Chapter 4. Thermochemistry

Summary

- **thermochemistry**: branch of thermodynamics dealing with **energy changes of chemical reactions**
- q, w, ΔU, and ΔH are calculated for chemical reaction processes
- **enthalpies of formation** are introduced
- because enthalpy is a **state function**:
  - enthalpies of formation for a few thousand compounds can be used for thermochemical calculations for millions of different chemical reactions
  - thermochemistry can be investigated without actually carrying out reactions (important for slow or non-spontaneous reactions)

Sections 4.1 to 4.3 Internal Energy and Enthalpy Changes of Chemical Reactions

previous Chapters: **physical processes**, such as heating, cooling, expanding, or compressing a system

What about systems with **chemical reactions**?

Example: $Fe_3O_4(s) + 4\,H_2(g) \xrightarrow{T,\,p} 3\,Fe(s) + 4\,H_2O(l)$

One mole of solid Fe_3O_4 and four moles of H_2 gas converted to three moles of solid iron and four moles of liquid water at a specified temperature and pressure.

All compounds assumed to be pure.

Thermodynamics of Chemical Reactions

At Constant Pressure

$\boxed{298\ \text{K},\ 1\ \text{bar}}$

$$\mathbf{Fe_3O_4(s) + 4\,H_2(g) \longrightarrow 3\,Fe(s) + 4\,H_2O(\mathit{l})}$$

$\boxed{\Delta n_g = -\,4\ \text{mol}}$

The **heat** absorbed by the reacting system can be determined using a calorimeter. Measure $\boxed{q_p = -24{,}800\ \ \text{J}}$

The **work** done (at constant pressure) is $-p\Delta V$. **Details:**

$$w_p = -\int_{V_i}^{V_f} p_{\text{external}}\,\mathrm{d}V = -\,p\int_{V_i}^{V_f}\mathrm{d}V = -\,p(V_f - V_i)$$

$$= -\,p[\,\underset{\text{negligible}}{\cancel{3V_{\text{m}}(\text{Fe,s})}} + \underset{\text{negligible}}{\cancel{4V_{\text{m}}(\text{H}_2\text{O},l)}} - \underset{\text{negligible}}{\cancel{V_{\text{m}}(\text{Fe}_3\text{O}_4,\text{s})}} - 4V_{\text{m}}(\text{H}_2, g)\,]$$

$$= -\,p[\,-4V_{\text{m}}(\text{H}_2, g)\,] = 4pV_{\text{m}}(\text{H}_2, g) = 4RT = -\Delta n_g RT$$

$$= 4\,(8.314\ \ \text{J}\ \ \text{K}^{-1}\ \text{mol}^{-1})\,(298\ \text{K}) = \boxed{9910\ \text{J mol}^{-1} = w_p}$$

$$\mathbf{Fe_3O_4(s) + 4\,H_2(g) \xrightarrow{\boxed{298\text{ K, 1 bar}}} 3\,Fe(s) + 4\,H_2O(\mathit{l})}$$ **(*cont.*)**

$$\Delta H = \Delta(U + pV) = \Delta U + p\Delta V \qquad \text{(constant pressure)}$$

$$= q_p + w_p + p\Delta V = q_p - p\Delta V + p\Delta V$$

$$\boxed{\Delta H = q_p = -24{,}800\ \text{J}}$$

$$\Delta U = q_p + w_p = -24{,}800\ \text{J} + 9{,}910\ \text{J}\ \boxed{= -14{,}890\ \text{J}}$$

chemical reactions
at <u>constant pressure</u>:

$$\Delta H = q_p$$

$$w_p = -p\Delta V = -RT\Delta n_g$$

$$\Delta U = \Delta H - RT\Delta n_g$$

Chemical Reactions at Constant Volume

"Bomb" Calorimeter

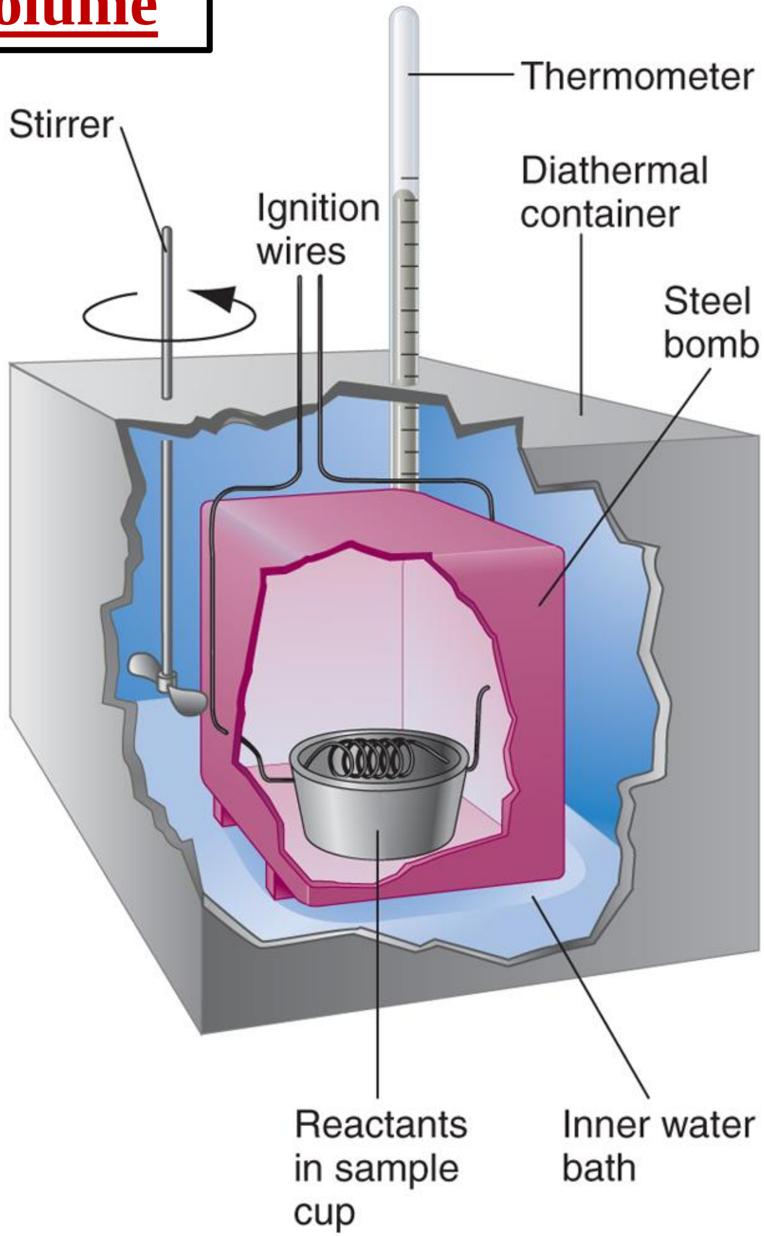
In a strong steel container **at constant volume:**

$$w_V = 0$$

$$\Delta U = q_V$$

$$\Delta H = \Delta(U + pV) = q_V + RT\Delta n_g$$

$q_V = C\Delta T$ is calculated from the measured temperature change ΔT and the calorimeter heat capacity C determined by calibration.



Thermochemical "Algebra"

Reaction: $\mathbf{Fe_3O_4(s) + 4\,H_2(g) \rightarrow 3\,Fe(s) + 4\,H_2O(\mathit{l})}$

$$\begin{aligned}\Delta H &= H_f - H_i \\ &= H(\text{products}) - H(\text{reactants}) \\ &= 3H_\text{m}(\text{Fe, s}) + 4H_\text{m}(\text{H}_2\text{O}, l) - H_\text{m}(\text{Fe}_3\text{O}_4\text{, s}) - 4H_\text{m}(\text{H}_2\text{, g})\end{aligned}$$

concise notation: $$\boxed{\Delta H = \sum_i \nu_i H_\text{m}(i)}$$

ν_i = **stoichiometry coefficient** of compound *i*

(positive for products, negative for reactants)

Example:

$\nu_{\mathbf{Fe3O4,s}} = -1$ (reactant)

$\nu_{\mathbf{H2,g}} = -4$ (reactant)

$\nu_{\mathbf{Fe,s}} = 3$ (product)

$\nu_{\mathbf{H2O,}l} = 4$ (product)

Thermochemical "Algebra"

similarly**:**

$$\boxed{\Delta U = \sum_i v_i U_\mathrm{m}(i)}$$

$$\boxed{\Delta V = \sum_i v_i V_\mathrm{m}(i)}$$

$$\boxed{\Delta C_p = \sum_i v_i C_{p\mathrm{m}}(i)}$$

subscript m refers to molar quantities

Reactions as Standard Pressure **(p^{o} = 1 bar)**

$$\boxed{\Delta H^{\mathrm{o}} = \sum_i v_i H^{\mathrm{o}}_{\mathrm{m}}(i)}$$

$$\boxed{\Delta U^{\mathrm{o}} = \sum_i v_i U^{\mathrm{o}}_{\mathrm{m}}(i)}$$

$$\boxed{\Delta V^{\mathrm{o}} = \sum_i v_i V^{\mathrm{o}}_{\mathrm{m}}(i)}$$

$$\boxed{\Delta C^{\mathrm{o}}_p = \sum_i v_i C^{\mathrm{o}}_{p\mathrm{m}}(i)}$$

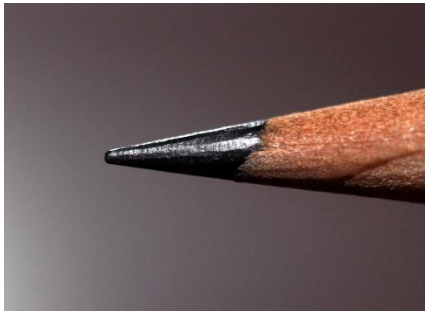
“standard” quantities denoted by superscript $^{\mathrm{o}}$

Enthalpy is a State Function

Important Consequence: ΔH for chemical reactions can be calculated ***without carrying out reactions!***

Example. Calculate ΔH for the reaction

$$\text{C(graphite)} \xrightarrow{25\ ^{o}\text{C, 1 bar}} \text{C(diamond)}$$



Big Problem**:** The reaction is immeasurably **slow**.

