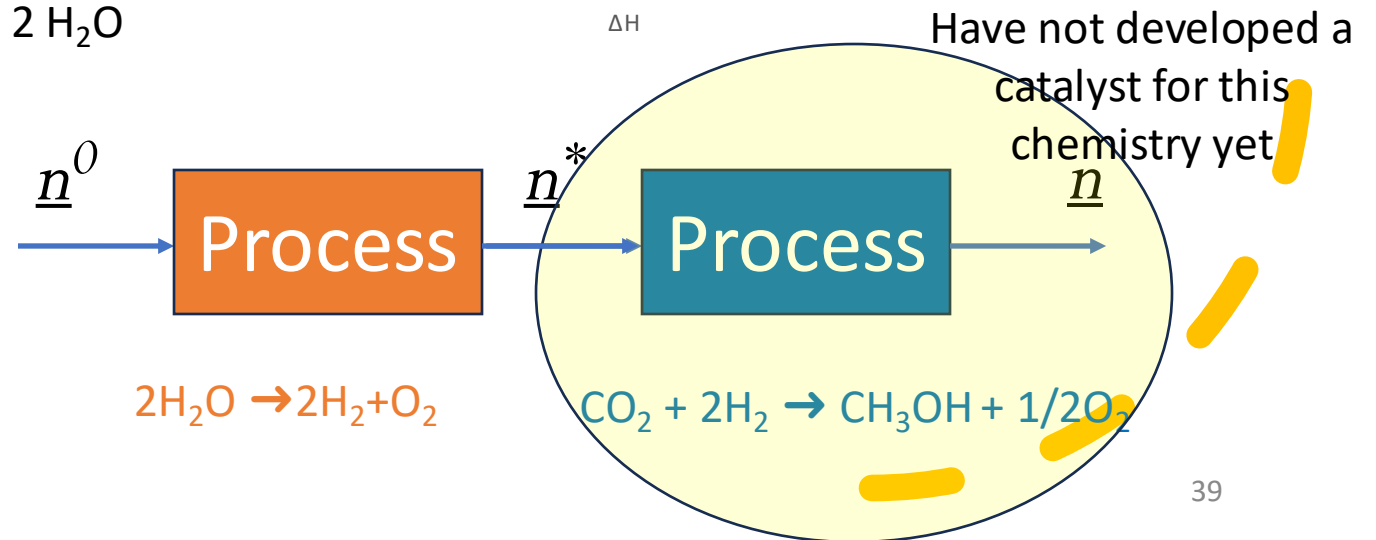
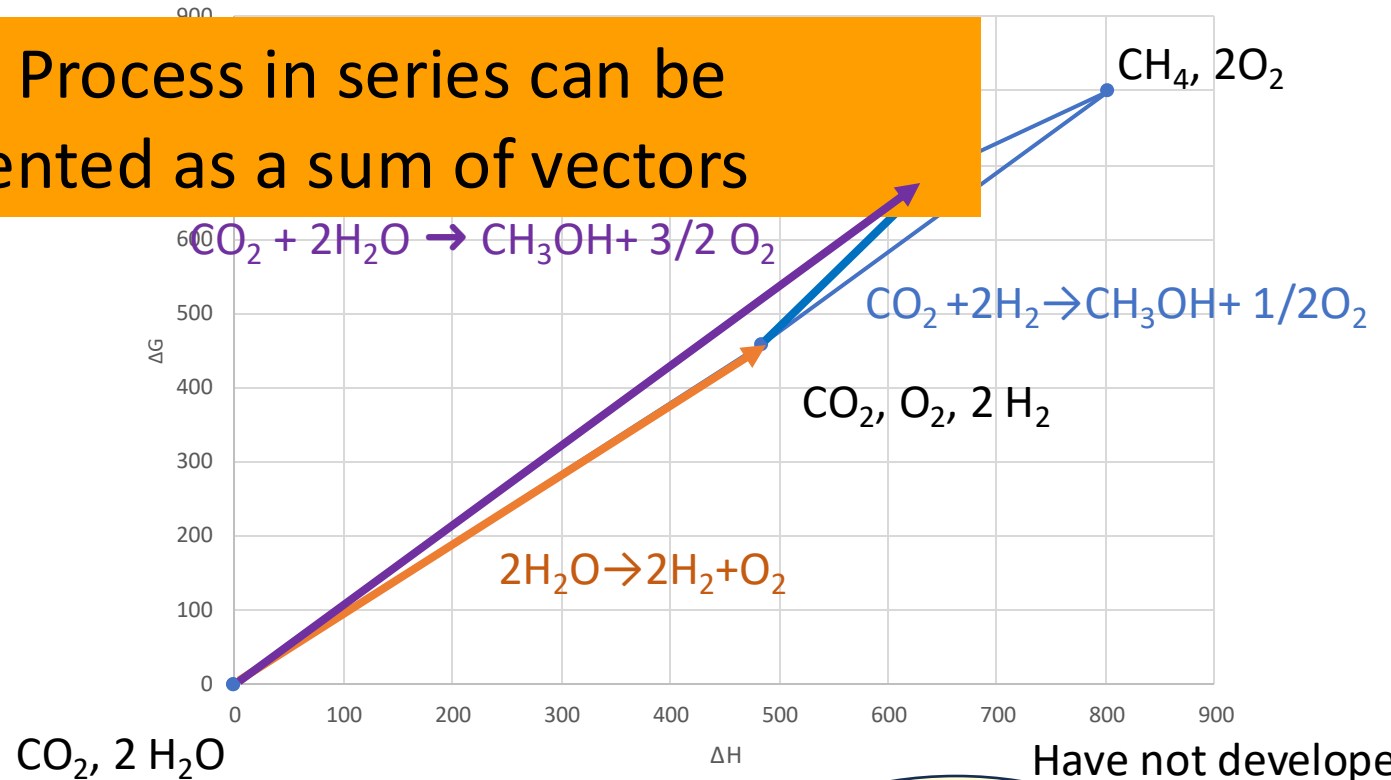
Result: A process can be represented
as a vector in the GH plot



