Feasibility Study of Venus Surface Cooling Using Chemical Reactions with the Atmosphere

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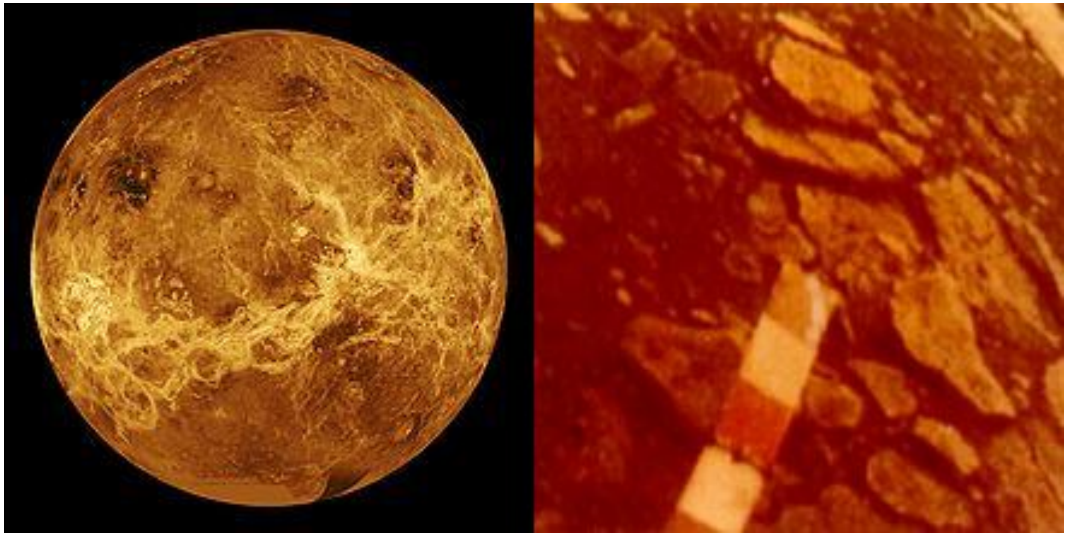
Background: Planet Venus

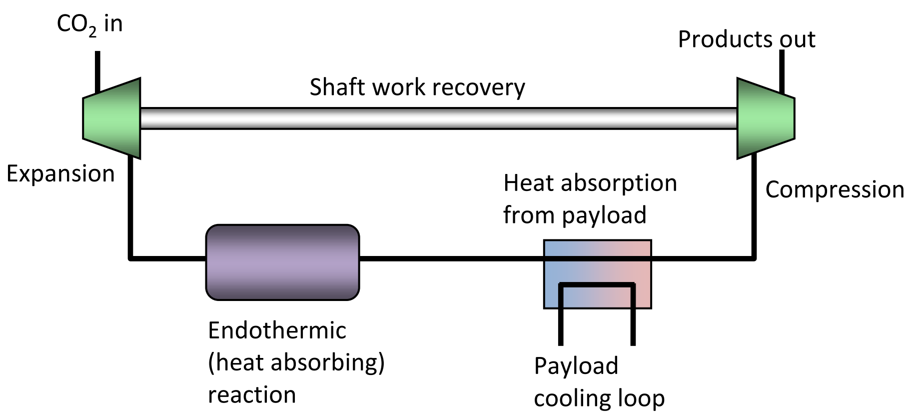


- Extremely harsh environment
  - Surface conditions:
    - P = 93 atm
    - T = 460°C (860°F)
    - Corrosive atmosphere
- High temperature is biggest issue
  - Causes electronics to overheat and fail
  - Previous landers have lasted hours at most
  - For extended missions, need powerful long-term cooling

Background: Heat Pumps

- Only viable method of long-term cooling
- Poor performance at Venus conditions
  - Performance limits determined by temperature difference (Carnot limit)
  - Massive power requirements
- Difficult to develop a system suited to Venus
  - Need materials, seals, working fluids suitable for environment

Is there another way?