(in fact, ***nonspontaneous*** at 25 ^{o}C, 1 bar)

C(graphite) → C(diamond) at 25 °C and 1 bar ***(cont.)***

Direct thermochemical measurement of Δ*H* impossible.

No problem. Enthalpy is a state function.

Δ*H* can be measured for **any path** connecting graphite and diamond.

A convenient two-step indirect path is:

$$\mathrm{C(graphite)} + \mathrm{O_2(g)} \xrightarrow{\boxed{\textbf{Step 1}}} \mathrm{CO_2(g)} \xrightarrow{\boxed{\textbf{Step 2}}} \mathrm{C(diamond)} + \mathrm{O_2(g)}$$

Why convenient? Δ*H* for Step 1 and Step 2 are easily measured:

$\Delta H_{\text{step 1}}$ = heat of combustion of graphite = –393.50 kJ

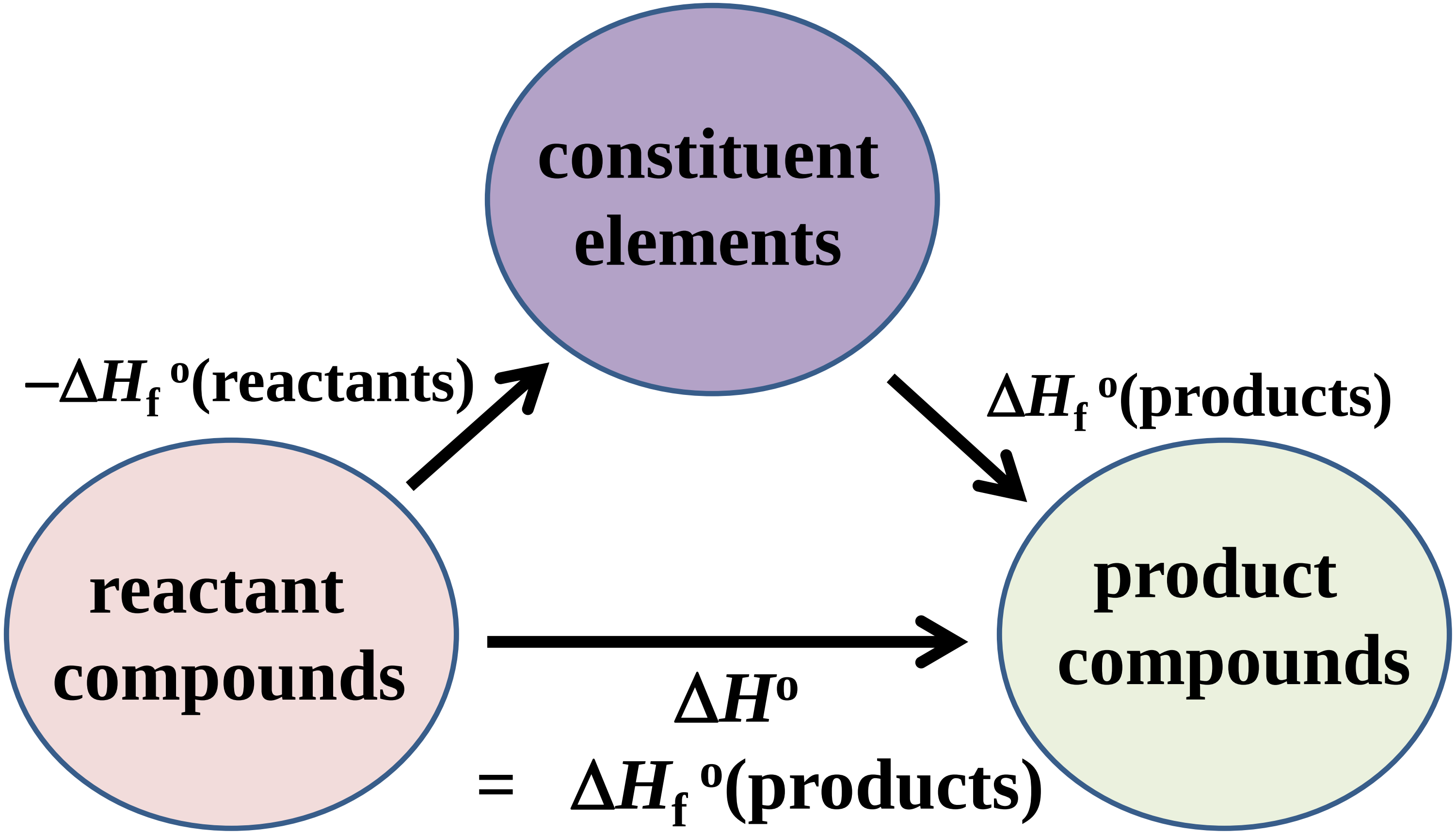
$\Delta H_{\text{step 2}}$ = – (heat of combustion of diamond) = 395.39 kJ

Δ*H*(graphite → diamond) = –393.50 + 395.39 = 1.89 kJ

Because enthalpy is a state function, another useful result:

Standard Enthalpies of Formation

ΔH for any chemical reaction is the enthalpy change for the formation of the products from the elements less the enthalpy change for the formation of the reactants from the elements



constituent elements

$-\Delta H_f^o$(reactants)

ΔH_f^o(products)

reactant compounds

product compounds

$$\Delta H^o = \Delta H_f^o(\text{products}) - \Delta H_f^o(\text{reactants})$$

Example: standard enthalpy of formation of methane at 25 $^{\mathrm{o}}$C

$$\mathbf{C(s,\ graphite) + 2\ H_2(g) \rightarrow CH_4(g)} \qquad \Delta H_f^{\mathrm{o}} = -74.81\ \mathrm{kJ\ mol^{-1}}$$

(use graphite, the most stable form of carbon at 25 $^{\mathrm{o}}$C, 1 bar)

Example: calculate ΔH^{o} at 25 $^{\mathrm{o}}$C for the reaction

$$\mathbf{CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(\mathit{l})}$$

$$\Delta H = \Delta H_f^{\mathrm{o}}(\mathrm{products}) - \Delta H_f^{\mathrm{o}}(\mathrm{reactants})$$

$$= \Delta H_{\mathrm{fm}}^{\mathrm{o}}(\mathrm{CO_2, g}) + 2\ \Delta H_{\mathrm{fm}}^{\mathrm{o}}(\mathrm{H_2O}, l) - \Delta H_{\mathrm{fm}}^{\mathrm{o}}(\mathrm{CH_4, g}) - 2\ \Delta H_{\mathrm{fm}}^{\mathrm{o}}(\mathrm{O_2, g})$$

$$= -393.5\ \mathrm{kJ\ mol^{-1}} + 2(-285.8\ \mathrm{kJ\ mol^{-1}}) - (-74.81\ \mathrm{kJ\ mol^{-1}}) - 2(0)$$

$$= -890.3\ \mathrm{kJ\ mol^{-1}}$$

Sections 4.4   Temperature Dependence of ΔH^{o}

Another useful result of enthalpy being a state function:

If ΔH^{o} for a reaction is known at a given temperature (*e.g.*, 25 $^{\mathrm{o}}$C), ΔH^{o} can be calculated at other temperatures.

$$\begin{tikzcd}
\text{Reactants at } T_2 \arrow[r, "\Delta H^{\mathrm{o}}(T_2)"] \arrow[d, "\int_{T_2}^{T_1} C_p^{\mathrm{o}}(\text{react.})\mathrm{d}T"'] & \text{Products at } T_2 \\
\text{Reactants at } T_1 \arrow[r, "\Delta H^{\mathrm{o}}(T_1)"] & \text{Products at } T_1 \arrow[u, "\int_{T_1}^{T_2} C_p^{\mathrm{o}}(\text{prod.})\mathrm{d}T"']
\end{tikzcd}$$

Temperature Dependence of ΔH^o

$$\begin{aligned}\Delta H^o(T_2) \;=\; & \Delta H^o \text{ (cool reactants from } T_2 \text{ to } T_1) \\ & + \Delta H^o(T_1) \text{ (carry out the reaction at } T_1) \\ & + \Delta H^o \text{ (heat products from } T_1 \text{ back to } T_2)\end{aligned}$$

Heating or cooling at constant pressure ($p = p^o$): $\mathrm{d}H = C_p \mathrm{d}T$

$$\Delta H^o(T_2) = \int_{T_2}^{T_1} C_p^o(\text{reactants})\mathrm{d}T + \Delta H^o(T_1) + \int_{T_1}^{T_2} C_p^o(\text{products})\mathrm{d}T$$

$$\Delta H(T_2) = \Delta H^o(T_1) + \int_{T_1}^{T_2} [C_p^o(\text{products}) - C_p^o(\text{reactants})]\mathrm{d}T$$

$$\boxed{\Delta H^o(T_2) = \Delta H^o(T_1) + \int_{T_1}^{T_2} \Delta C_p^o \mathrm{d}T}$$

$$\boxed{\Delta C_p^o = \sum_i \nu_i C_{pm}^o(i)}$$

Temperature Dependence of ΔH^{o}

$$\boxed{\Delta H^{o}(T_2) = \Delta H^{o}(T_1) + \int_{T_1}^{T_2} \Delta C_p^{o} \mathrm{d}T}$$

So what?