Interpretation
of the AR^T

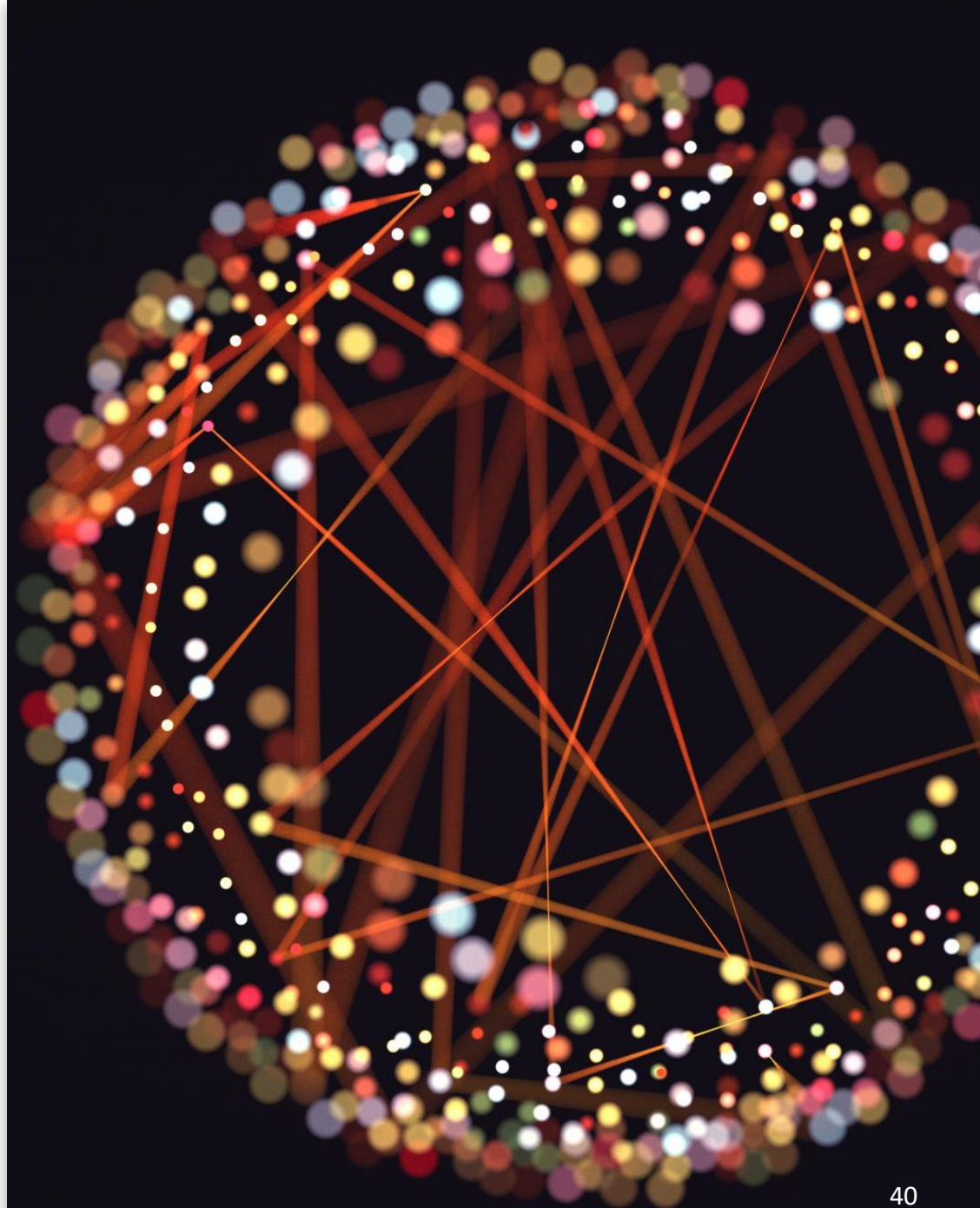
Processes in
Series

Result: Process in series can be represented as a sum of vectors

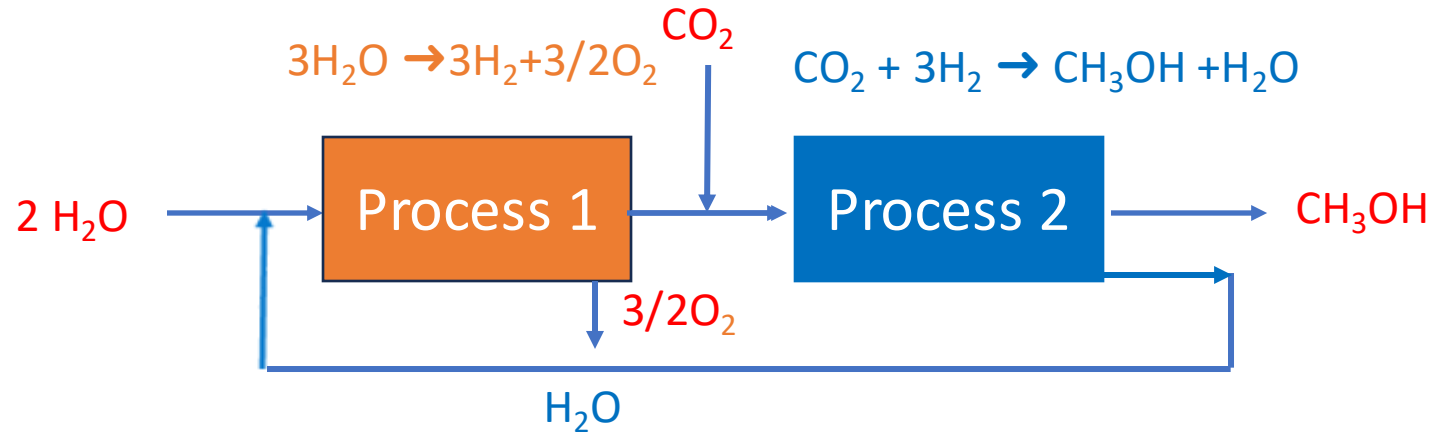


Putting this all together

- We have introduced the following concepts
 - The Mass Balance Attainable Region AR^{MB}
 - The Thermodynamic Attainable Region AR^T
 - Representing process heat and work flows as vectors
 - Representing processes as vectors
- How do we put this all together?



Example: Production of green methanol using existing catalytic chemistry

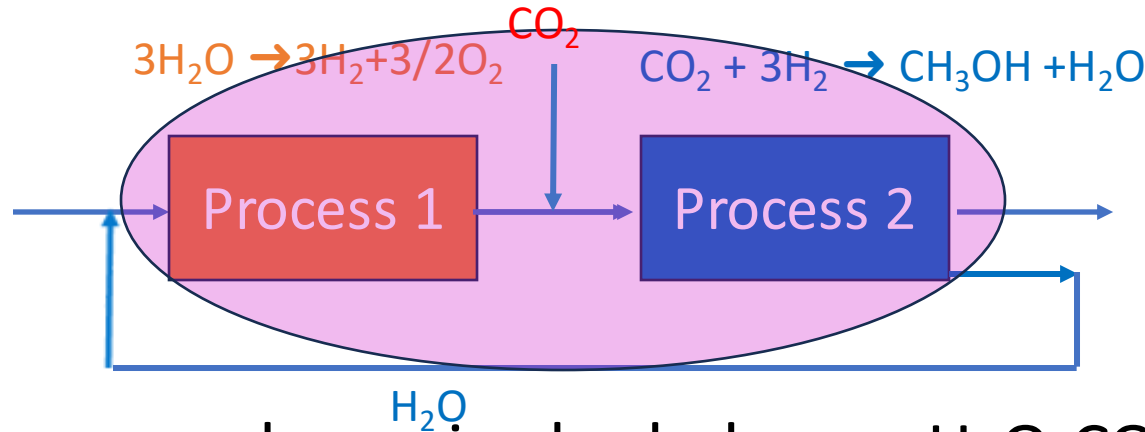
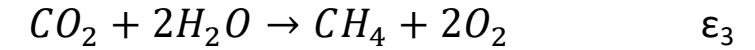
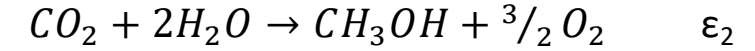


- Currently, we have catalysts for the reaction: $\text{CO}_2 + 3 \text{ H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$
- To use this chemistry, we need to electrolyze 3 moles H_2O to produce 3 moles of H_2 and $3/2$ moles of O_2 :
- We then react the 3 moles of H_2 with 1 mole CO_2 to produce 1 mole CH_3OH and 1 mole H_2O
- The water produced in methanol synthesis can be recycled to give the overall material balance:



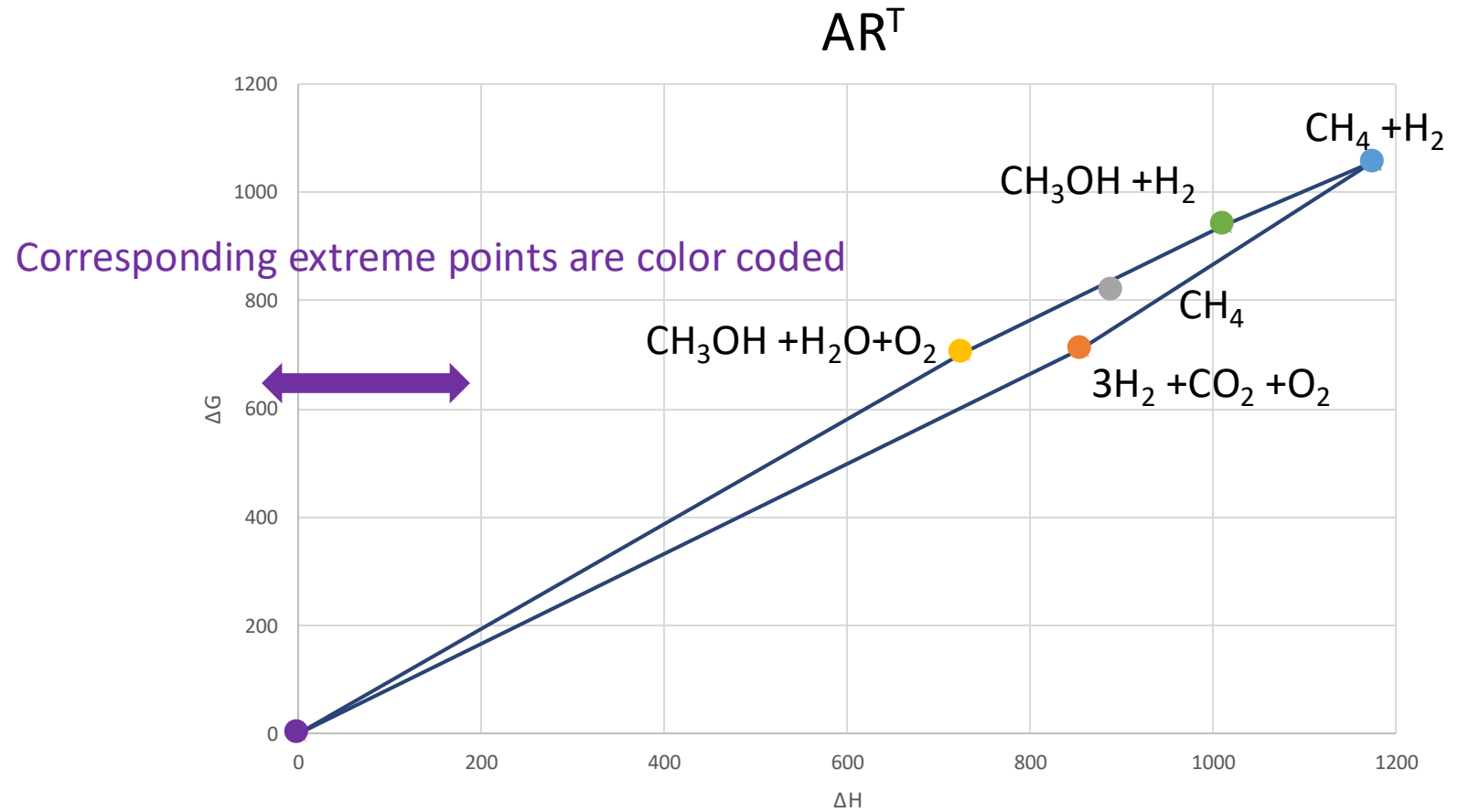
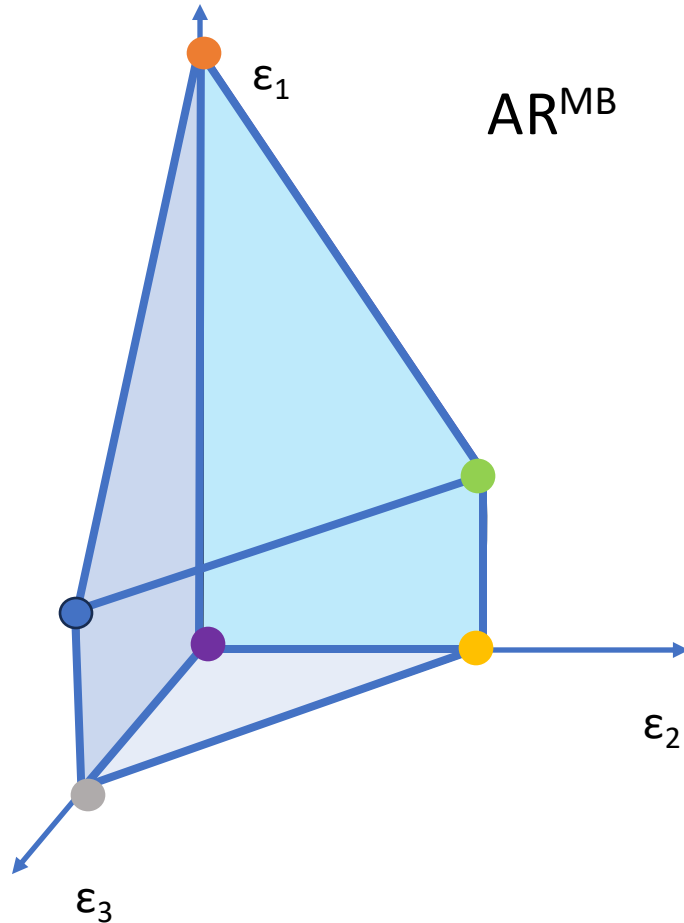
Finding the AR^{MB} and AR^T

Independent Material Balances:



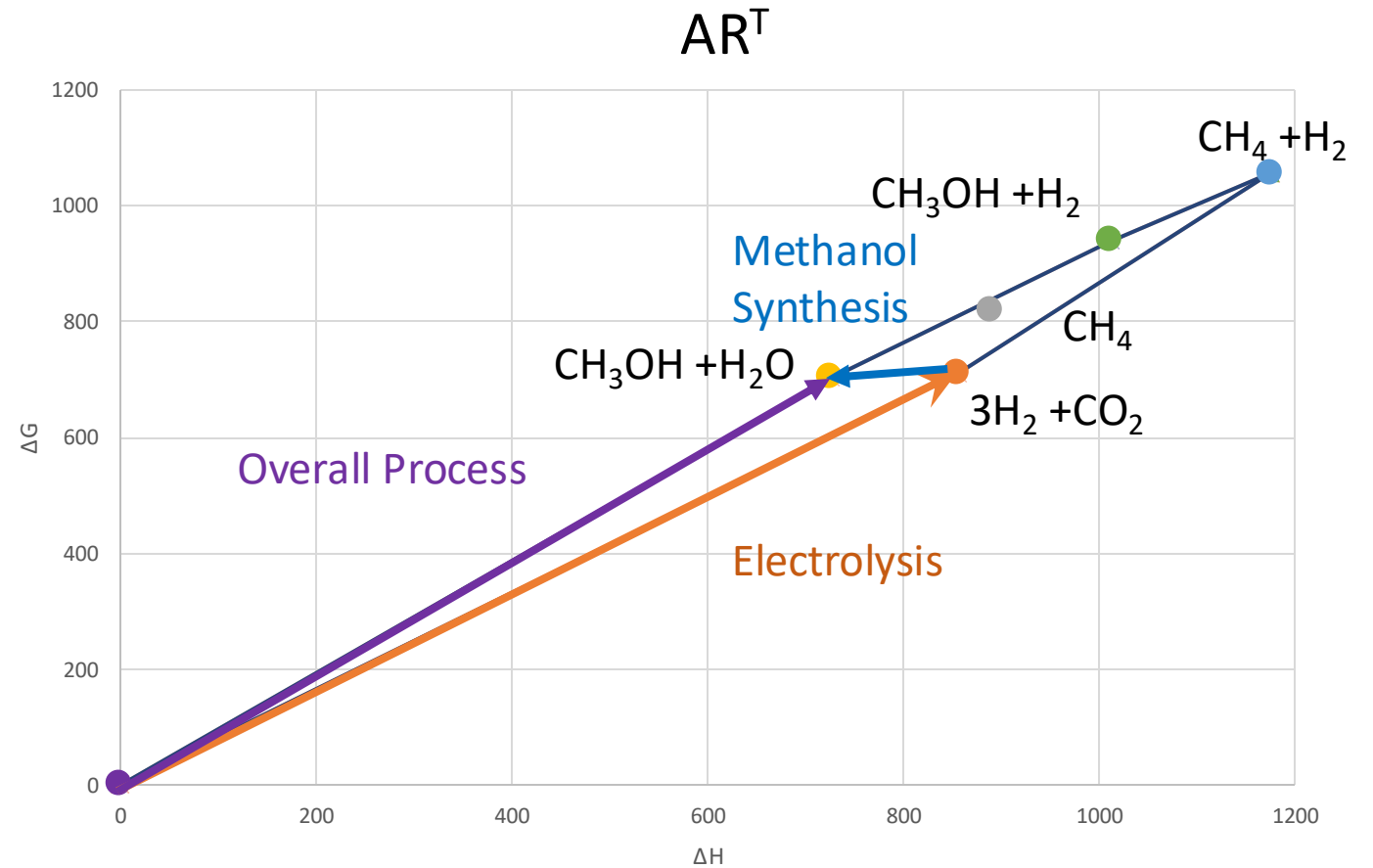
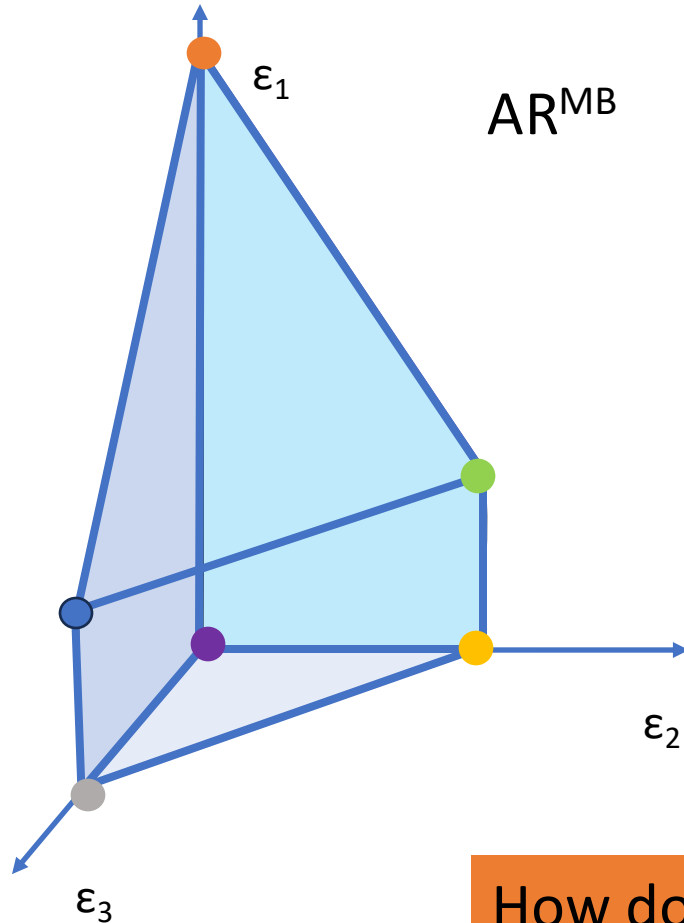
- Feed to process shown in shaded area: $H_2O:CO_2 = 3:1$
- Process 1
 - Require $\epsilon_1 = 3$ giving $3H_2O \rightarrow 3H_2 + 3/2O_2$
- Process 2:
 - Require $\epsilon_1 = -3$ $\epsilon_2 = 1$ giving $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$
- Overall Process
 - Described by $\epsilon_1 = 0$; $\epsilon_2 = 1$; $\epsilon_3 = 0$ giving $CO_2 + 2H_2O \rightarrow CH_3OH + 3/2O_2$

AR^{MB} and AR^T for a feed of: 1 mole CO_2 and 3 moles H_2O



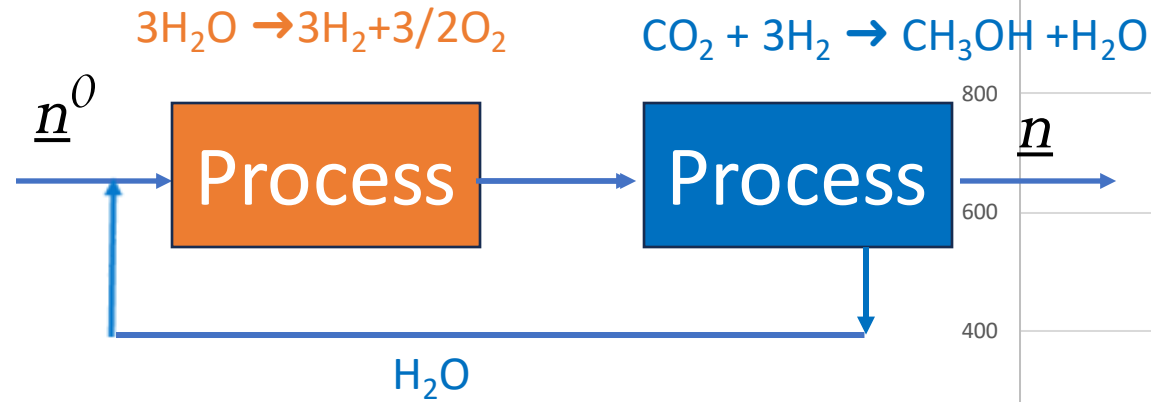
Please note: I will leave O_2 out of labels going forward