Concept

- Chemically reform CO2 from the atmosphere into other compounds, absorbing heat in the process
  - Novel method of providing cooling for a Venus surface mission
  - Venus atmosphere has abundant CO2 – "in-situ" resource utilization
  - Reforming CO2 into simpler compounds is generally endothermic
  - "Reverse combustion"

$$\mathbf{CO2 \rightarrow C + O2}$$
$$\mathbf{CO2 \rightarrow CO + \tfrac{1}{2}O2}$$

- Ideal system would require only energy input (no consumables), and could function as long as ambient CO_2 is available
  - Could be implemented as an enhancement to a conventional heat pump, or as a stand-alone system
- Expands options for cooling system design
- Chemical reformation techniques subject to different performance limits than conventional heat pumps
  - Fuel cells outperform Carnot heat engines
  - Could a chemical cooling system outperform a Carnot heat pump?

Research Questions

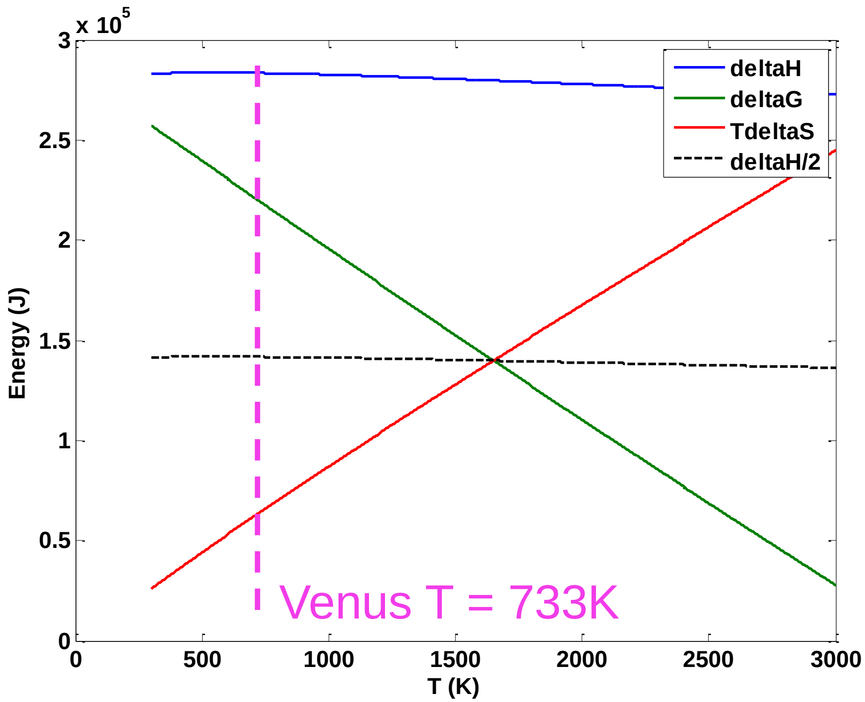
- Is it possible to provide cooling by promoting endothermic reactions of materials from the environment?
- Is this approach practical on Venus using atmospheric CO_2?
  - What techniques could be used to achieve this in practice?
  - How well might such a system perform?
- Could this technique be useful in other environments that we might encounter in the future?

Reformation Options

- Goal is to produce an endothermic CO_2 reaction
- Two viable routes for CO_2 decomposition:
  - Solid carbon route: **$CO_2 \rightarrow C + O_2$**
    - +More endothermic → more cooling ability
    - -Forms solid carbon – difficult to handle
  - Carbon monoxide route: **$CO_2 \rightarrow CO + \frac{1}{2}O_2$**
    - -Less endothermic → less cooling ability
    - +All products are gases – easy to handle
  - Other carbon compounds too unstable
- Easier handling makes “carbon monoxide route” preferable
- Reaction can be done in one step or multiple

Venus Theoretical Limits

- Unconventional application of chemistry
- Governing equation: $\Delta H = \Delta G + T\Delta S$
- For the reaction $CO_2 \rightarrow CO + \frac{1}{2}O_2$:



$$COP = \frac{\text{Heat removed}}{\text{Work input}} = \frac{T\Delta S}{\Delta G}$$