Significance: If heat capacity data are available, ΔH^{o} for chemical reactions measured by calorimetry *at a single temperature* can be used to calculate ΔH^{o} *over a range of temperatures*, in some cases up to extremely high temperatures where calorimetry is difficult.

In practice, heat capacity measurements are easier than reaction ΔH measurements. Also, heat capacities can be calculated using molecular energy levels predicted by quantum mechanics (Chem 332).

Pressure Dependence of ΔH

ΔH^{o} data for reactions at standard pressure (p^{o} = 1 bar) are widely available. What about ΔH for reactions at other pressures?

$\Delta H(T, p)$ = ΔH (de-pressurize reactants from p to p^{o})

+ $\Delta H^{o}(T, p^{o})$ (carry out the reaction at p^{o})

+ ΔH (pressurize products from p^{o} back to p)

$$\Delta H(T,p) = \int_{p}^{p^{o}} \left(\frac{\partial H}{\partial p}\right)_T (\text{reactants})\mathrm{d}p + \Delta H^{o}(T,p^{o}) + \int_{p^{o}}^{p} \left(\frac{\partial H}{\partial p}\right)_T (\text{products})\mathrm{d}p$$

for pressure changes at constant temperature: $\mathrm{d}H = V\mathrm{d}p$

$$\boxed{\Delta H(T,p) = \Delta H^{o}(T,p^{o}) + \int_{p^{o}}^{p} \Delta V\mathrm{d}p}$$

$$\boxed{\Delta V = \sum_i v_i V_{\mathrm{m}}(i)}$$

Isothermal Reactions

Example:

$$\mathrm{CH_4(g) \; + \; 2\,O_2(g) \;\xrightarrow{25\ ^{o}C}\; CO_2(g) \; + \; 2\,H_2O(}l\mathrm{)}$$

But how can the <u>combustion</u> of methane occur at 25 ºC?

$$q_p = \Delta H = = \; -890.3\ \mathrm{kJ\ mol^{-1}}$$

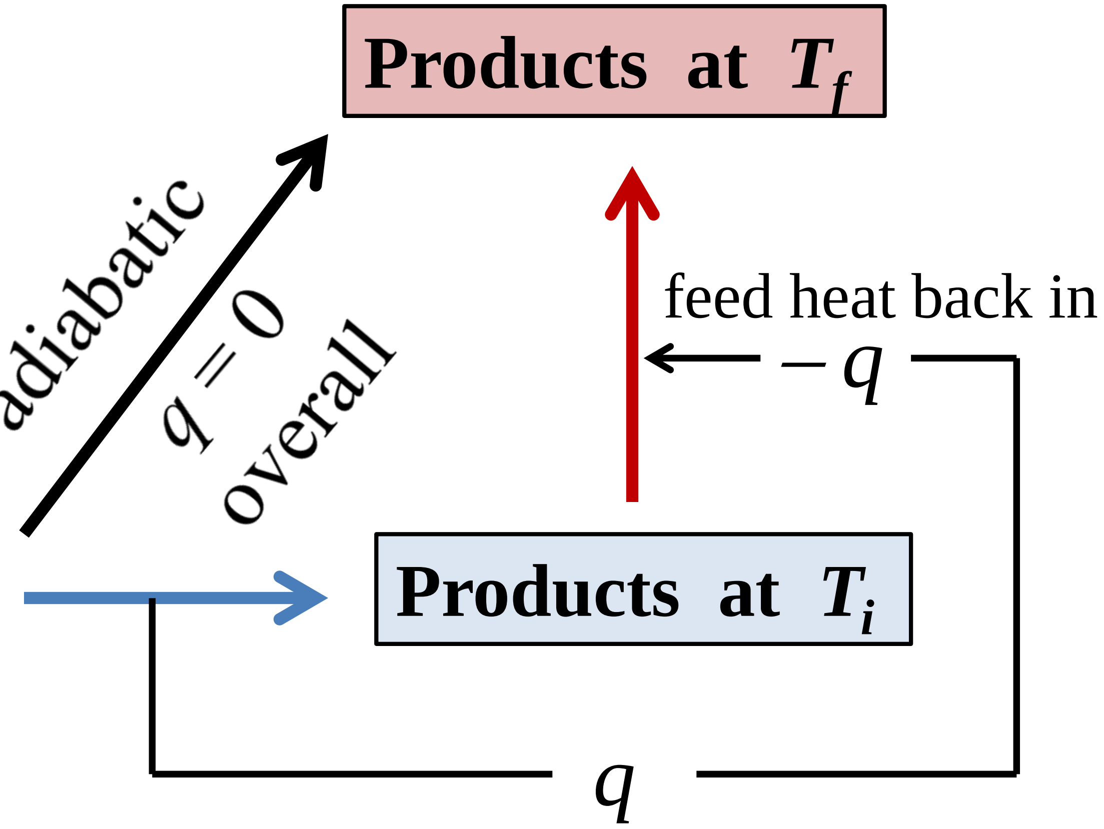
Heat is lost to the surroundings (exothermic reaction).

Warning! Many chemical reactions are <u>not isothermal</u>:

- rapid reactions (no time for heat transfer)
- systems thermally insulated from the surroundings

Adiabatic Flame Temperature

For the reaction products to reach maximum temperature, no heat is allowed to escape (adiabatic reaction).



Products at T_f

adiabatic

$q = 0$

overall

feed heat back in

$-q$

Reactants at T_i

Products at T_i

q

Adiabatic Flame Temperature

Step 1
react

Step 2
heat

Reactants at T_i → **Products at T_i** → **Products at T_f**

$$q_1 = \Delta H(T_i) \qquad q_2 = -\Delta H(T_i)$$

$$-\Delta H^{\text{o}}(T_1) \;=\; \int_{T_i}^{T_f} C_p^{\text{o}}(\text{products})\,\mathrm{d}T \;\approx\; C_p^{\text{o}}(\text{products})(T_f - T_i)$$

assuming constant C_p^{o}(products)

$$\boxed{T_f \approx T_i - \frac{\Delta H^{\text{o}}(T_i)}{C_p^{\text{o}}(\text{products})}}$$

hottest flames:

- large negative $\Delta H(T_i)$ (exothermic)
- small C_p(products) (*e.g.*, diatomics)
- large T_i (pre-heat reactants)

Adiabatic Flame Temperature of Cyanogen (N≡C–C≡N)

$$\boxed{C_2N_2(g) \;+\; O_2(g) \;\rightarrow\; 2\,CO(g) \;+\; N_2(g)}$$

Data at T_i = 298 K: $\Delta H^o(298\text{ K}) = -1096\text{ kJ mol}^{-1}$

CO and N_2 heat capacities (assume no vibration):

$$C_{pm} = C_{Vm} + R = C_{Vm}(\text{trans.}) + C_{Vm}(\text{rot.}) + R$$
$$= (3/2)R + R + R = (7/2)R$$

Note:
Constant $C_p{}^o$(products) assumed. Not an accurate approximation for large ΔT (≈ 13,000 K)

$$T_f \approx T_i - \frac{\Delta H^o(T_i)}{C_p^o(\text{products})}$$

$$T_f \approx 298\text{ K} - \frac{1{,}096\text{ kJ mol}^{-1}}{3\text{ mol} \times \frac{7}{2} \times 8.314\text{ J K}^{-1}\text{mol}^{-1}}$$

$$\boxed{T_f \approx 298\text{ K} + 12{,}600\text{ K} = \mathbf{12{,}900\text{ K}} \qquad \textit{HHHOT !!!}}$$

Adiabatic Flame Temperatures

Molecules start vibrating when they get hot, increasing C_{pm}

For accurate flame temperature calculations, include vibrational heat capacities:

C_2N_2	in O_2	4800 K
C_4N_2 *	in O_2	5260 K**
H_2	in O_2	3470 K***
H_2	in air	2480 K***
C_2H_2 (acetylene)	in O_2	3750 K
C_2H_2 (acetylene)	in air	2770 K
CH_4	in air	2220 K
C_3H_8 (propane)	in air	2250 K

*** Why are flame temperatures lower for burning fuel in air instead of oxygen?

* dicyanoacetylene (N≡C–C≡C–C≡C)