Representing the processes as vectors in the GH space

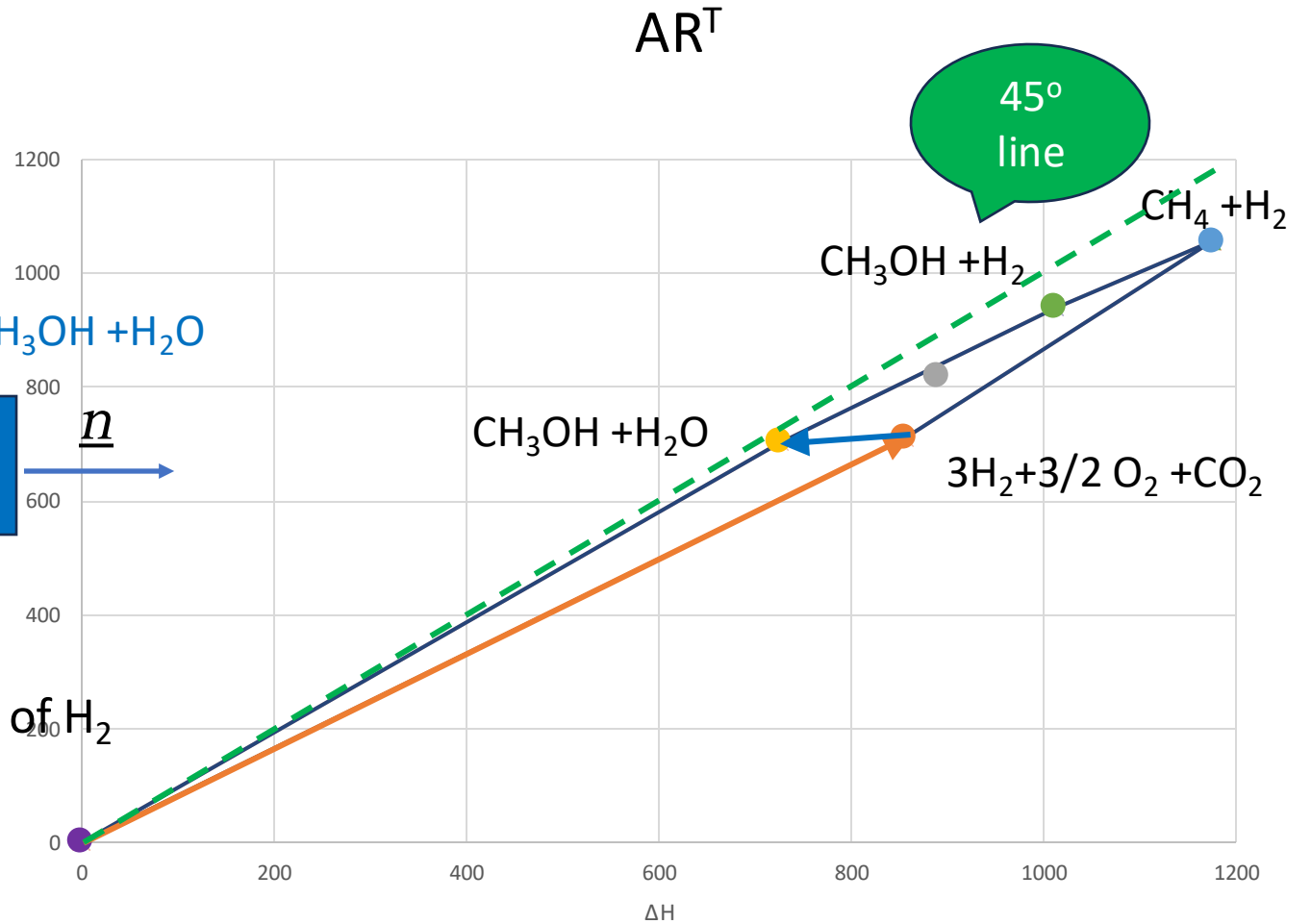


How do we add or reject heat and work in this process?

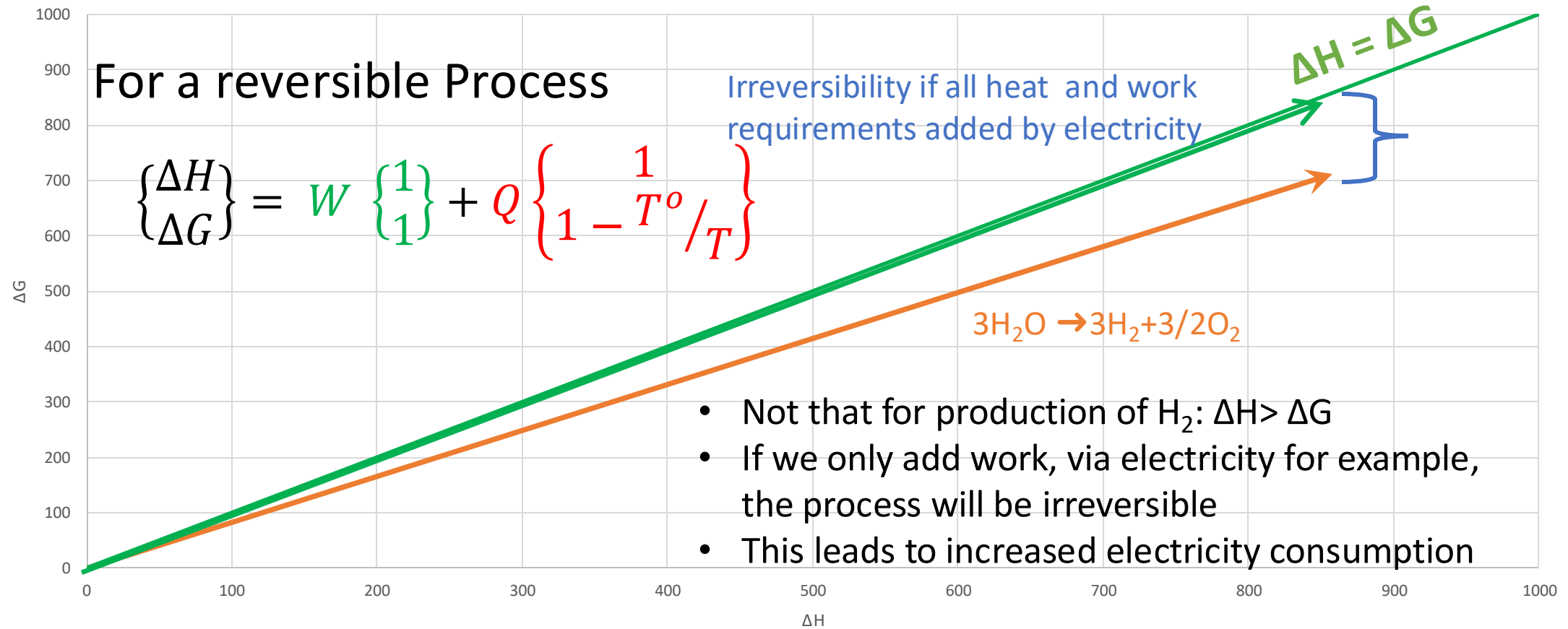
Electrolysis: matching heat and work vectors to the process vector