For T = 733K

Chemical cooling COP ≤ 0.29

Heat pump $COP_{Carnot} \approx 0.8 - 1$

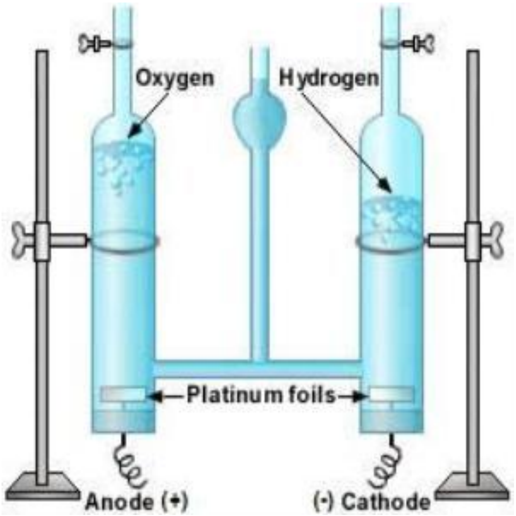
Not a practical method of cooling at Venus conditions.

– Would require higher temperatures or different atmospheric composition

CO_2 Reformation Techniques

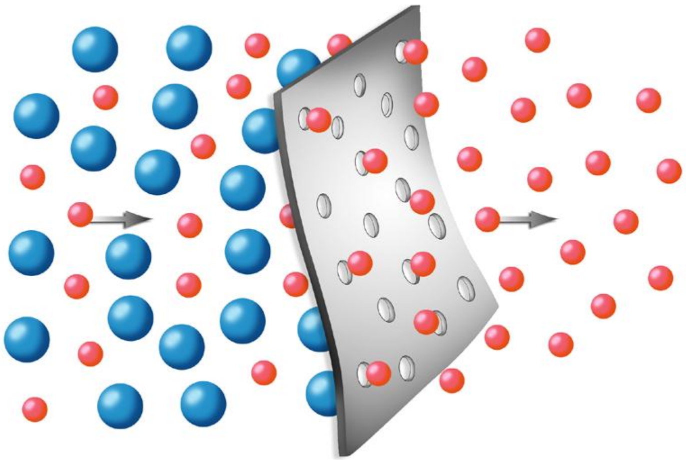
- One step
  - Electrolysis, regenerative fuel cell, radiation, electric discharge, etc.
  - At relevant temperatures, cooling effect outweighed by energy cost
  - Separation of products could improve performance, but need a sink to reject products
- Multi-step
  - Lower theoretical efficiency, but often easier to achieve in practice
  - Ferrites, Bosch reaction, Sabatier reaction, Zn/ZnO cycle, etc.
  - Many more examples

Most Useful Techniques



- Electrochemistry
  - Use electrical energy to “push” a chemical reaction
  - Examples: electrolysis, regenerative fuel cells
  - Simple, reliable systems
    - Can be as simple as a pair of electrodes
    - No moving parts
  - Products easily separated
  - Evolving technology

- Separation of products
  - Selectively removing products disrupts equilibrium, allowing a reaction to proceed past normal limits
  - Allows reaction to be driven with only heat input
  - Work generally required to separate products and expel to environment
    - Most feasible if a property difference exists: density, phase change, magnetism, selective membranes