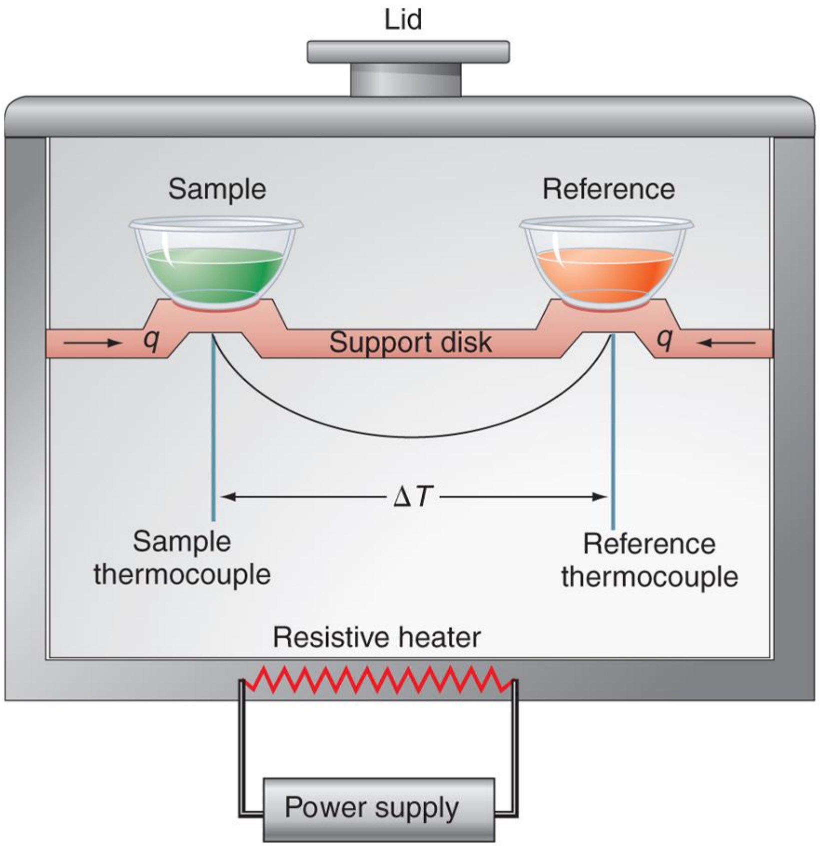
** almost as hot as the surface of the sun (5600 K)

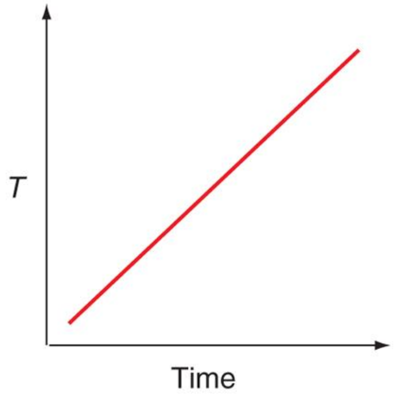
Section 4.6 Differential Scanning Calorimetry (DSC)

- practical form of calorimetry
- important technique for characterizing materials
- relatively inexpensive
- measurements are rapid and convenient
- DSC units commercially available

How does Differential Scanning Calorimetry Work?

- a small sample (< 1 g) and an inert reference material* are heated at a steady rate in an insulated enclosure
- a sensitive thermocouple thermometer monitors the temperature difference ΔT between the sample and reference



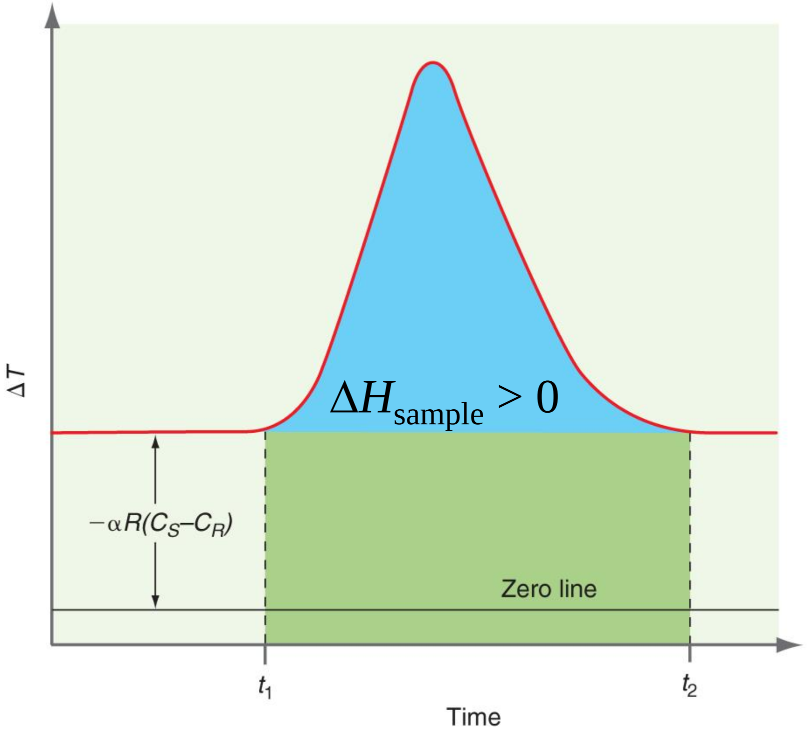


*such as solid alumina (Al_2O_3)

How does Differential Scanning Calorimetry Work?

- The difference in the heat capacities of the sample and reference generates a steady temperature difference $\Delta T = T_{\text{sample}} - T_{\text{reference}}$
- an exothermic sample reaction (warming the sample) produces a positive peak
- an endothermic sample reaction (cooling the sample) produces a negative peak
- the peak area is proportional to ΔH

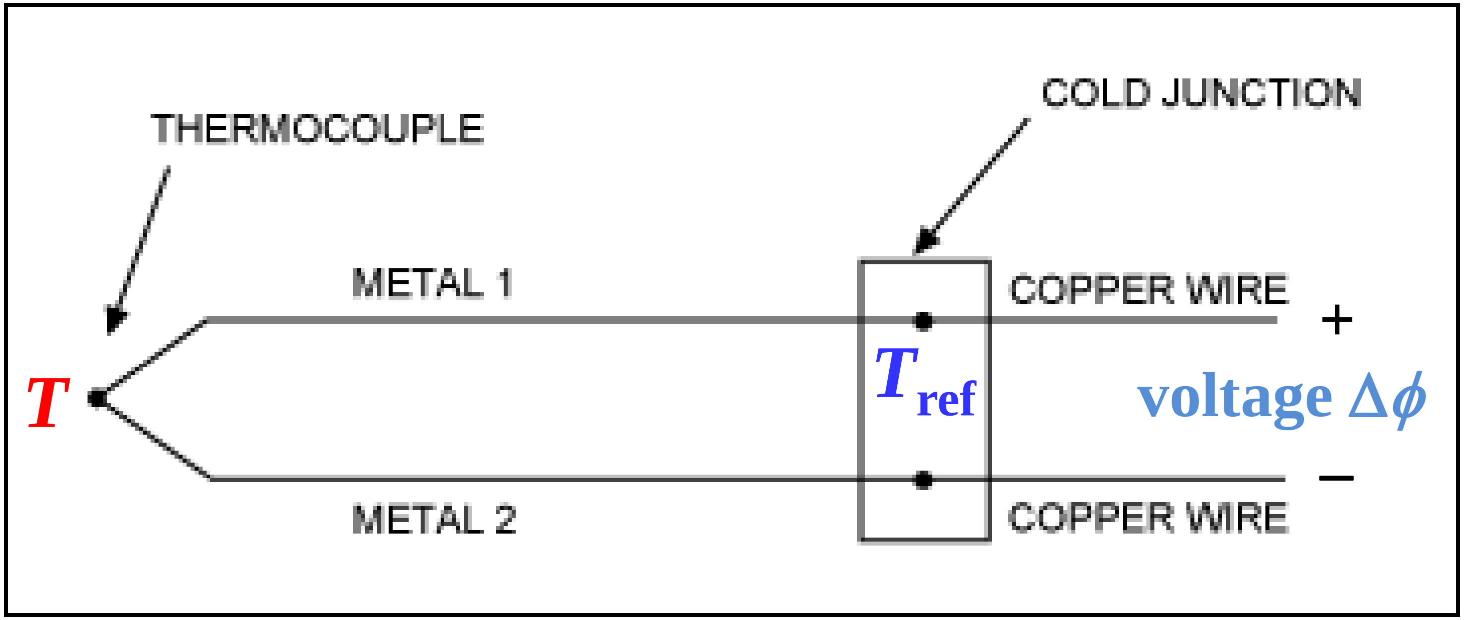
Exothermic DSC Peak



What's a "Thermocouple"