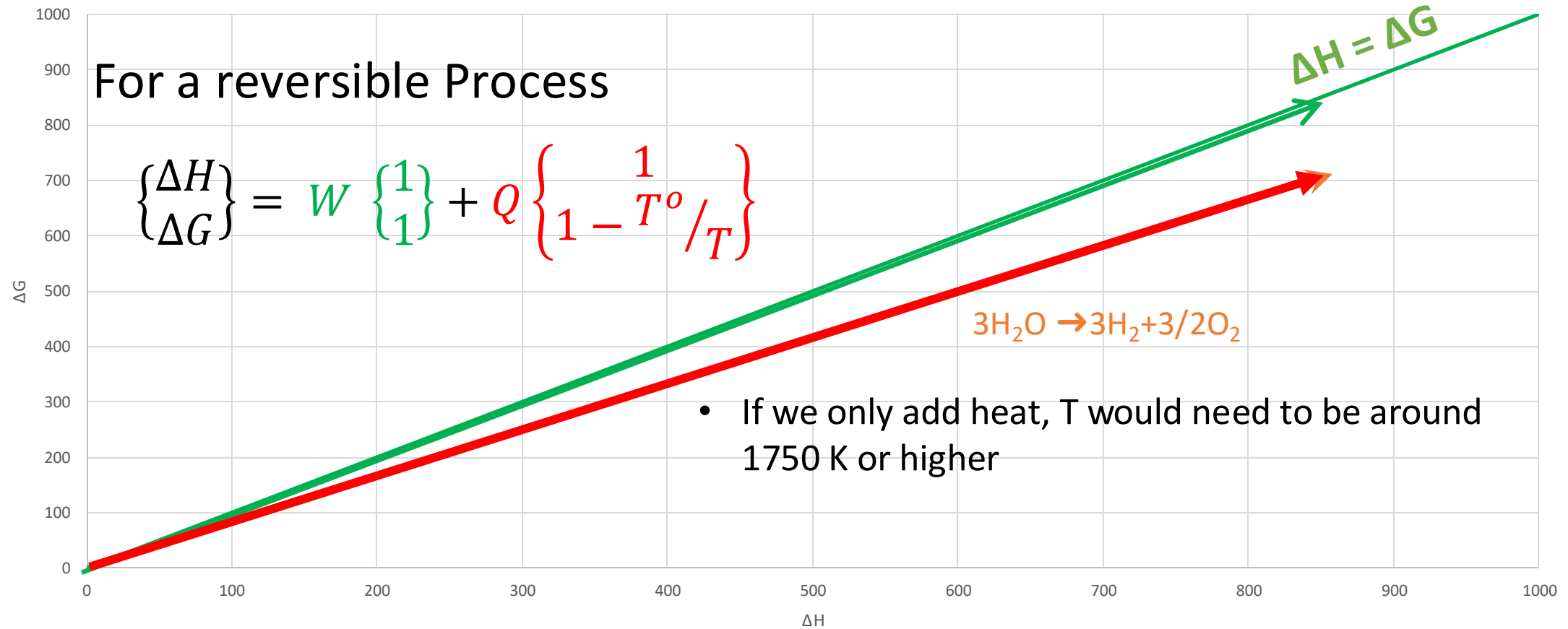
- The orange vector represents the production of H_2
- Both ΔG and $\Delta H > 0$
 - Requires work and heat addition,
 - But $\Delta G < \Delta H$
- Can we add heat and work reversibly?



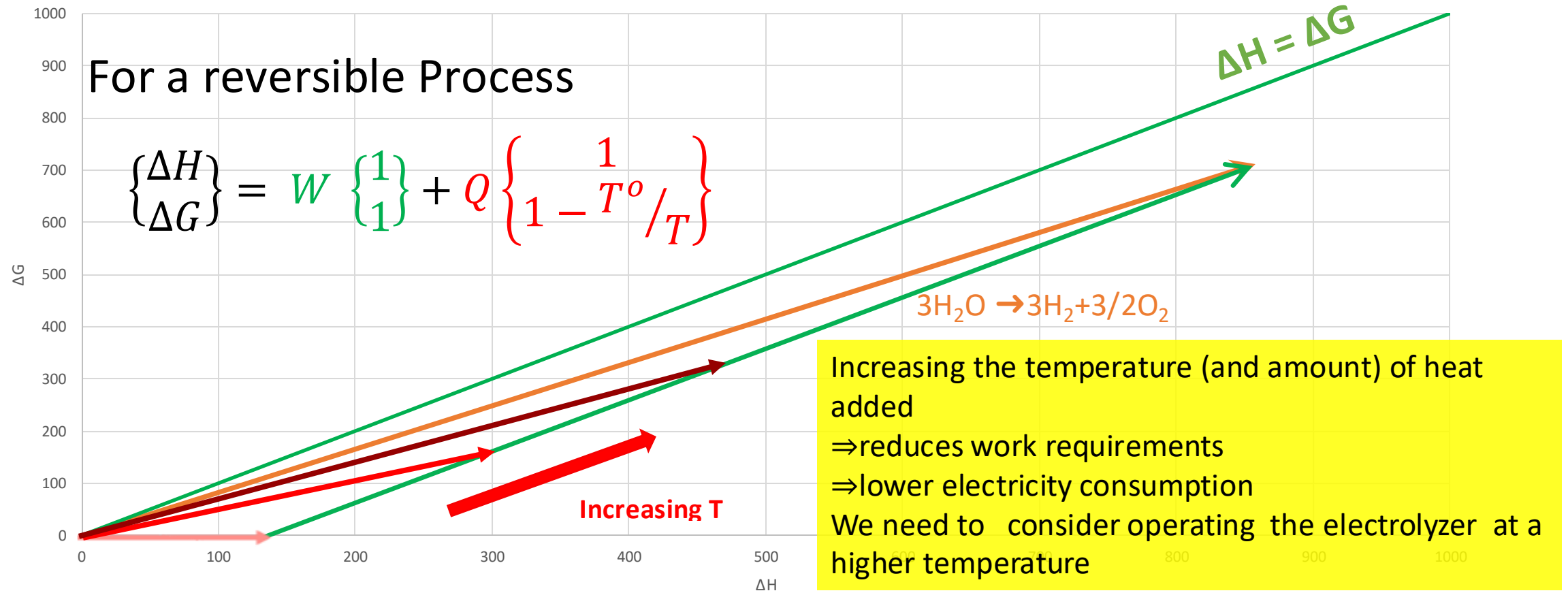
Consider Adding Work only for H₂ Production



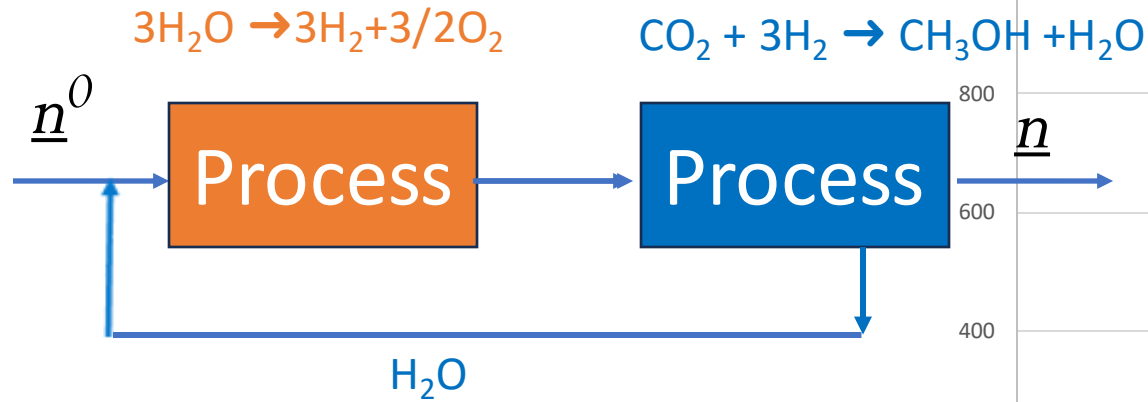
Consider Adding Heat Only for H₂ Production



