

Ch 1b Lecture 12

February 4th, 2013

Next few lectures – Still on the road to chemical reactivity, circa mid-1800s.

Today: The First Law of Thermodynamics.
(or, “Attack of the killer partial derivatives”)

Reading: OGC Chapter 12, esp. through section 12.5

Ranger says: “Thermo makes me sleepy.”



Ch 1b - A Thermodynamics Primer/Review

We've spent most of Ch1a+b learning about the microscopic world, one that is defined by quantum mechanics. Such understanding has emerged only relatively recently within the history of chemistry, much of what we know about the transformation of chemical systems was gleaned from studies of macroscopic samples before the advent of the Schrödinger equation.

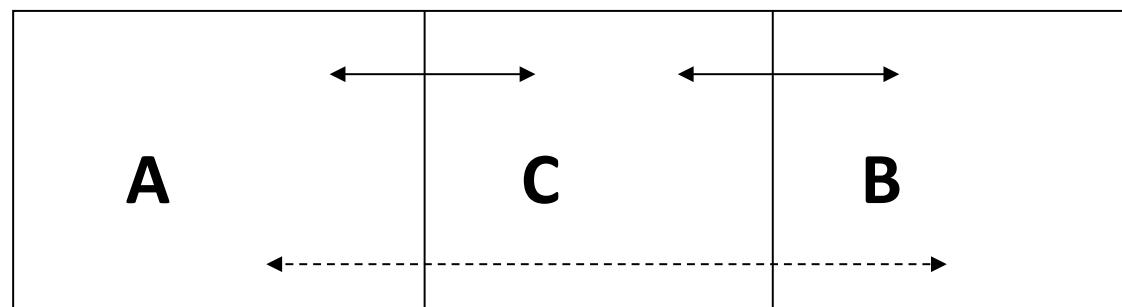
Chief among these advancements was *thermodynamics*. The power of this discipline lies in its generality. The field developed from observations of the natural world, it stands on its own. No molecular details of the system under study enter into classical thermodynamic analyses. The desire to bridge the macroscopic and microscopic worlds lies at the heart of *statistical thermodynamics*, a subject you will consider in Ph 2.

This week we'll briefly outline the fundamental "laws" of thermodynamics, and provide some simple examples of their applications to chemistry.

Ch 1b - The “Zeroth” Law of Thermodynamics

The quantitative concepts of temperature, work, internal energy, and heat play an important role in the understanding of chemical phenomena. The need to define an absolute temperature scale was not recognized until after the first and second laws of thermodynamics were established. Briefly, it states:

For three systems A, B, and C, if A is in thermal equilibrium with C and B is also in thermal equilibrium with C; then A and B are in thermal equilibrium with each other.



Ch 1b - Thermodynamic State Variables/Functions

When a system is at equilibrium under a given set of conditions, it is said to be in a definite state. State variables include things like pressure, volume and temperature (P , V , T). Those variables that depend on the size of the system are referred to as *extensive* (such as V , energy); those that do not are referred to as *intensive* (P , T , for example). Extensive variables can be converted into intensive variables by dividing by a measure of the amount of substance (the molar volume, for example).

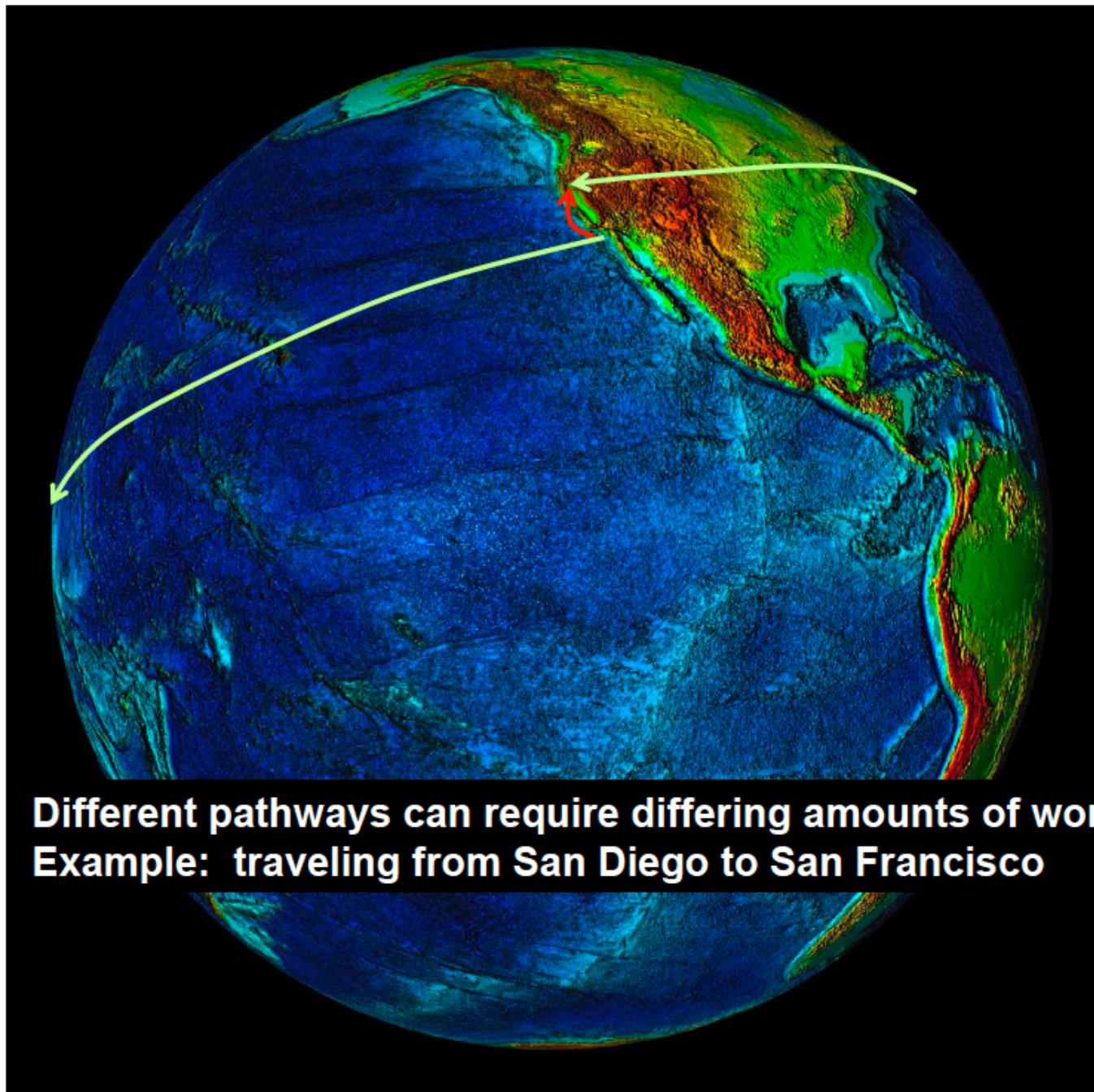
As we'll see next, certain quantities do not depend upon the path taken by the system; these are called state functions. Some thermodynamic state functions we will be concerned with include:

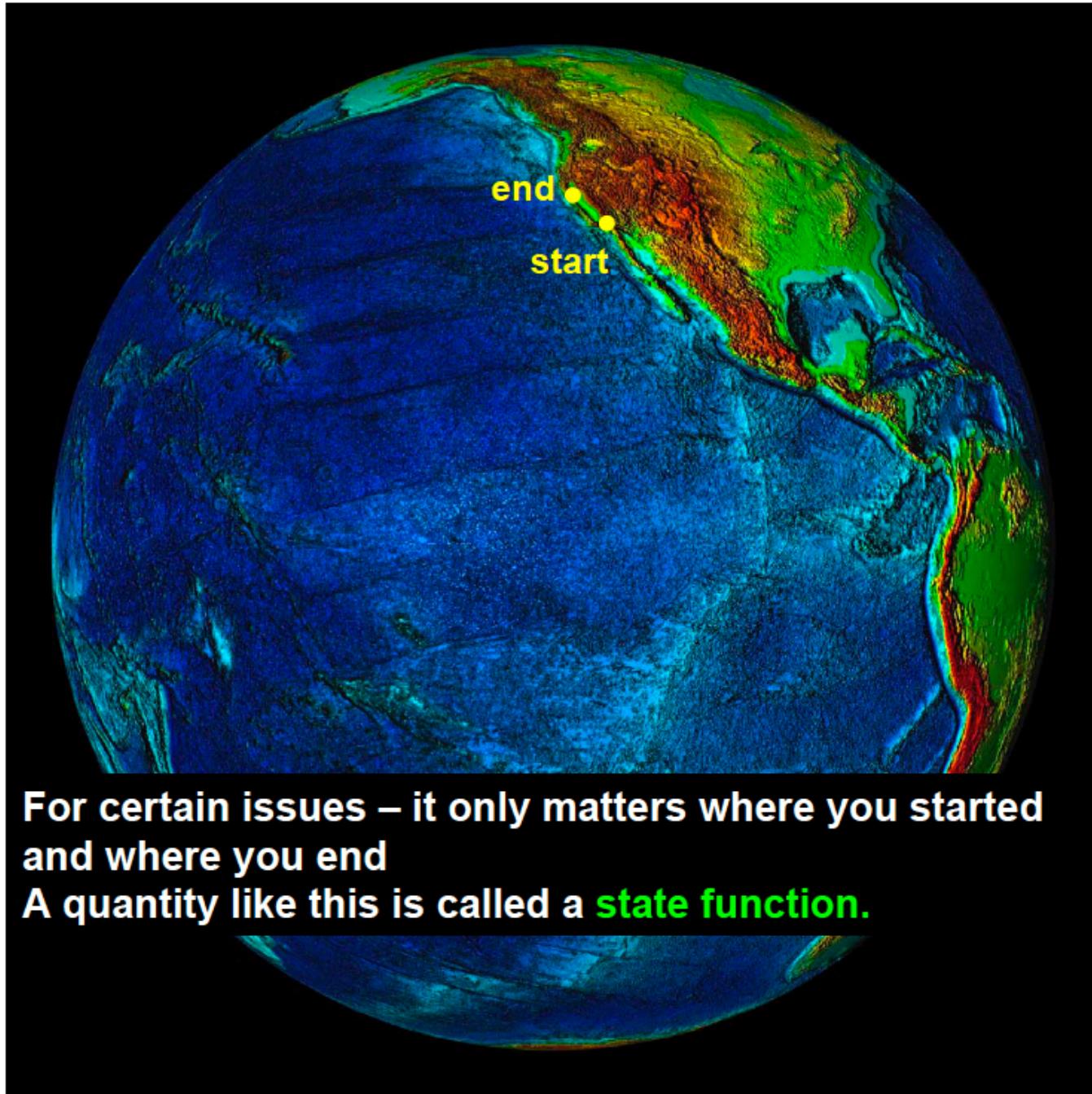
U = internal energy

H = enthalpy (classically, $U + PV$)

S = entropy

G = Gibbs free energy = $H - TS$





For certain issues – it only matters where you started
and where you end

A quantity like this is called a **state function**.

Thermodynamic Processes and Thermochemistry

The goal of thermodynamics:

predict what chemical and physical processes are possible, and under what conditions, and to calculate quantitatively the properties of the equilibrium state that ensues when a process is carried out.

Much of thermodynamics involves first defining the system

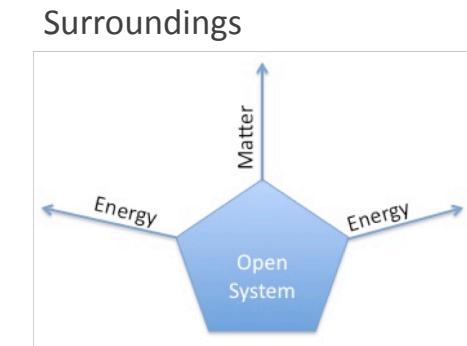
- Can heat get in or out of the system?
- Can mass get in or out of the system?
- Can the system expand or contract?
- Can the # of particles inside the system change?
- Is the system changing?

- What is outside the system?

These (and other) aspects are all important

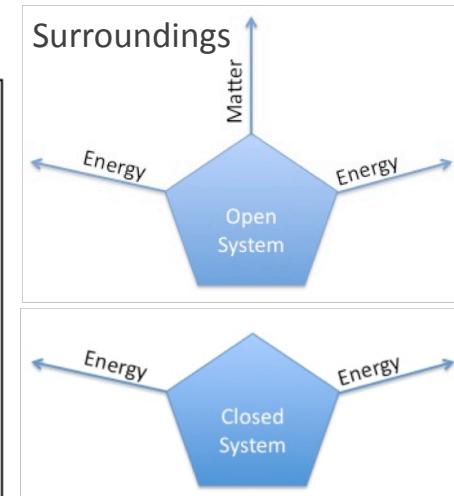
Thermodynamic Systems: Definitions

- (a) **An open system** can exchange matter and energy with its surroundings.



Thermodynamic Systems: Definitions

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- (b) **A closed system** can exchange energy with its surroundings, but it cannot exchange matter.



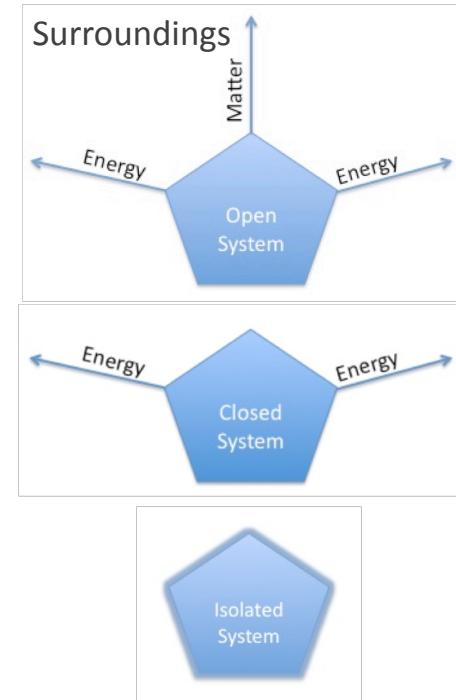
CLOSED SYSTEM

A lid has been placed on the coffee cup



Thermodynamic Systems: Definitions

- (a) **An open system** can exchange matter and energy with its surroundings.
- (b) **A closed system** can exchange energy with its surroundings, but it cannot exchange matter.
- (c) **An isolated system** can exchange neither energy nor matter with its surroundings.



