Chapter 16

Energy

Thermodynamics

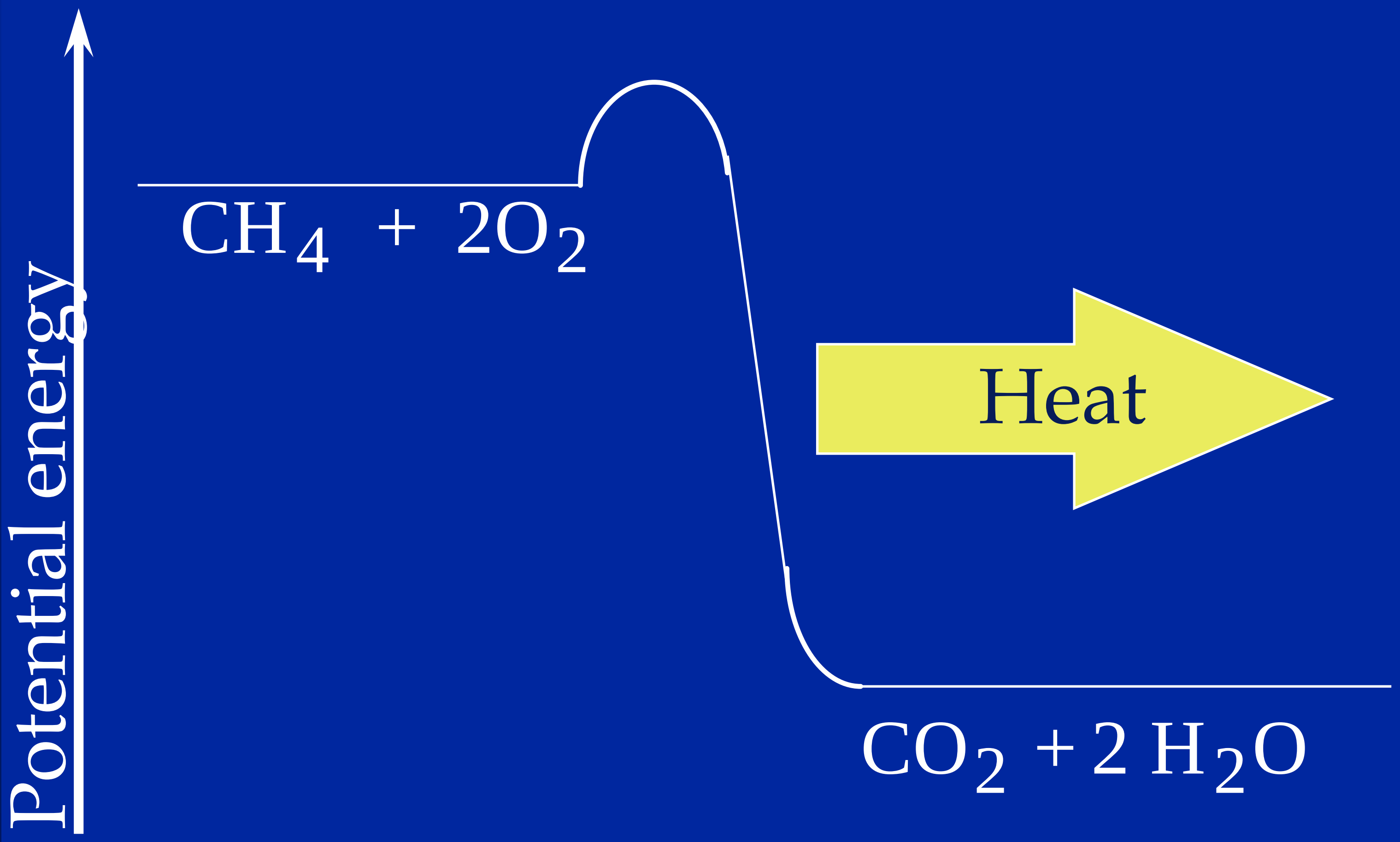
Energy is...

- The ability to do work.
- Conserved.
- made of heat and work.
- a state function.
- independent of the path, or how you get from point A to B.
- Work is a force acting over a distance.
- Heat is energy transferred between objects because of temperature difference.