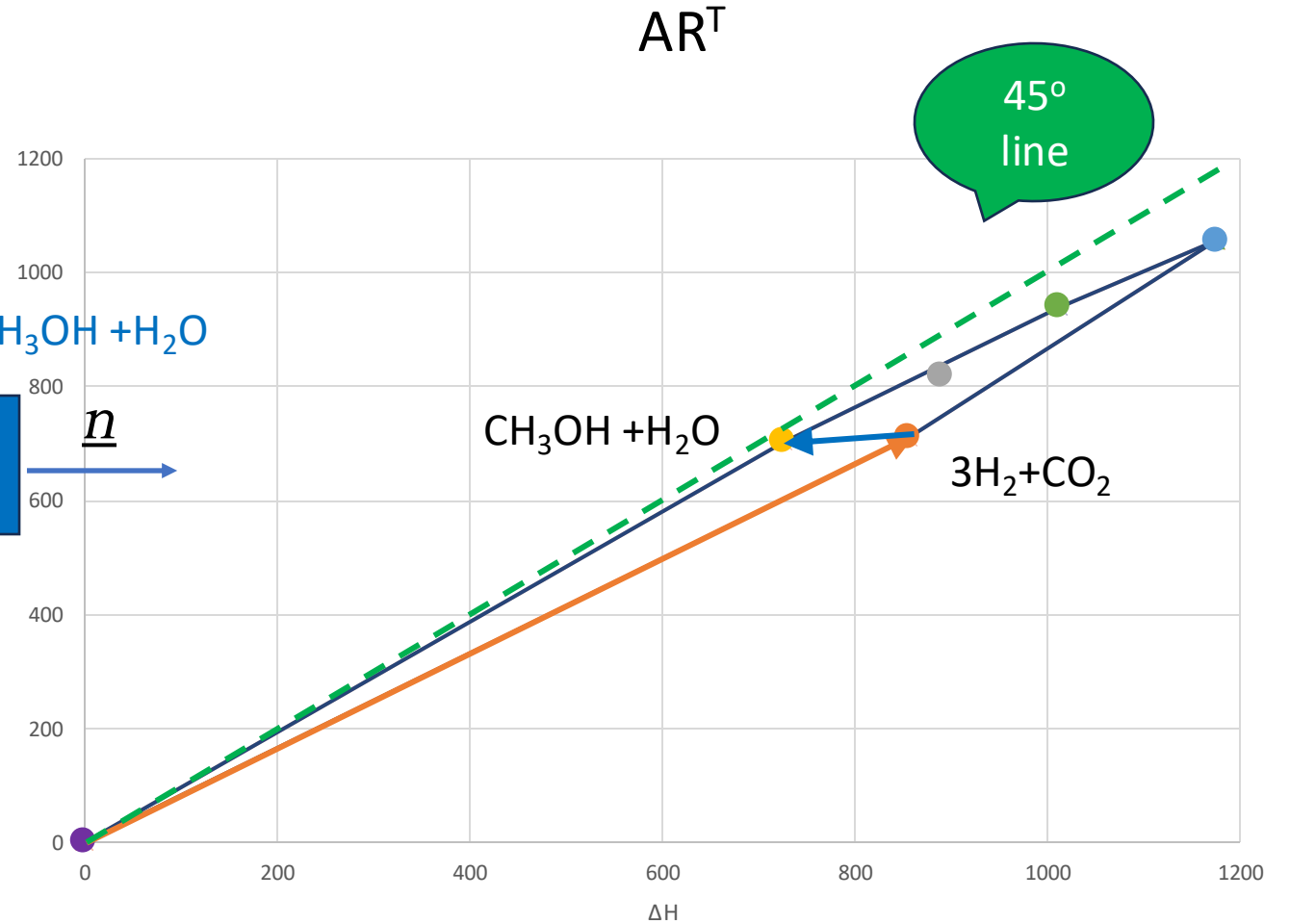
Adding Heat and Work to H₂ Production: Improves Process Reversibility



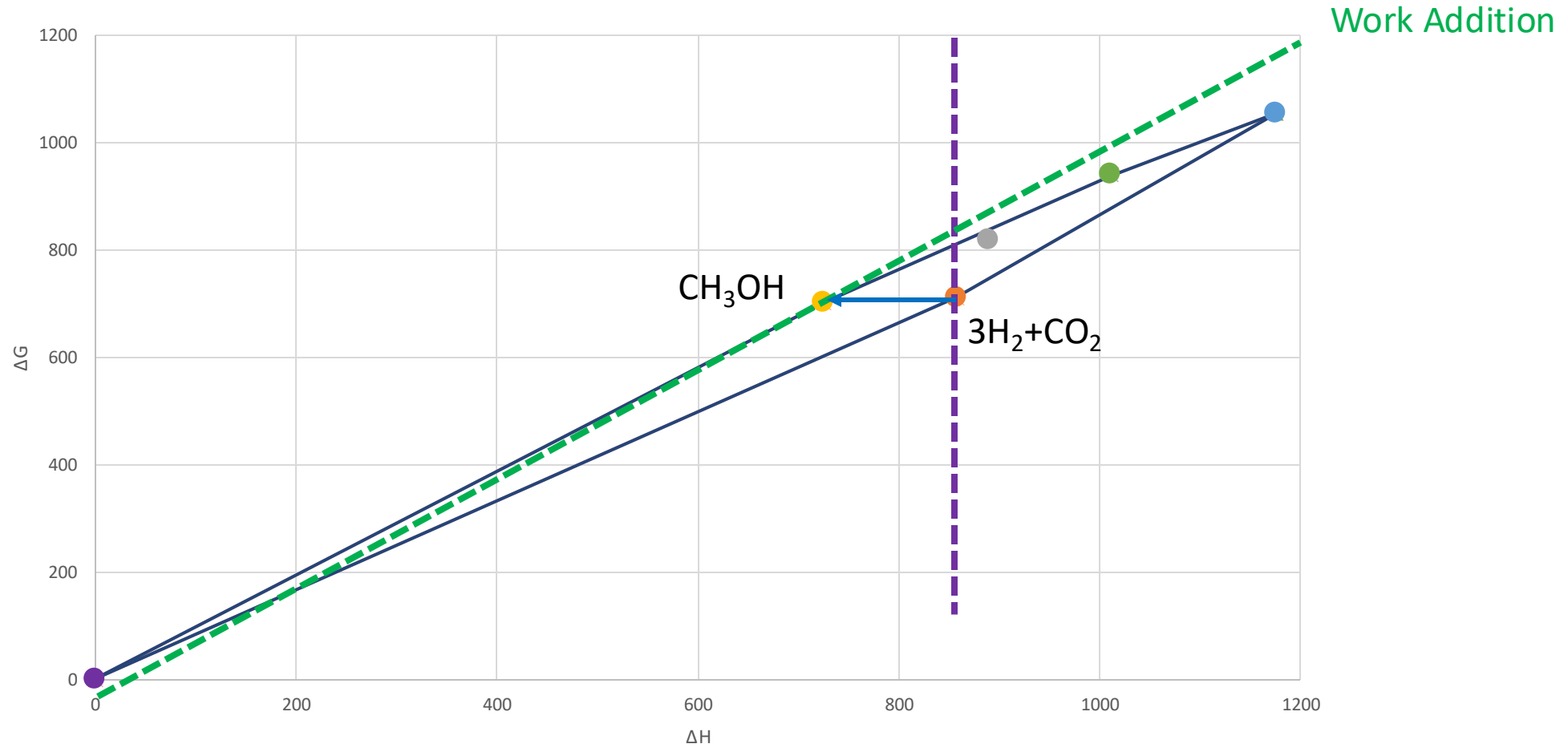
Synthesis: matching heat and work vectors to the process vector