The coffee has
been placed into
a thermos.



Macroscopic Properties of Systems

- An **extensive property** is one that can be written as the sum of the properties of subsystems formed by dividing the system into smaller compartments (**examples: volume, mass, energy**)

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- An **extensive property** is one that can be written as the sum of the properties of subsystems formed by dividing the system into smaller compartments (**examples: volume, mass, energy**)
- An **intensive property** of the system is one that is the same as the corresponding properties of each of the subsystems (**examples: temperature, pressure**)

Equations of State

- A thermodynamic state is a macroscopic condition of a system whose properties are uniquely determined by the laboratory apparatus that holds them at selected fixed values independent of time. **It can be described by the variables n, P, V, T**
- When the system has been prepared subject to the constraints, all disturbances have ceased, and none of its properties are changing with time, the system is said to have reached equilibrium.

Diathermic and Adiabatic Systems

(a) A **diathermic system** allows energy to escape as heat through its boundary if there is a temperature difference between the system and its surroundings.

(b) An **adiabatic system** does not permit the passage of energy as heat through its boundary even if there is a temperature difference between the system and its surroundings.



The coffee cools to the outside temperature.



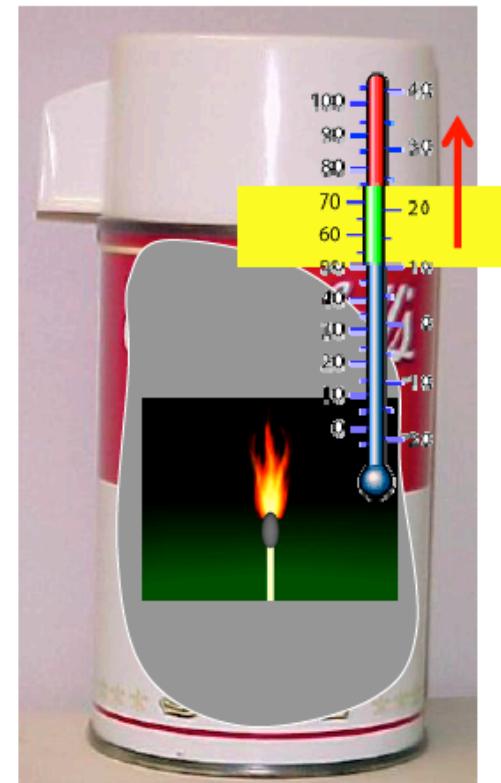
Hot coffee inside,
cold air outside.

Endothermic and Exothermic Processes

(a) When an **endothermic process** occurs in an **adiabatic system**, the temperature falls

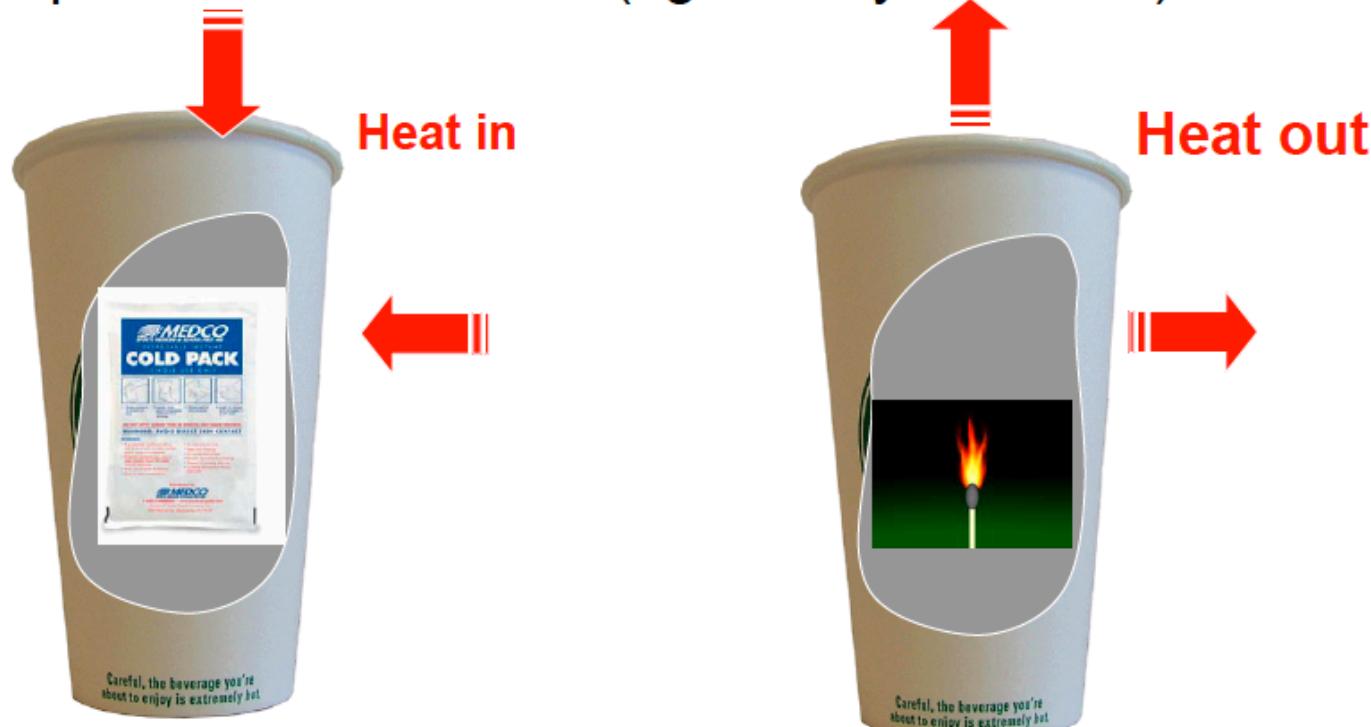


(b) if the process is **exothermic**, then the temperature rises.