http://web.ornl.gov/info/ornlreview/v38_1_05/article06.shtml

Alternate Venus Concept: Limited-use System

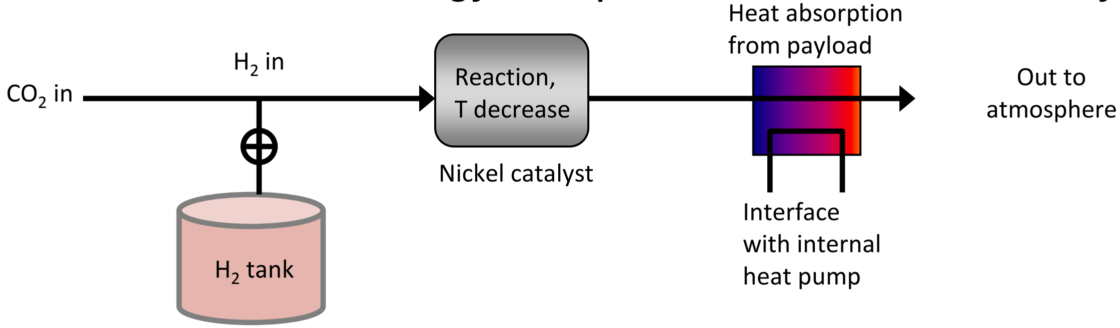
- Original concept would have no consumables and run as long as energy lasted
  - Revised concept: carry a supply of consumable reactants to allow limited-term operation
- Reverse water-gas shift

$$H_2 + CO_2 \rightarrow H_2O + CO$$

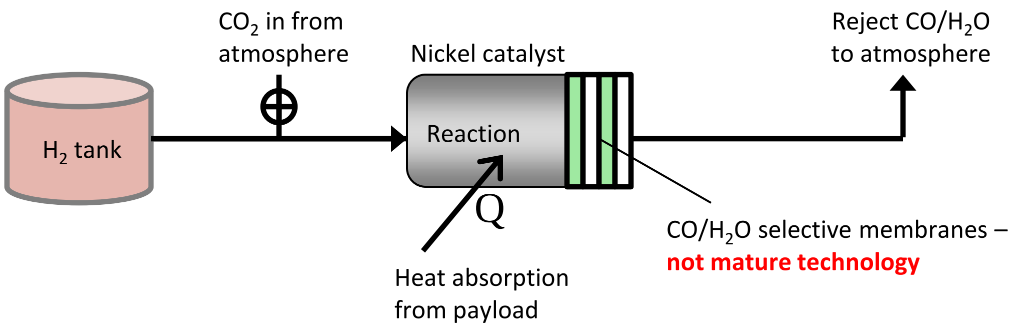
  - Studied by ECLSS for life support
  - Equilibrium does not favor products at low temperatures
    - However, can push the reaction to run by using uneven quantities of H2/CO2
  - Carry hydrogen tank, take CO_2 from Venus atmosphere
- More potent than phase-change material
  - Hydrogen tank used in this context has over 5x the heat rejection capacity of an equivalent mass of water
  - May not trade well on a volume basis

Limited-use System Implementations

- Enhancement to heat pump
  - Use trickle of H2 and excess of CO2
  - Improves performance of a conventional heat pump
  - Feasible with current technology, but performance benefits may be small



- Analogue to phase-change material
  - Use excess of H2 and trickle of CO2
  - Requires membranes that have not yet been developed, may not produce low enough temperatures for electronics



Beyond Venus

- Under what circumstances is cooling via chemical reformation an effective strategy?
  - Particular atmospheric conditions exist
    - Chemical composition, temperature, pressure
    - Needs case-by-case evaluation
  - Products of reaction are valued
  - Design simplicity and robustness are important enough to trade some level of performance
- Another tool for the toolbox
  - Ideal situations for chemical cooling may be rare
  - Provides an alternative to heat pumps in some cases

Conclusions

- It is possible to provide cooling by promoting endothermic reactions of chemicals from an environment.
  - In most cases, performance is likely to be lower than a conventional heat pump.
- On Venus, cooling via chemical reformation is not a practical strategy.
  - Possible, but performance will be lower than a conventional heat pump.
  - An electrochemical system could be simpler than a heat pump, but more development is needed.
- This approach to cooling is most viable when favorable conditions exist, when the products of reaction are valued, or when design simplicity and robustness are valued enough to trade some performance.