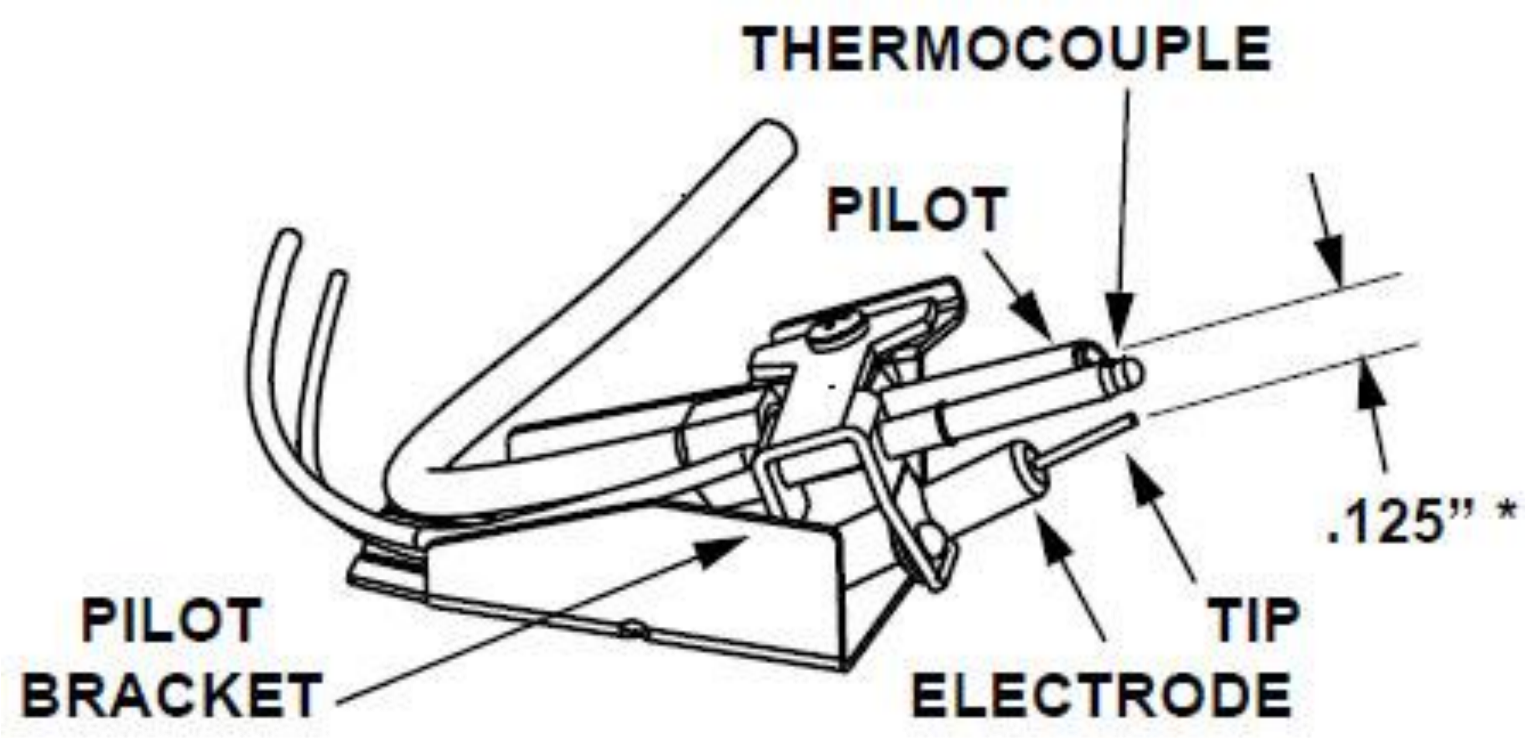
- junction between two different electronic conductors (usually metals)
- a temperature difference produces a voltage difference
- used to measure temperatures
- run in reverse, an applied voltage produces a temperature difference

(*solid-state refrigerator!*)



$$\text{voltage } \Delta\phi = \text{constant} \times (T - T_{\text{ref}})$$

Another Application: Gas Shut-Off Valve



If the gas supply to the burner is temporarily interrupted and the pilot light goes out, the thermocouple cools, dropping the voltage to zero and closing a gas supply valve.

Chapter 5. Entropy and the Second Law of Thermodynamics

Summary

- the **First Law of Thermodynamics** describes energy changes for physical and chemical processes
- no exceptions to the First Law and the conservation of energy have been discovered

But many processes obeying the First Law ***never occur***.

Why?

- the **Second Law of Thermodynamics** and the entropy are introduced to predict spontaneous processes
- combining the First and Second Laws unleashes the full power of thermodynamics

First Law of Thermodynamics

The change in internal energy of a system (ΔU) equals the heat absorbed from the surroundings (q) plus the work done on the system (w) by the surroundings.

$$\boldsymbol{\Delta U = q + w}$$

The energy of an isolated system (no contact with the surroundings, ($q = w = 0$) is constant.

$$\boldsymbol{\Delta U = 0 \text{ (isolated system)}}$$

(conservation of energy)

Section 5.1 Spontaneous Processes

First Law calculations:

$$\Delta U \qquad q \qquad w \qquad \Delta H$$

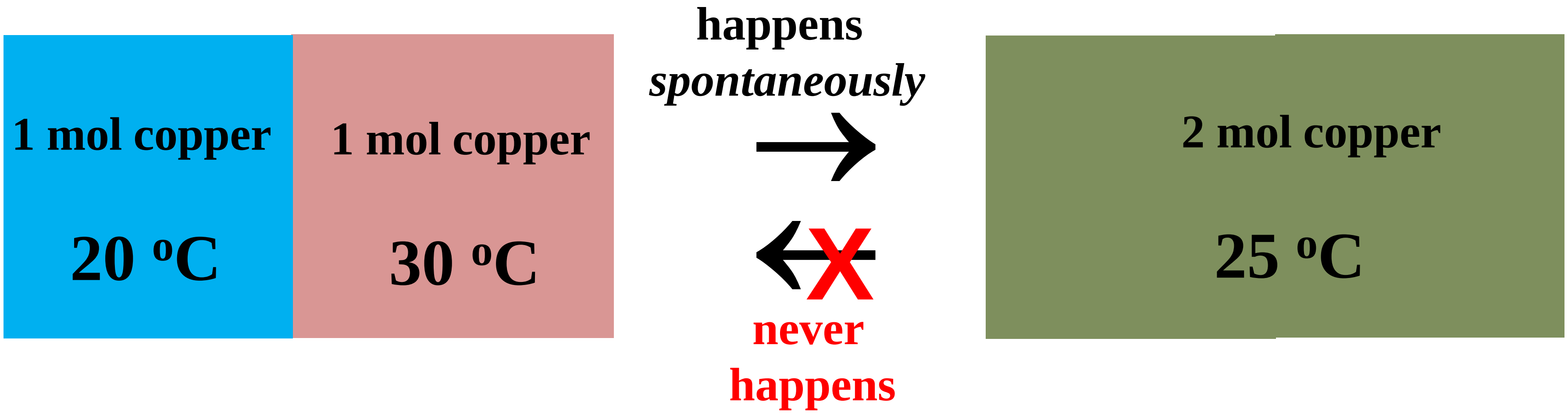
for physical and chemical processes.

But from everyday experience, many processes consistent with the First Law never occur. Others occur "spontaneously".

Why ?

Mystery: Some __heat flow__ processes obeying the First Law never occur, others occur spontaneously

isolated system ($\Delta U = 0$):



1 mol copper

20 ^{o}C

1 mol copper

30 ^{o}C

happens *spontaneously*

$\rightarrow$

$\cancel{\leftarrow}$

never happens

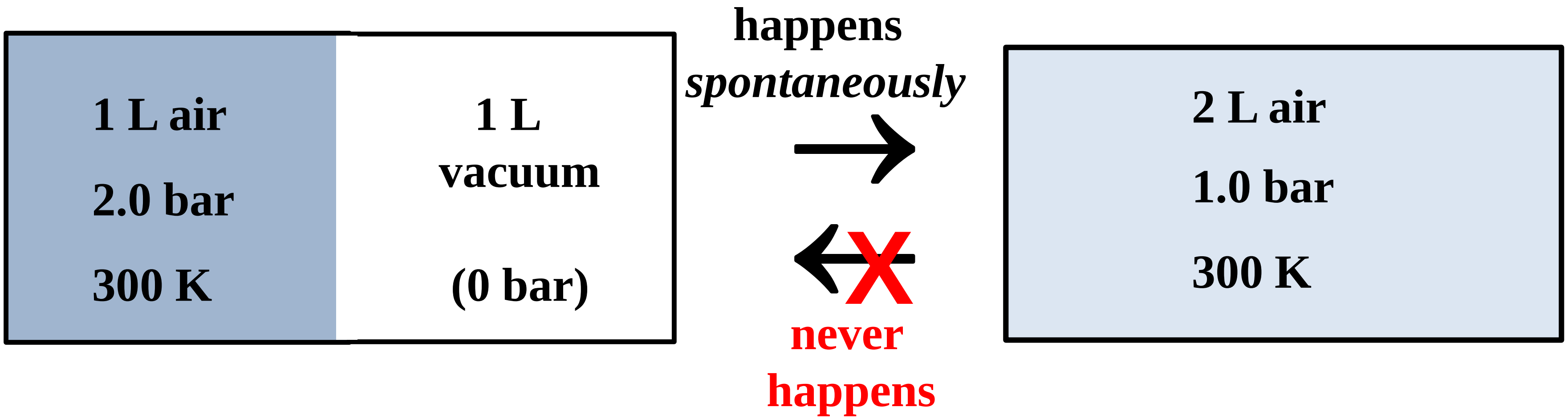
2 mol copper

25 ^{o}C

- the forward and reverse processes both obey the First Law
- the forward process __**occurs spontaneously**__ (“by itself”)
- the reverse process __**is never observed**__ (for an isolated system)