Endothermic and Exothermic Processes

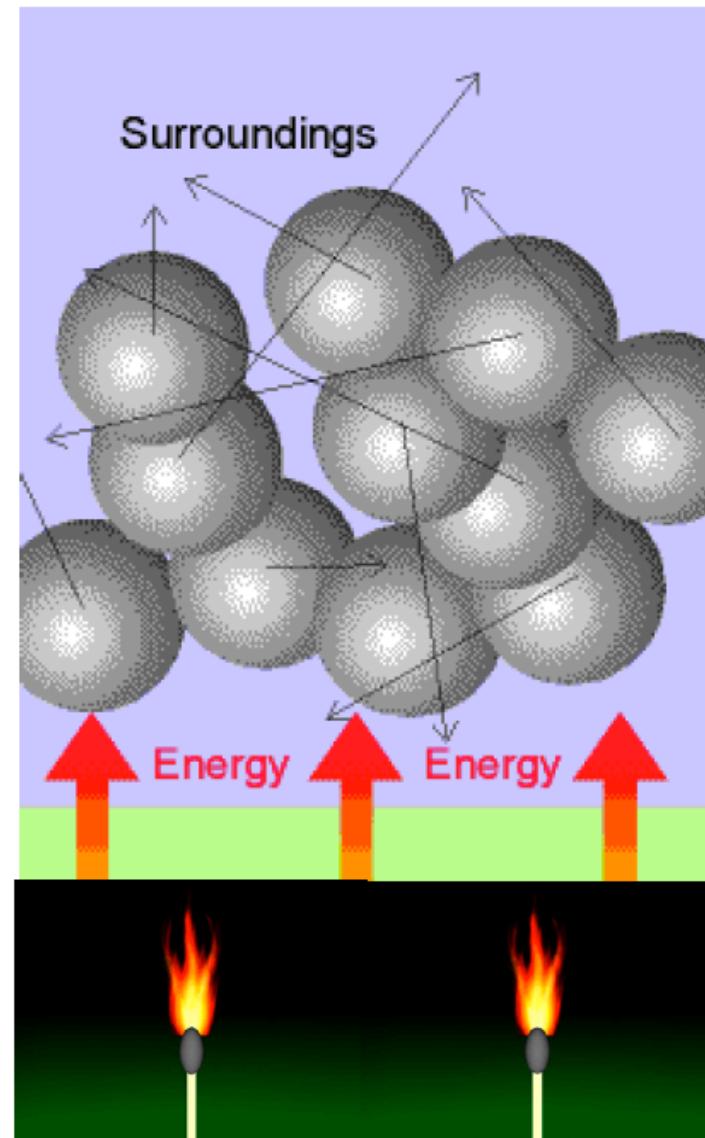
- (c) When an **endothermic process** occurs in a **diathermic container**, energy enters as heat from the surroundings, and the system remains at the same temperature (may take a little time)
- (d) If the process is **exothermic**, then energy leaves as heat, and the process is isothermal (again may take time).



Energy transfer, **as Heat**, between a system and it surroundings

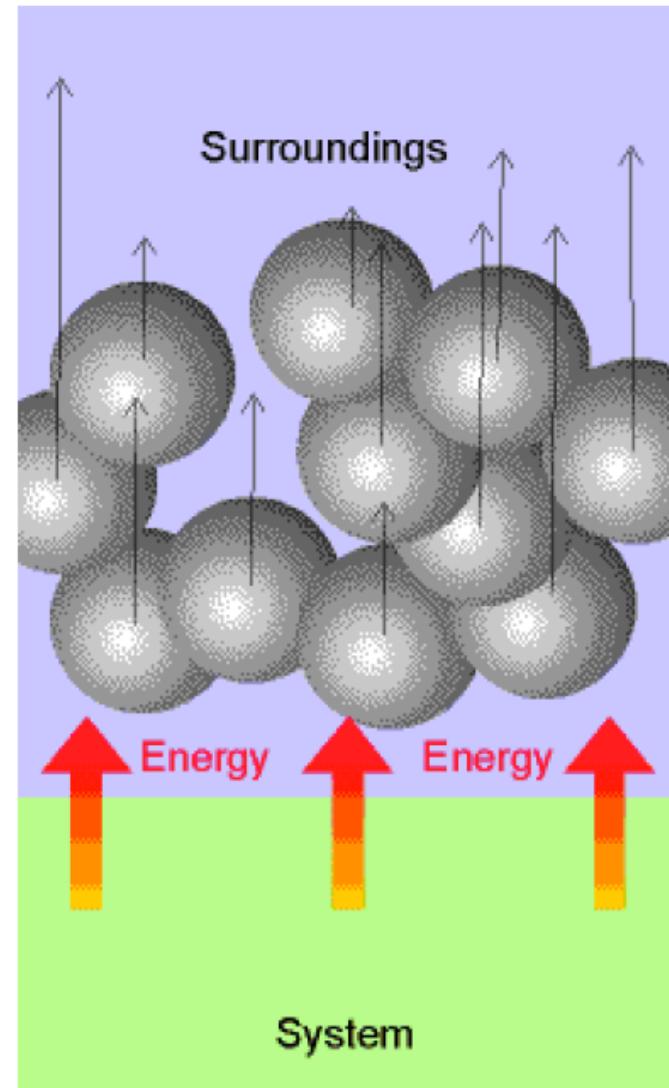
When energy is transferred to the surroundings as heat, the transfer stimulates disordered, thermal motion of the atoms in the surroundings.

Drawing not
to scale



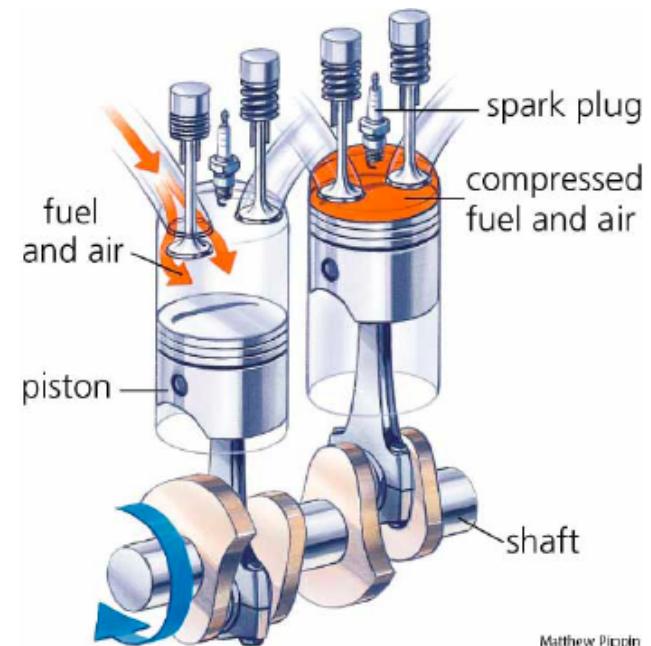
Energy Transfer, **as work**, between a system and its surroundings

When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.



A system may be able to adjust its volume as heat is added:

When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat.



Matthew Pippin

Units?



James Joule (1818-1889)
(a.k.a. Santa Claus)

English Physicist

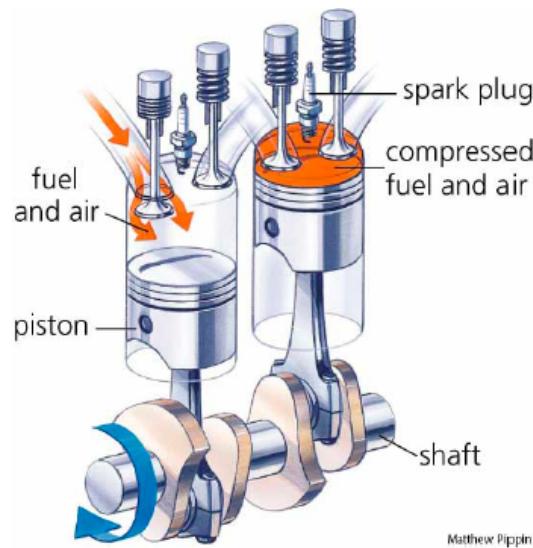
Determined the mechanical equivalent of heat by measuring change in temperature produced by the friction of a paddlewheel attached to a falling weight in the 1840s.