Backup Slides

One-step Reformation

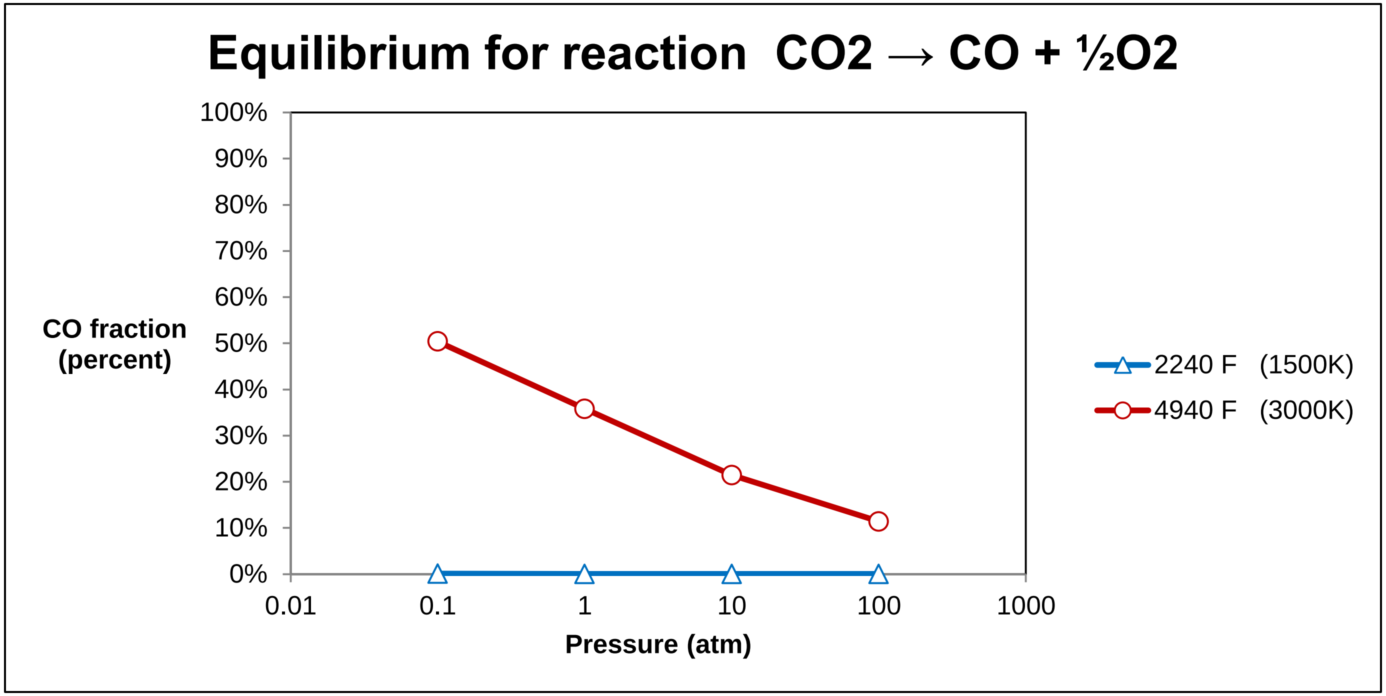
- Goal is to produce one of two reactions:

$$CO_2 \rightarrow C + O_2$$

$$CO_2 \rightarrow CO + \tfrac{1}{2}O_2$$

  - One step process examples: catalytic reaction, electrolysis, electric discharge, etc.
- Does not appear viable for cooling with current technology
  - Performance is temperature-dependent
    - Good cooling ability at high T (~1500C)
    - Poor cooling ability at Venus conditions (460C)
- Separation of products
  - Separation of products allows heat to drive reaction
  - Existing O2 selective membranes require excessively high temperatures
  - CO selective membranes exist, but seem immature
  - Low-temperature, efficient CO & O2 selective membranes needed
  - Atmosphere is at equilibrium already. Must use energy to push products out.