Mystery: Some mechanical processes obeying the First Law never occur, others occur spontaneously

isolated system ($\Delta U = 0$):



1 L air

2.0 bar

300 K

1 L vacuum

(0 bar)

happens *spontaneously*

never happens

2 L air

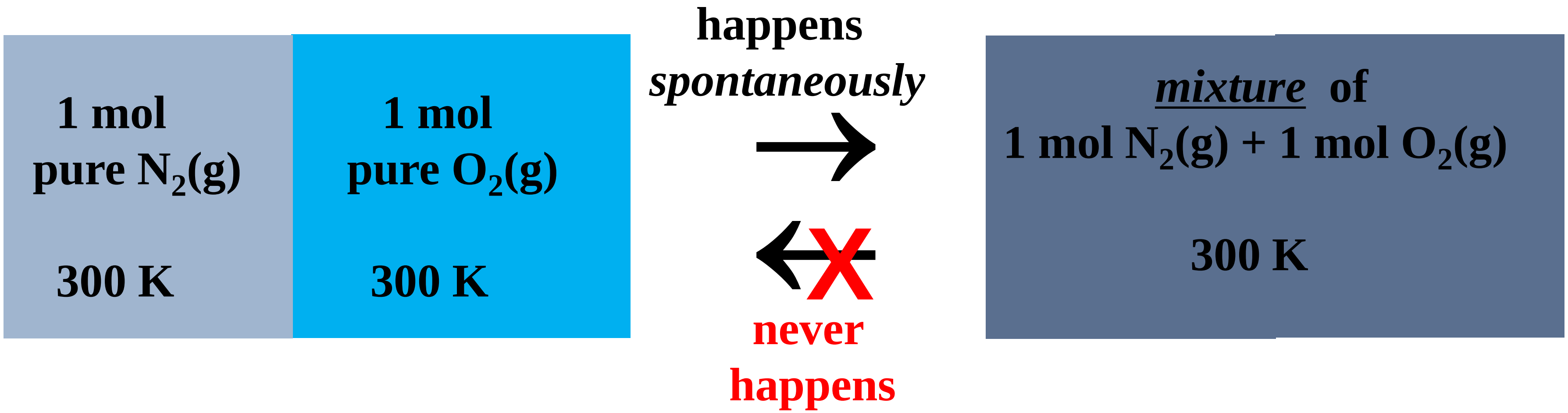
1.0 bar

300 K

- the forward and reverse processes both obey the First Law
- the forward expansion process **occurs spontaneously**
- the reverse process **is never observed** for an isolated system

Mystery: Some mixing processes obeying the First Law never occur, others occur spontaneously

isolated system ($\Delta U = 0$):



1 mol
pure $N_2(g)$
300 K

1 mol
pure $O_2(g)$
300 K

happens
spontaneously

$\rightarrow$

$\nleftarrow$

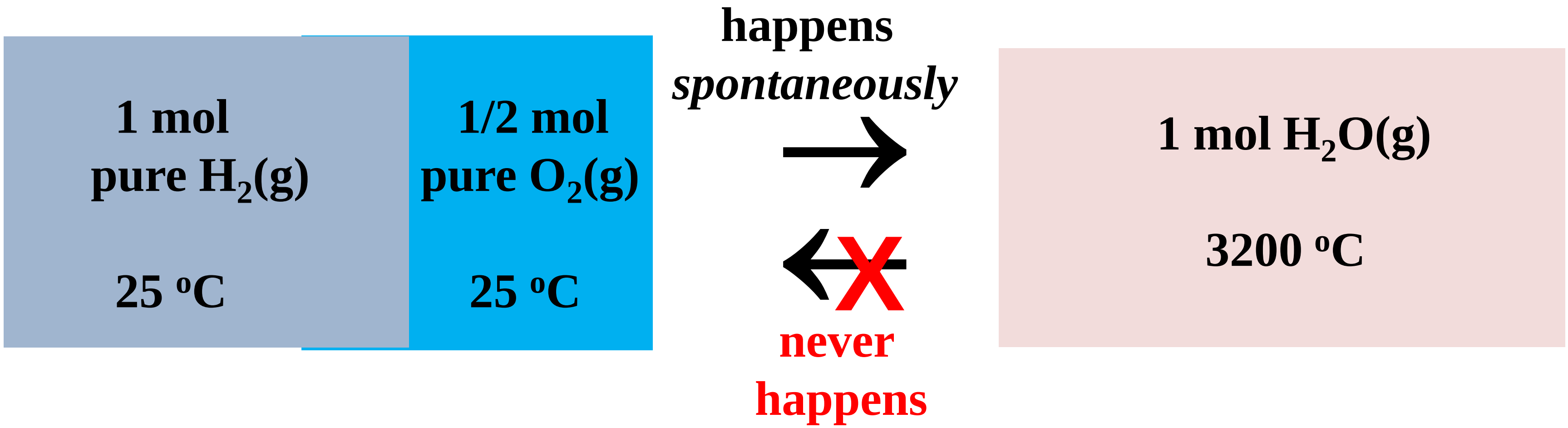
never
happens

mixture **of**
1 mol $N_2(g)$ + 1 mol $O_2(g)$
300 K

- the forward and reverse processes both obey the First Law
- the forward mixing process **occurs spontaneously**
- the de-mixing process **is never observed** for an isolated system

Mystery: Some chemical reactions obeying the First Law never occur, others occur spontaneously

isolated system (Δ*U* = 0):



1 mol pure $H_2(g)$ 25 °C

1/2 mol pure $O_2(g)$ 25 °C

happens *spontaneously*

$\longrightarrow$

$\not\longleftarrow$

never happens

1 mol $H_2O(g)$ 3200 °C

- the forward and reverse processes both obey the First Law
- the forward reaction process **occurs spontaneously**
- the reverse reaction **is never observed** for an isolated system

***Big* Mysteries:**

Many physical and chemical processes obey the First Law of Thermodynamics (conservation of energy) but never happen, others occur spontaneously.

Why?

Something important must be missing from thermodynamics based on the First First Law.

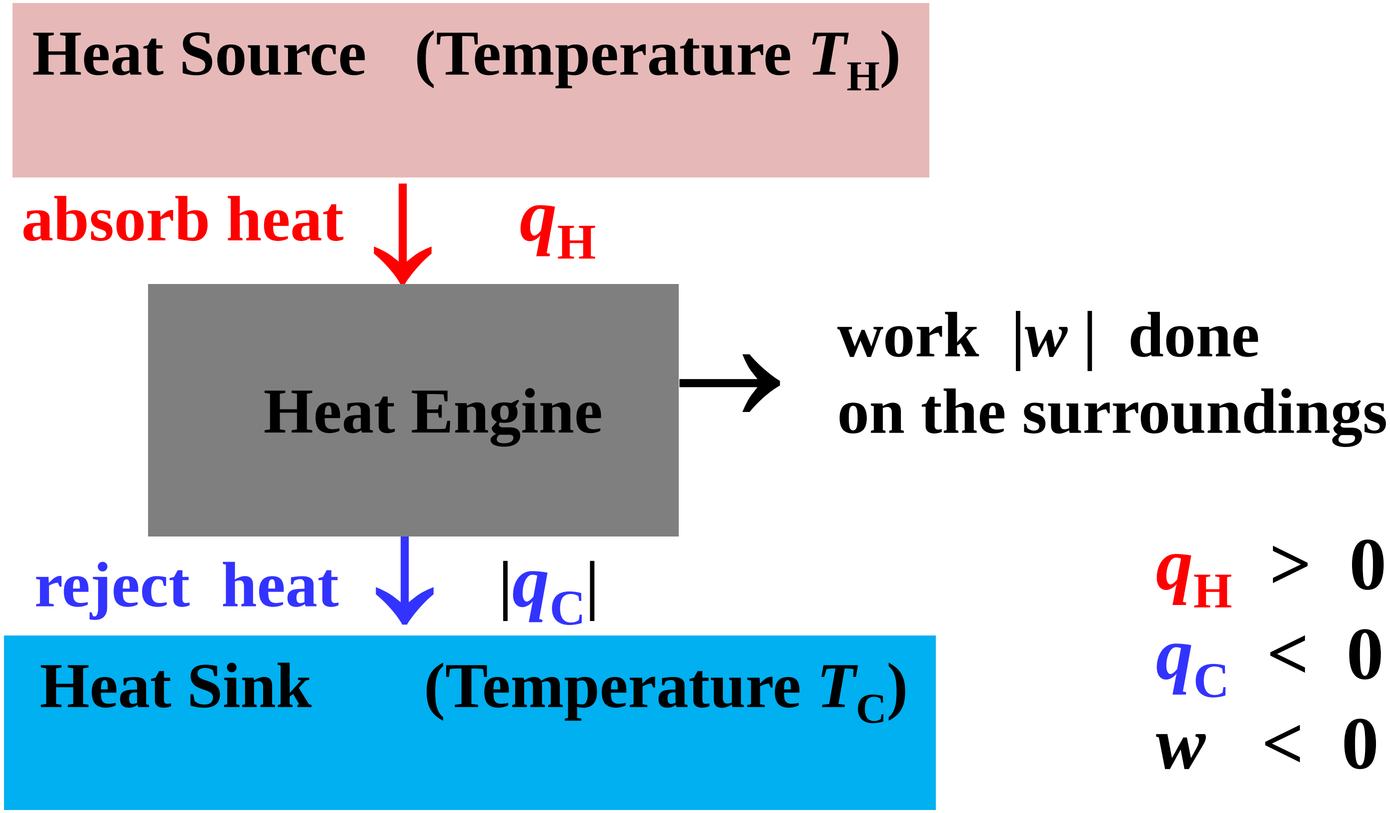
These concerns led to the discovery of entropy and the Second Law of Thermodynamics, one of the most important advances in the history of science.