772 pound weight falling one foot would raise the temperature of one pound of water by 1° F. **What a great definition!**

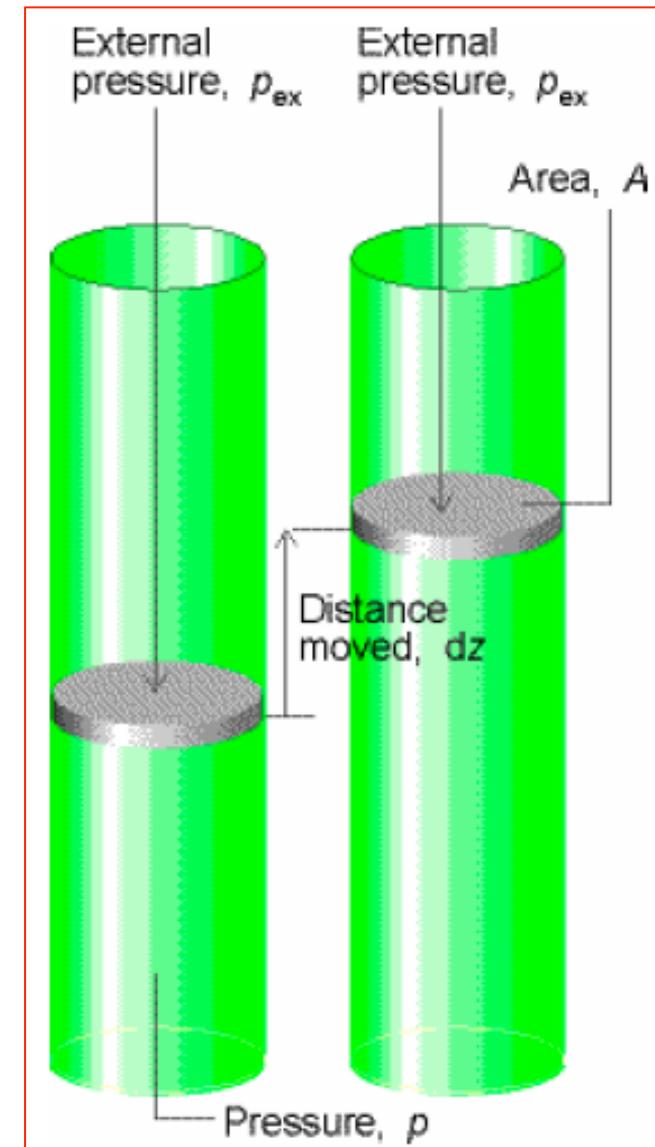
$(772 \text{ ft lbs})(1.356 \text{ J/ft lb}) = 59453.6 \text{ Calories}$, or 1 cal = 4.15 Joules, in close agreement with the current accepted value of 1 cal = 4.184 J.

Expansion of a Gas:

When a piston of area A moves out through a distance dz , it sweeps out a volume $dV = A dz$. The external pressure, p_{ex} , is equivalent to a weight pressing on the piston, and the force opposing expansion is $F = p_{ex} A$.

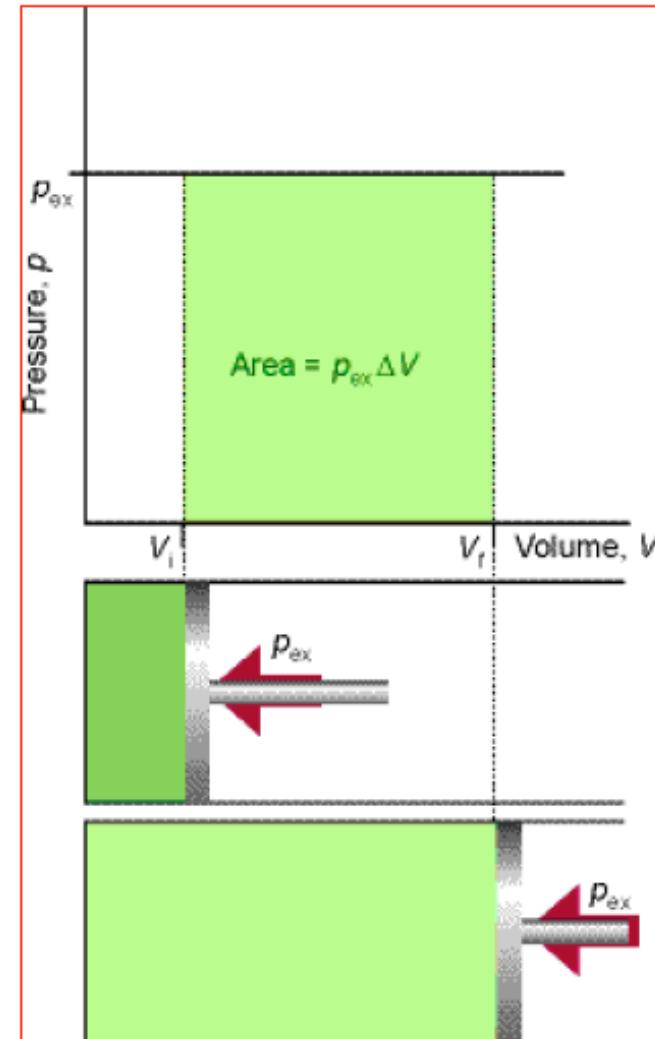
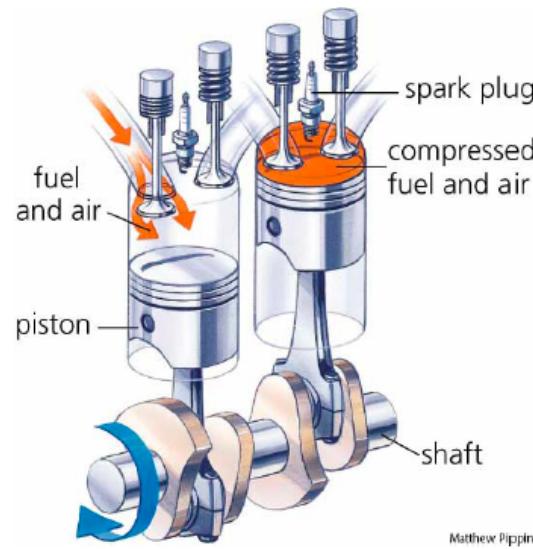


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Work due to Gas Expansion:

The work done by a gas when it expands against a constant external pressure, p_{ex} , is equal to the shaded area in this diagram ($p_{\text{ex}}\Delta V$).