Catalyst Limitations



- Can only bring reaction to equilibrium
- If products can be removed, the reaction will no longer be at equilibrium. Conversion can then continue.
  - Separation of products is the key issue
  - Studies have used membrane separation of O_2 to push reaction past equilibrium

Multi-step Reformation

- Use sequence of reactions
  - Often easier to achieve in practice
  - Lower theoretical efficiency
- Examples
  - Zinc/Zinc oxide cycle

$$Zn + CO_2 \rightarrow ZnO + CO$$

$$ZnO + heat \rightarrow Zn + O_2$$

  - Ferrites
    - 1: iron takes oxygen from CO2
    - 2: H2 used to regenerate iron
- Literature search is ongoing
  - Body of resources greater than expected
  - Access to resources less than expected
  - Will continue search in our own time

Nickel Ferrite Nanocatalysts

- Promising material for “solid carbon route”

$$CO_2 \rightarrow C + O_2$$

- Not a true catalyst, but a regenerable reducing agent
  - Carbon deposits as a solid
  - Oxygen combines with metal (oxidation)
  - Hydrogen treatment regenerates the material
    - Can recover used hydrogen to close loop
- “Low” temperature: 300° C (572° F)
- Carbon buildup eventually disables the material
  - Able to reform large quantities of CO_2 before failure
  - Removal of carbon may be feasible
- Thermodynamics not fully investigated

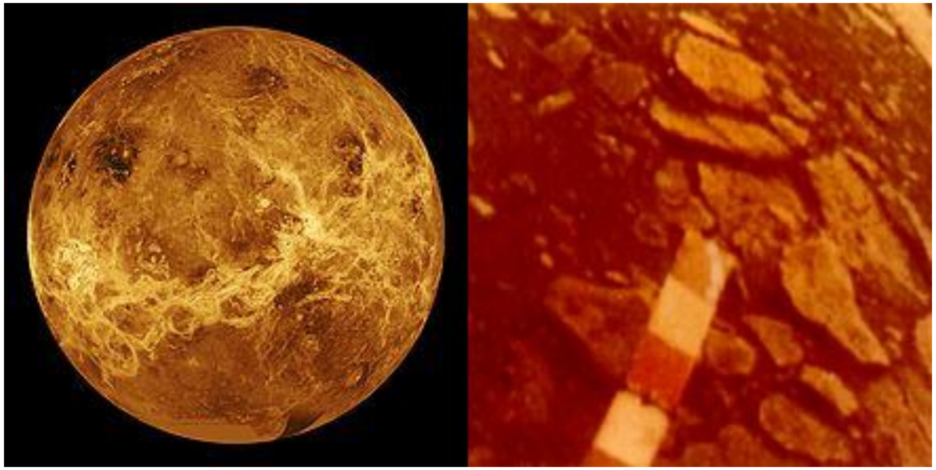
Conclusions

- Research indicates cooling via atmospheric reformation is not viable on Venus
  - Chemical reformation based cooling is outperformed by conventional heat pumps
- In a general sense, cooling via atmospheric reformation is possible, however applicability may be limited
  - Performance depends on atmospheric temperature and composition
  - Need particular circumstances for good performance
- Literature search uncovered several technologies of potential use to ECLSS, Mars ISRU and other applications
  - Ferrites
    - Materials that decompose CO2 at low temperatures, and can be regenerated
  - CO selective adsorbent materials
  - CO selective membranes
  - O2 selective membranes

Venus Surface Cooling System

Project Summary

Principal Investigator: Christopher Evans/EV34
Co-Investigator(s):
Project Category: II
Initial TRL: 1
Final TRL: 2
Project Summary:
This project examined the feasibility of providing cooling for an extended mission to the Venus surface by endothermically reforming CO_2 from the atmosphere into other compounds.



Planet Venus. Left: Magellan radar map.
Right: Venera 13 surface image.

Budget History

FY12:
Labor: 0.2 FTE / $27,471

Milestones and accomplishments

- Performed survey of CO_2 reformation techniques
- Determined theoretical performance limits of a cooling system based on reforming CO_2 from the Venus atmosphere
- Developed concept for a system using consumable reactants with greater cooling capacity than phase-change material
- Identified technologies of use to ECLSS, Mars exploration, and others

Forward Plans and Opportunities

- Continue research into multi-step processes
- Develop conference paper