Sections 5.2 Heat Engines and the Second Law

Analysis of the **efficiency of heat engines** (how much work can be done per ton of coal burned?) was used to develop the **Second Law** of thermodynamics, useful for predicting spontaneous processes.

"The steam engine has done more for science than science has ever done for the steam engine."

Heat Engine



Heat Source (Temperature T_H)

absorb heat q_H

Heat Engine

work $|w|$ done on the surroundings

reject heat $|q_C|$

Heat Sink (Temperature T_C)

$q_H > 0$

$q_C < 0$

$w < 0$

First Law :

$$q_H + q_C + w = 0$$

(conservation of energy)

Reversible Carnot Engine Cycle

Step I Isothermal Expansion at T_H

$V_1 \rightarrow V_2$ absorb heat q_H

Step II Adiabatic Expansion

$V_2 \rightarrow V_3$ $q = 0$

Step III Isothermal Compression at T_C

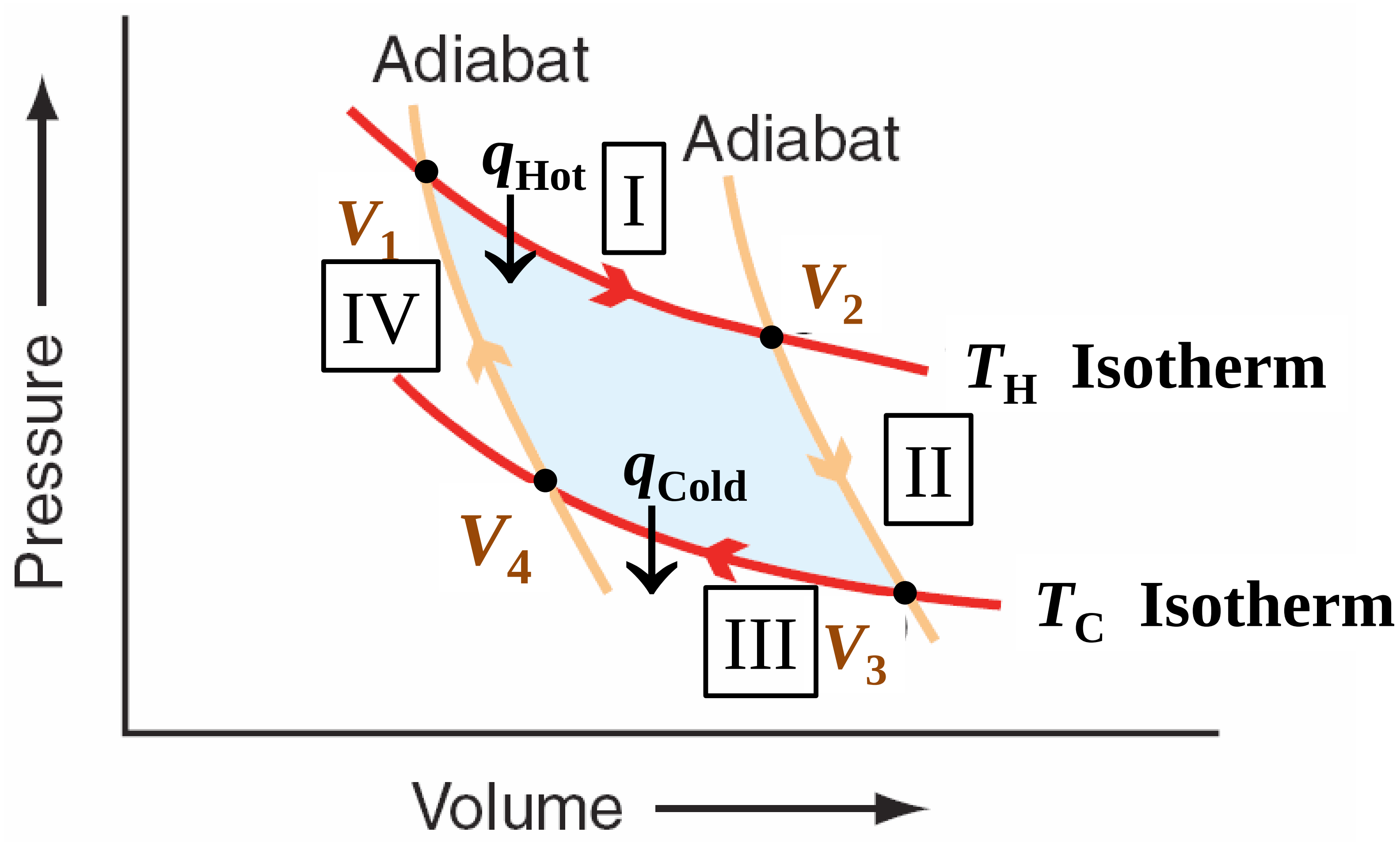
$V_3 \rightarrow V_4$ reject heat $|q_\text{C}|$

Step IV Adiabatic Compression

$V_4 \rightarrow V_1$ $q = 0$

Reversible Carnot Cycle

Steps I, II, III, IV



Reversible Carnot Engine Cycle – *the details*

system: *n* moles of ideal gas (the "working fluid" in the engine)

Step I Isothermal Expansion at $\boldsymbol{T}_{\mathbf{H}}$ $V_1 \rightarrow V_2$

$w_{\mathrm{I}} = -nRT_{\mathrm{H}}\ln(V_2/V_1)$ $\Delta U_{\mathrm{I}} = 0$ $q_{\mathrm{I}} = -w_{\mathrm{I}}$

Step II Adiabatic Expansion $\boldsymbol{T}_{\mathbf{H}} \rightarrow \boldsymbol{T}_{\mathbf{C}}$ $V_2 \rightarrow V_3$

$w_{\mathrm{II}} = C_V(T_{\mathrm{C}} - T_{\mathrm{H}}) = \Delta U_{\mathrm{II}}$ $q_{\mathrm{II}} = 0$

Step III Isothermal Compression at $\boldsymbol{T}_{\mathbf{C}}$ $V_3 \rightarrow V_4$

$w_{\mathrm{III}} = -nRT_{\mathrm{H}}\ln(V_4/V_3)$ $\Delta U_{\mathrm{III}} = 0$ $q_{\mathrm{III}} = -w_{\mathrm{III}}$

Step IV Adiabatic Compression $\boldsymbol{T}_{\mathbf{C}} \rightarrow \boldsymbol{T}_{\mathbf{H}}$ $V_4 \rightarrow V_1$

$w_{\mathrm{IV}} = C_V(T_{\mathrm{H}} - T_{\mathrm{C}}) = \Delta U_{\mathrm{IV}}$ $q_{\mathrm{IV}} = 0$

Relation between volumes V_1, V_2, V_3, V_4 (*will be useful later*):

Steps II and IV [reversible ($p = p_{\text{external}}$) and adiabatic ($q = 0$)]

$$\mathrm{d}U = \mathrm{d}w + \cancelto{0}{\mathrm{d}q}$$

$$C_V \mathrm{d}T = -p\mathrm{d}V$$

$$C_V \mathrm{d}T = -\frac{nRT}{V}\mathrm{d}V$$

$$C_V \frac{dT}{T} = -nR\frac{dV}{V}$$

$$\int_{T_\mathrm{C}}^{T_\mathrm{H}} C_V \frac{\mathrm{d}T}{T} = -nR\int_{V_4}^{V_1}\frac{\mathrm{d}V}{V} = -\int_{T_\mathrm{H}}^{T_\mathrm{C}} C_V \frac{\mathrm{d}T}{T} = nR\int_{V_2}^{V_3}\frac{\mathrm{d}V}{V}$$

$$-\ln\frac{V_1}{V_4} = \ln\frac{V_3}{V_2}$$

$$\boxed{\begin{array}{c} \boldsymbol{V_1 / V_4 = V_2 / V_3} \\ \\ \boldsymbol{V_2 / V_1 = V_3 / V_4} \end{array}}$$