Work due to Volume Changes (Gases):

$$w = -P_{\text{ext}} \Delta V$$

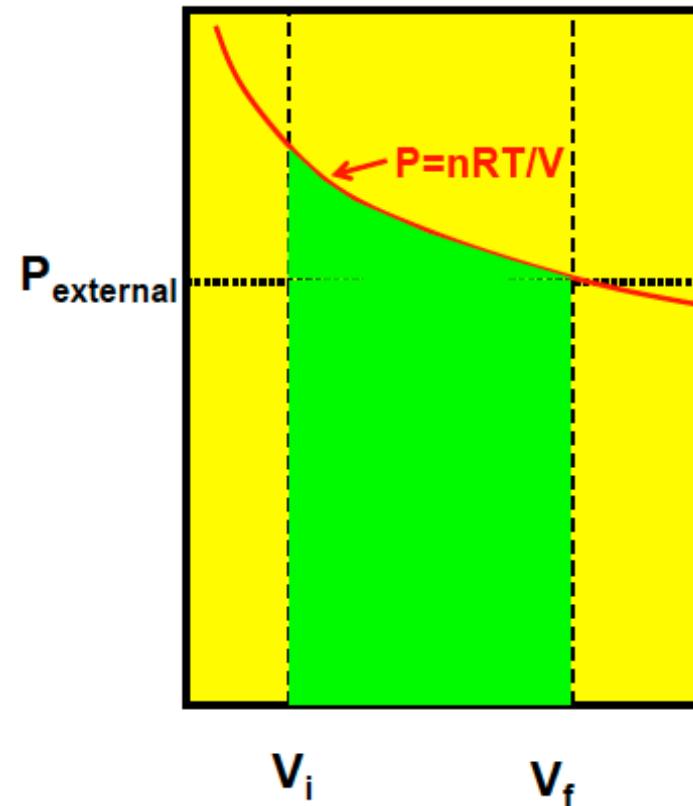
By convention, for an expansion, $\Delta V > 0$, so $w < 0$ and the system does work; it pushes back the surroundings. If the gas is compressed, $w > 0$.

Note: Not all texts follow this convention!!

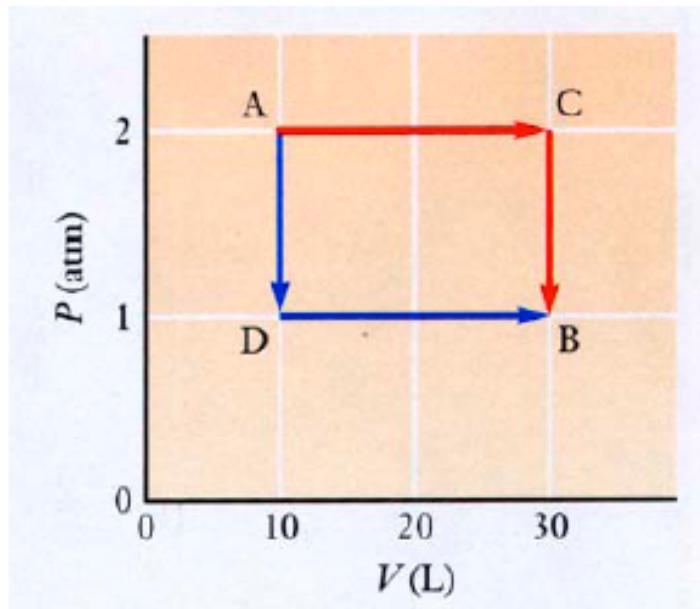
Work due to Gas Expansion:

The work done by a perfect gas when it expands **reversibly** and **isothermally** is equal to the area under the isotherm $PV=nRT$.

We will come back to what the term **reversibly** means, thermodynamically speaking, in the next lecture.



Paths and State Functions:



We will look at the difference in the paths A-C-B and A-D-B in some detail, and find different work and heat flow for each path.

Clearly, the n_i, V_i, P_i, T_i and n_f, V_f, P_f, T_f are equal for the two paths (because they are state functions).

This implies a state function that is concerned only with the difference between the initial and final conditions!

That state function is ΔU , and it is called the internal energy (some texts refer to this state function as ΔE).

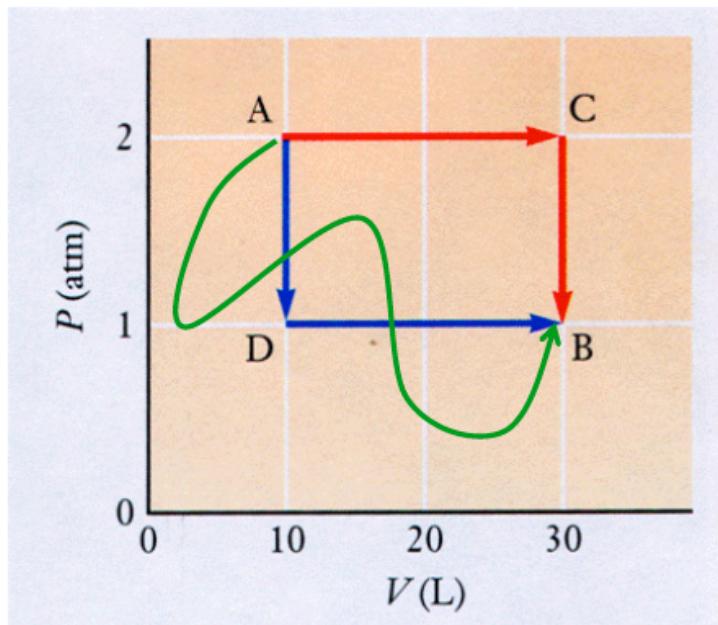
The First Law of Thermodynamics:

$$\Delta U = q + w$$

The change in internal energy of a system is equal to the sum of the heat added to the system and the work done on the system.

Although q and w depend *individually* on the path followed between a given pair of states, their **sum** does not.

The First Law of Thermodynamics:



Other Pathways

How about the green path?

Why?

Because ΔU is a state function – it is pathway independent

$$\Delta U_{Green} = q + w = 15l \cdot atm = 1520J$$

Path	q	w	$q+w$
ACB	5570 J	-4050 J	1520 J
ADB	3550 J	-2030 J	1520 J

= all pathways A → B

Calculating q, w ?

Heat Capacities:

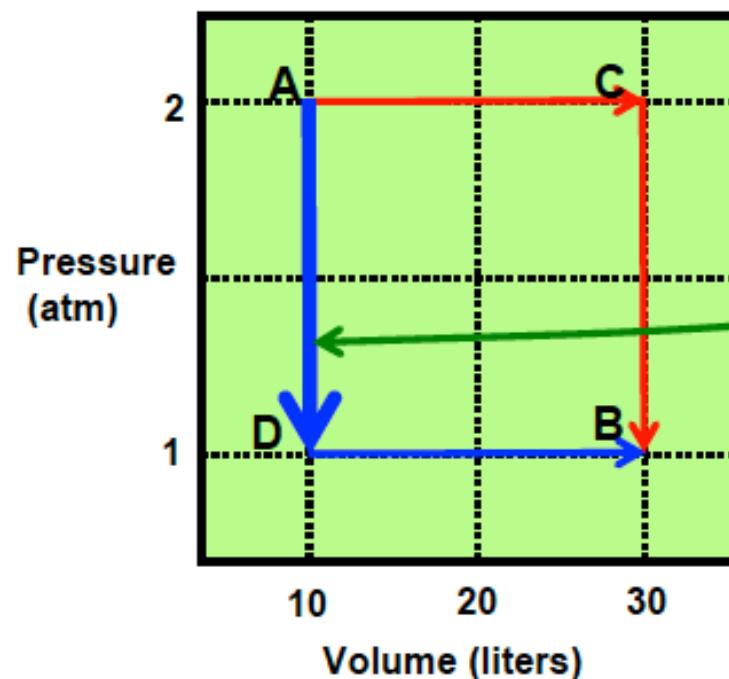
Why is $C_v = 3R/2$?