- The blue vector represents the process of converting CO_2 and H_2 to produce methanol
- Note that ΔG is slightly negative
- Process rejects heat and a bit of work

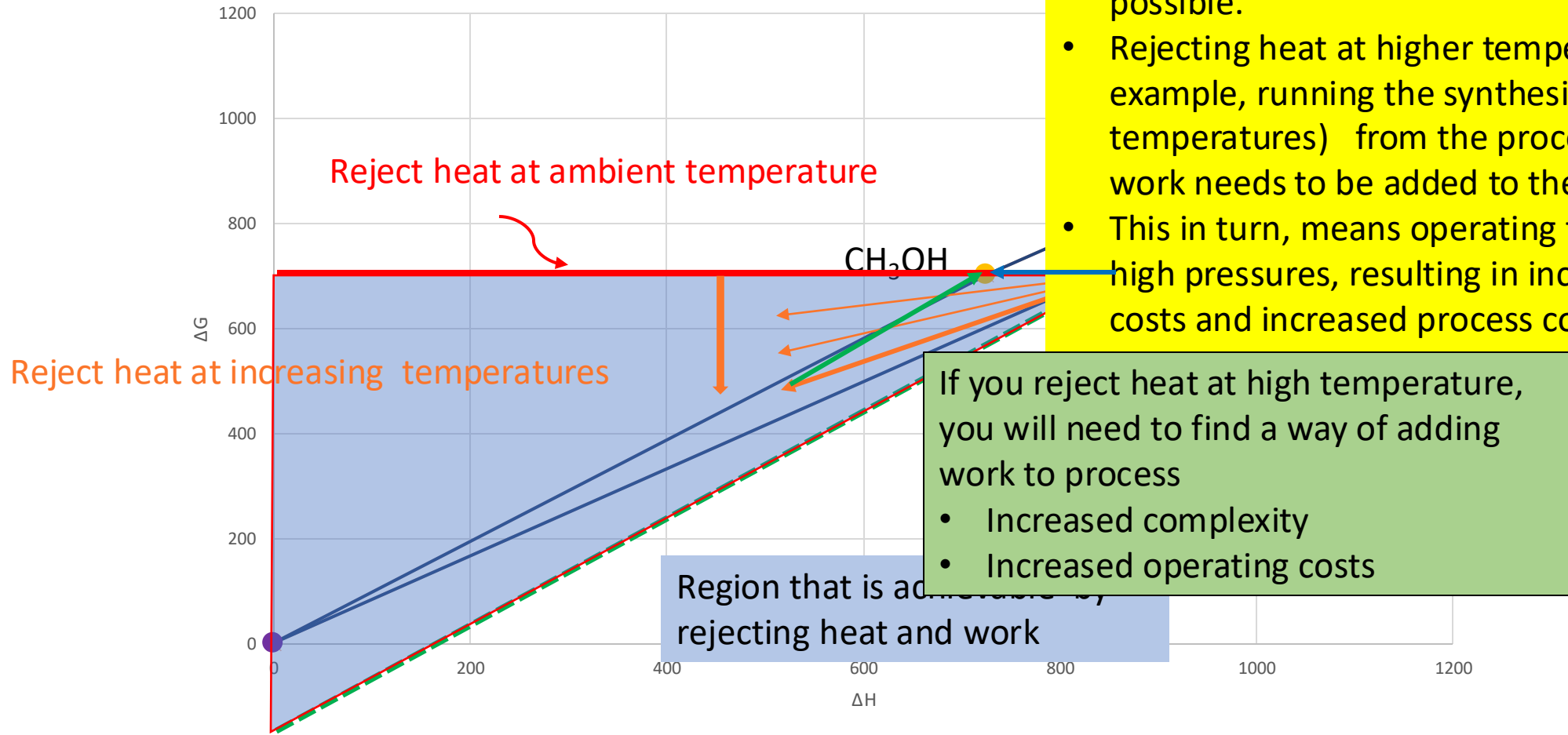


Matching Process Vector with Heat and Work Flows



Impact of rejecting heat at high tem

- Ideally, heat from the process should be rejected at as close to ambient temperature as possible.
- Rejecting heat at higher temperatures (for example, running the synthesis reactor at high temperatures) from the process means that work needs to be added to the process,
- This in turn, means operating the reactors at high pressures, resulting in increased operating costs and increased process complexity



Applications of this approach

- By applying these techniques, we can improve the methane-to-methanol process

	Tons of CH ₄ Consumed/ Ton of Methanol produced	Tons of CO ₂ Emitted/ Ton of Methanol produced
Current Processes	0.53	0.09
New Process*	0.47	-0.11
Target (without incorporating renewable energy)	0.43	-0.19

Putting this into practice

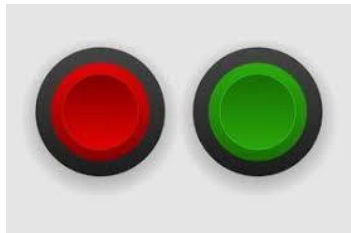
- In 2006 we were asked if we could develop a CTL technology for China
 - China at that time was short of fuel and electricity (similar to SA)
- We started by designing a pilot plant,
 - Tight schedule (18 months), tight budget
- We were responsible:
 - Process Synthesis
 - Project Management
 - Catalyst selection
 - Overseeing commissioning and operation
- Pilot plant using conventional semi-batch coal gasification
 - Located in Shaanxi, China
 - Commissioned in 2008, 5 bpd
- Demonstrated that we could reduce CO₂ emissions compared to conventional technologies and reduce operating and capital costs.



And more recently

How small can we make an XTL process?

- Worked together with ThyssenKrupp SA
 - A feasibility study was done (late 2013) on a 500 bpd GTL plant in TX, US
 - CAPEX in \$/bpd is close to a recent (2012) ~100,000 bpd GTL case in US
- Can we design a 1 ton per day waste to electricity or fuel process?
 - Robust, simple process



Conclusions

- We have introduced a simple graphical representation of processes
- We can use vectors in a simple G-H plot to represent
 - Heat and workflows
 - Process
 - Chemical transformations
- You would like to match the heat and workflow vectors to the process vectors.
 - This implies that the heat and work added to the process is incorporated into the chemical transformations
 - Helps with screen chemistries, catalysts, and equipment choices

Conclusions Continued

- Reversibility sets the target for process performance
 - It allows one to determine the room for improvement in existing technologies
 - It allows one to determine sources of process inefficiencies
 - It allows one to set performance targets for new processes
- As energy costs increase, the balance in design will probably move towards reducing “energy” consumption, perhaps at the expense of increased capital costs.
 - It is, therefore, important during the early stages of process development to try to minimize inefficiencies resulting from choices of process operating conditions.



Acknowledgements

The ideas presented have been developed over many years, with contributions from many different people.

Thanks, in particular, to Celestin Sempuga, James Fox, Ephraim Llana, Ralph Muvhiiwa, David Glasser, Brendon Hausberger, Bilal Patel.

We would like to thank the funders, which include:

Rutgers University

University of the Witwatersrand

University of South Africa

National Research Foundation of SA



Questions?