Reversible Carnot Engine Cycle – First Law Analysis

Internal Energy Change for One Cycle (I → II → III → IV → I)

$$\oint_{1}^{1} \mathrm{d}U = \Delta U_{\mathrm{I}} + \Delta U_{\mathrm{II}} + \Delta U_{\mathrm{III}} + \Delta U_{\mathrm{IV}}$$

$$= 0 + C_V(T_{\mathrm{C}} - T_{\mathrm{H}}) + 0 + C_V(T_{\mathrm{H}} - T_{\mathrm{C}})$$

$$= U_{\mathrm{I}} - U_{\mathrm{I}}$$

$$\Delta U_{\mathrm{cycle}} = 0$$

Reversible Carnot Engine Cycle – First Law Analysis

Work Done for One Cycle (I → II → III → IV → I)

$$\oint_{1}^{1} \mathrm{d}w = w_{\mathrm{I}} + w_{\mathrm{II}} + w_{\mathrm{III}} + w_{\mathrm{IV}}$$

$$= -nRT_{\mathrm{H}} \ln\frac{V_2}{V_1} + \cancel{C_V (T_{\mathrm{C}} - T_{\mathrm{H}})} - nRT_{\mathrm{C}} \ln\frac{V_4}{V_3} + \cancel{C_V (T_{\mathrm{H}} - T_{\mathrm{C}})}$$

use
$V_4 / V_3 = V_1 / V_2$

$$= -nRT_{\mathrm{H}} \ln\frac{V_2}{V_1} + 0 + nRT_{\mathrm{H}} \ln\frac{V_2}{V_1} + 0$$

$$w_{\mathrm{cycle}} = -nR(T_{\mathrm{H}} - T_{\mathrm{C}}) \ln\frac{V_2}{V_1}$$

Reversible Carnot Engine Cycle – First Law Analysis

Heat Absorbed for One Cycle (I → II → III → IV → I)

$$\oint_{1}^{1} \mathrm{d}q \;=\; q_{\mathrm{I}} + q_{\mathrm{II}} + q_{\mathrm{III}} + q_{\mathrm{IV}}$$

$$=\; nRT_{\mathrm{H}} \ln\frac{V_2}{V_1} \;+\; 0 \;-\; nRT_{\mathrm{C}} \ln\frac{V_3}{V_4} \;+\; 0$$

use
$V_3 / V_4 = V_2 / V_1$

$$q_{\mathrm{cycle}} \;=\; nR(T_{\mathrm{H}} - T_{\mathrm{C}}) \ln\frac{V_2}{V_1}$$

Check: Can you verify that $q_{\mathrm{cycle}} + w_{\mathrm{cycle}} = 0$ $(= \Delta U_{\mathrm{cycle}})$?

Efficiency ε of a Reversible* Carnot Engine

$$\varepsilon = \frac{\text{work done on the surroundings}}{\text{heat absorbed from the hot reservoir}}$$

$$= \frac{-w_{\text{cycle}}}{q_{\text{H}}}$$

$$= \frac{nR(T_{\text{H}} - T_{\text{C}})\ln(V_2/V_1)}{nRT_{\text{H}}\ln(V_2/V_1)}$$

$$\boxed{\varepsilon = \frac{T_{\text{H}} - T_{\text{C}}}{T_{\text{H}}} = 1 - \frac{T_{\text{C}}}{T_{\text{H}}}}$$

So What?

This result is a big deal!

It places a <u>fundamental limit</u> on heat engine efficiency.

*reversible heat engine: infinitesimal temperature and pressure differences between the gas and the surroundings

Efficiency ε of a Reversible* Carnot Engine

Example: Calculate the efficiency of a reversible steam engine operating between **T_H = 373 K** (the boiling point of water at 1 bar) and **T_C = 293 K**. How much work is done if 10.0 MJ of heat is absorbed at 373 K?

$$\varepsilon = 1 - \frac{T_C}{T_H} = 1 - \frac{293\ \text{K}}{373\ \text{K}} = 0.214 = 21.4\,\%$$

$$\varepsilon = \frac{-w}{q_H} = 0.214 = \frac{-w}{10.0\ \text{MJ}}$$

$-w = 0.214 \times 10.0$ MJ $= 2.14$ MJ work done on the surroundings*

*this is the maximum amount of work that can be done – real engines are less efficient than reversible engines

Section 5.3 Important Consequences of the Carnot Cycle

For one complete cycle, all steps reversible, it was noticed that:

$$\oint \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \int_1^2 \frac{\mathrm{d}q}{T} + \int_2^3 \frac{\mathrm{d}q}{T} + \int_3^4 \frac{\mathrm{d}q}{T} + \int_4^1 \frac{\mathrm{d}q}{T}$$

$$= \frac{q_{\mathrm{H}}}{T_{\mathrm{H}}} + 0 + \frac{q_{\mathrm{C}}}{T_{\mathrm{C}}} + 0$$

$$= \frac{nRT_{\mathrm{H}}\ln(V_2/V_1)}{T_{\mathrm{H}}} + \frac{nRT_{\mathrm{C}}\ln(V_4/V_3)}{T_{\mathrm{C}}}$$

$$= nR\ln(V_2/V_1) + nR\ln(V_4/V_3) = nR\ln(V_2/V_1) - nR\ln(V_2/V_1)$$

$$= 0$$

So what?

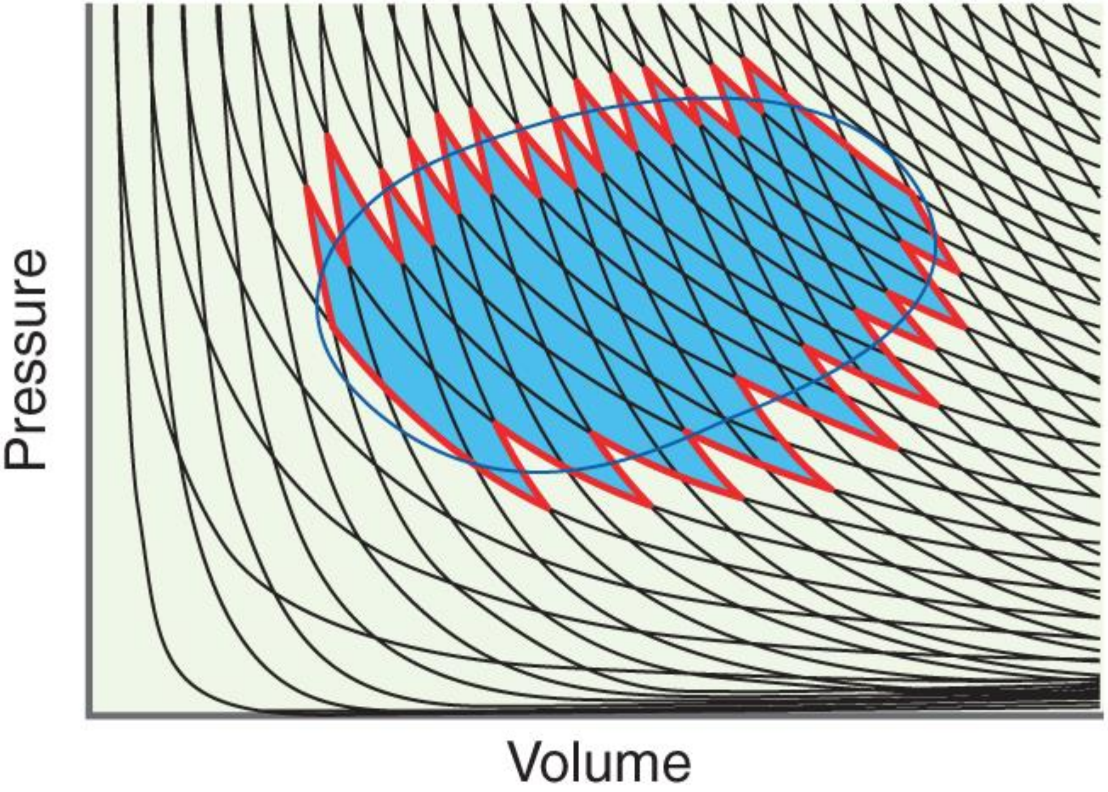
Important Consequences from the Carnot Cycle

A. The Entropy *S* (A New State Function!)

The result

$$\boxed{\oint \frac{dq_{\text{rev}}}{T} = 0}$$

can be generalized
to **any reversible cycle**
for **any system**.



Important Consequences from the Carnot Cycle

A. The Entropy *S* (A New State Function)

Conclusion:

The entropy *S* defined by

$$\boxed{\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T}}$$

is a function of the state of the system (like the internal energy *U* and the enthalpy *H* state functions).

Important Consequences from the Carnot Cycle

B. Clausius Inequality – *the breakthrough !*

For a **reversible** Carnot cycle, from the First Law

$$\Delta U_{\text{cycle}} = q_{\text{H}} + q_{\text{C}} + w = 0$$

so $$-w = q_{\text{H}} + q_{\text{C}}$$

$$\varepsilon = \frac{-w}{q_{\text{H}}} = \frac{q_{\text{H}} + q_{\text{C}}}{q_{\text{H}}} = 1 - \frac{T_{\text{C}}}{T_{\text{H}}}$$

multiply by $T_{\text{H}}q_{\text{H}}$

$$T_{\text{H}}q_{\text{H}} + T_{\text{H}}q_{\text{C}} = T_{\text{H}}q_{\text{H}} - T_{\text{C}}q_{\text{H}}$$

divide by $T_{\text{H}}T_{\text{C}}$

$$\left(\frac{q_{\text{H}}}{T_{\text{H}}} + \frac{q_{\text{C}}}{T_{\text{C}}}\right)_{\text{reversible}} = 0$$

generalizes to

$$\boxed{\oint \frac{\mathrm{d}q_{\text{rev}}}{T} = 0}$$