29

$U = 3/2k_B T$ per particle; $=3/2nRT$ for a molar amount of particles

So: $\Delta U = 3/2nR\Delta T$

Also $\Delta U = q + w = \text{heat} + \text{work}$ and $q = nc_{v,p}\Delta T$



For a constant volume change of an ideal gas, we use c_v

For a constant pressure expansion/compression of an ideal gas, we use c_p

Constant volume change: work = 0
Since $\Delta U = q+w$, then $\Delta U = q$

So $\Delta U = 3/2nR\Delta T = q = nc_v\Delta T$
And $c_v = 3/2R$

Heat Capacities:

Why is $C_p = 5R/2$?

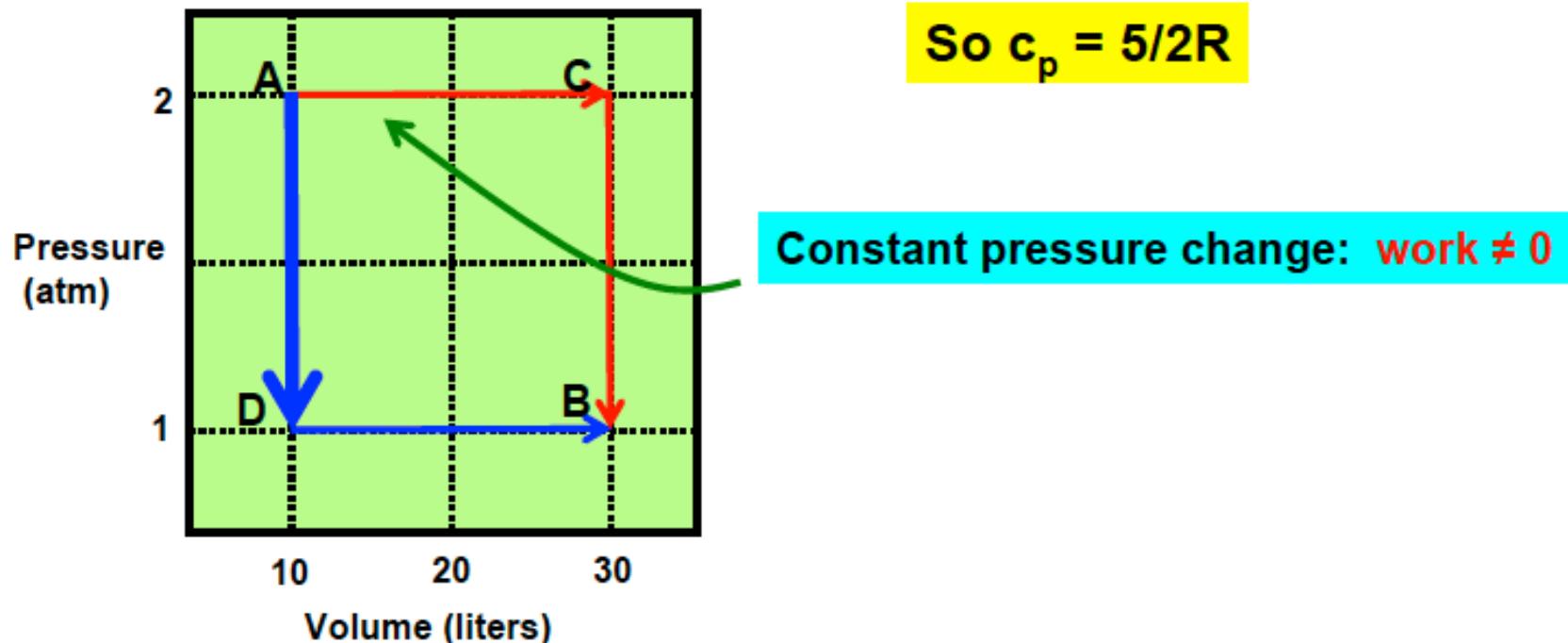
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$$\Delta U = 3/2nR\Delta T = q + w = \text{heat} + \text{work} \quad \text{and} \quad q = r$$

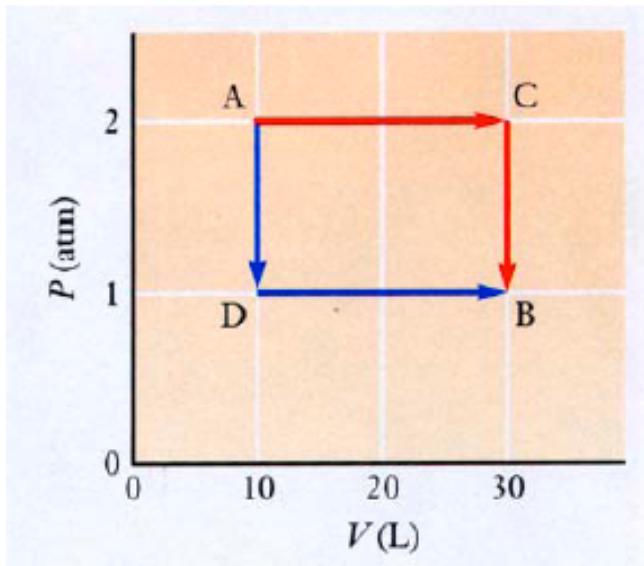
For a constant pressure expansion/compression of an ideal gas, use c_p

$$q+w = \Delta U (= 3/2 nR\Delta T) = nc_p\Delta T - P_{\text{ext}}\Delta V = nc_p\Delta T - nR\Delta T$$

$$\text{SO } 3/2nR\Delta T = nc_p\Delta T - nR\Delta T$$



The First Law of Thermodynamics:



$$w_{AC} = -P_{ex}\Delta V = -P_A (=2\text{atm}) (V_B - V_A) = -40 \text{ liter}\cdot\text{atm}$$

$$\Delta q = nc_P\Delta T = 5/2nR(T_C - T_A)$$

$$nc_P\Delta T = 5/2 nRP (V_C/nR - V_A/nR)$$

$$= 5/2 P(V_C - V_A) = 5/2 (2 \text{ atm}) (20 \text{ liters})$$

For C to B there is no ΔV , and hence no work.

$$q_V = 3/2R\Delta T = 3/2R (P_B - P_A) 30 \text{ liters} = -45 \text{ liter}\cdot\text{atm}$$

Thus,

$$\Delta U = q + w = (100 - 45) + (-40) = 15 \text{ liter atm}$$

Now, the conversion to Joules is $8.314/0.08206 = 101.316$,
and $\Delta U = 1520$ Joules, as stated in slide 28.

Enthalpy:

Why do we care? Many chemical reactions are carried out at constant pressure, in air for example.

Our work so far suggests that there is another state function that may be quite useful, tied to heat and especially under constant pressure, say P_{ext} . That is, let's look at:

$$\Delta U = q_P + w = q_P - P_{ext} \Delta V = q_P - P \Delta V$$

Enthalpy:

$$\Delta U = q_P + w = q_P - P_{ext} \Delta V = q_P - P \Delta V$$

Thus, rearranging:

Subscript implies constant P

$$q_P = \Delta U + P \Delta V = \Delta(U + PV)_P = \Delta H$$

Note that q_P is in terms of U , P and V – state functions all. Thus, q_P is also a state function, and is called the **enthalpy**, or H :

$$H = U + PV$$

Enthalpy (defined more generally):

$$\Delta H = \Delta U + \Delta(PV)$$

$$= nc_V \Delta T + \Delta(PV)$$

$$= nc_V \Delta T + nR\Delta T = n\Delta T(c_V + R)$$

$$= nc_P \Delta T$$

$$\boxed{\Delta H = nc_P \Delta T}$$

Enthalpy (defined more generally):

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = nc_P\Delta T$$

Why does ΔH have to be a state function?

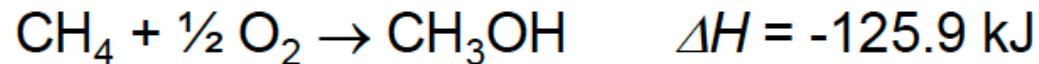
Because **U, P, and V are all state functions.**

**Enthalpy is very important –
we will refer back to it several times**

Thermochemistry:

Goal is to generate energy (& thus work) via chemistry.

For 1.00 mol CH₄ reacting with 0.5 mol of O₂ at 25 °C and 1 atm



From Appendix D of OGC:

ΔH_f° of CH₄ is -74.81 kJ·mol⁻¹

ΔH_f° of CH₃OH_(g) is -200.66 kJ·mol⁻¹

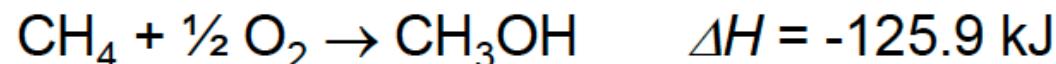
Thus, one can calculate the ΔH of the reaction.

(Question: Why is ΔH_f° of O₂ zero?)

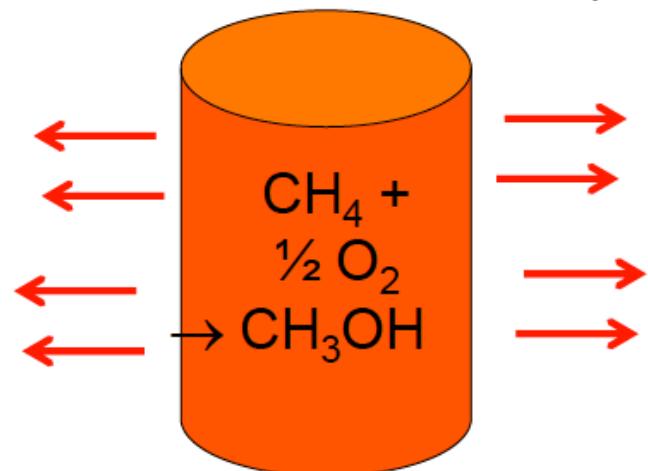
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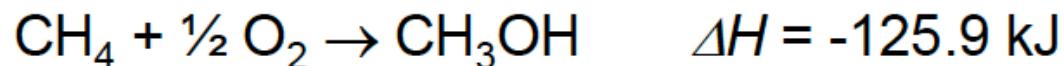
Heat (q) is given off; reaction is **exothermic**
($\Delta H < 0$)



If $\Delta H > 0$; reaction is **endothermic**

Thermochemistry:

Goal is to generate energy (& thus work) via chemistry.



ΔH_f° of CH_4 is $-74.81 \text{ kJ}\cdot\text{mol}^{-1}$

ΔH_f° of $\text{CH}_3\text{OH}_{(g)}$ is $-200.66 \text{ kJ}\cdot\text{mol}^{-1}$

Standard state enthalpies

Standard State (SS): thermodynamically stable state at $P= 1 \text{ atm}$ and at temp T

Standard State (SS): dissolved species = 1 M soln' at $P = 1 \text{ atm}$

Standard State (SS): elements in their stable form at 298.15K

enthalpy = 0

ΔH_f° of a compound is the enthalpy change for the reaction that produces 1 mole of the compound from its elements in their standard states at 298.15K and 1 atm.

Thermochemistry:

Goal is to generate energy (& thus work) via chemistry.

Enthalpies are additive

$$\Delta H_{rxn}(25^{\circ}C) = \sum_{products} \Delta H_f^0 - \sum_{reactants} \Delta H_f^0$$

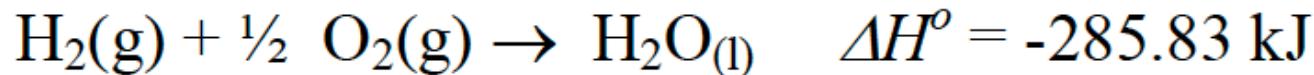
example



$$\Delta H^0 = c\Delta H_f^0(C) + d\Delta H_f^0(D) - a\Delta H_f^0(A) - b\Delta H_f^0(B)$$

Thermochemistry:

Goal is to generate energy (& thus work) via chemistry.



$$\Delta H_f^\circ[\text{H}_2\text{O}_{(\text{l})}] = -285.83 \text{ kJ mol}^{-1}$$

Principle of hydrogen powered vehicles and H₂ storage of energy

Enthalpies are additive



$$\Delta H_{rxn}(25^\circ\text{C}) = \sum_{\text{products}} \Delta H_f^0 - \sum_{\text{reactants}} \Delta H_f^0$$

Thermochemistry:

Goal is to generate energy (& thus work) via chemistry.

Eventually we need to deal with the making and breaking of chemical bonds.

How best to deal with chemical reactivity?

Energetics of individual steps described by bond enthalpies



Bond energies and bond enthalpies related by:

$$\Delta H = \Delta E + \Delta(PV)$$

Bond enthalpies & chemical reactivity are related: weaker bonds are easier to break and thus more reactive (in general)

	Bond Broken	$\Delta H^\circ (\text{kJ mol}^{-1})$
Methane	$\text{CH}_4 \rightarrow \cdot\text{CH}_3 + \text{H}\cdot$ (primary C-H bond)	439
Ethane	$\text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\cdot + \text{H}\cdot$ (secondary C-H bond)	421
Propane	$(\text{CH}_3)_2\text{CH}_2 \rightarrow (\text{CH}_3)_2\text{CH}\cdot + \text{H}\cdot$ (secondary C-H bond)	413
Isobutane	$(\text{CH}_3)_3\text{CH} \rightarrow (\text{CH}_3)_3\text{C}\cdot + \text{H}\cdot$	400

(Isobutane most reactive.)