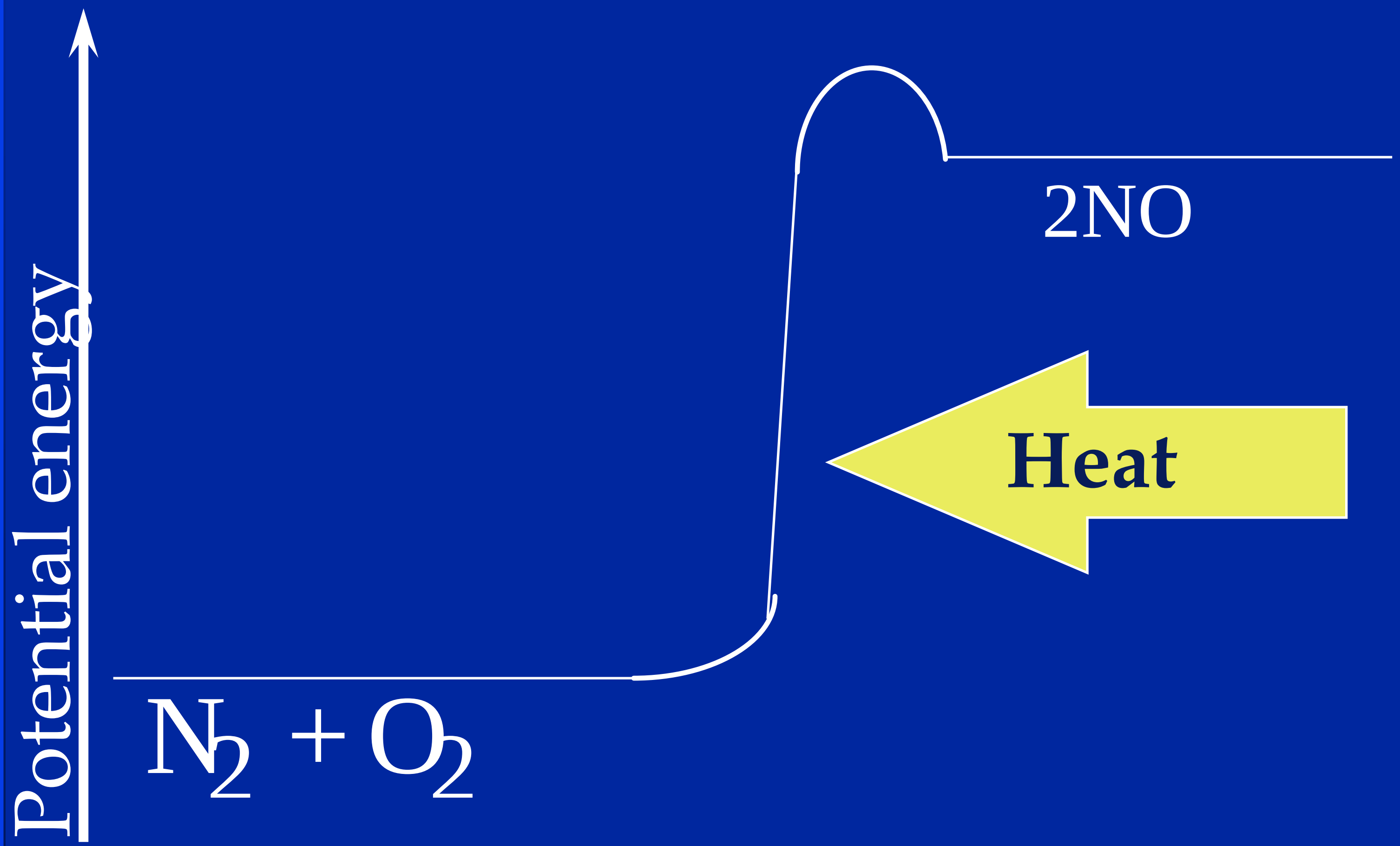
The universe

- is divided into two halves.
- the system and the surroundings.
- The system is the part you are concerned with.
- The surroundings are the rest.
- Exothermic reactions release energy to the surroundings.
- Endo thermic reactions absorb energy from the surroundings.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{Heat}$$



$N_2 + O_2 + heat \rightarrow 2NO$

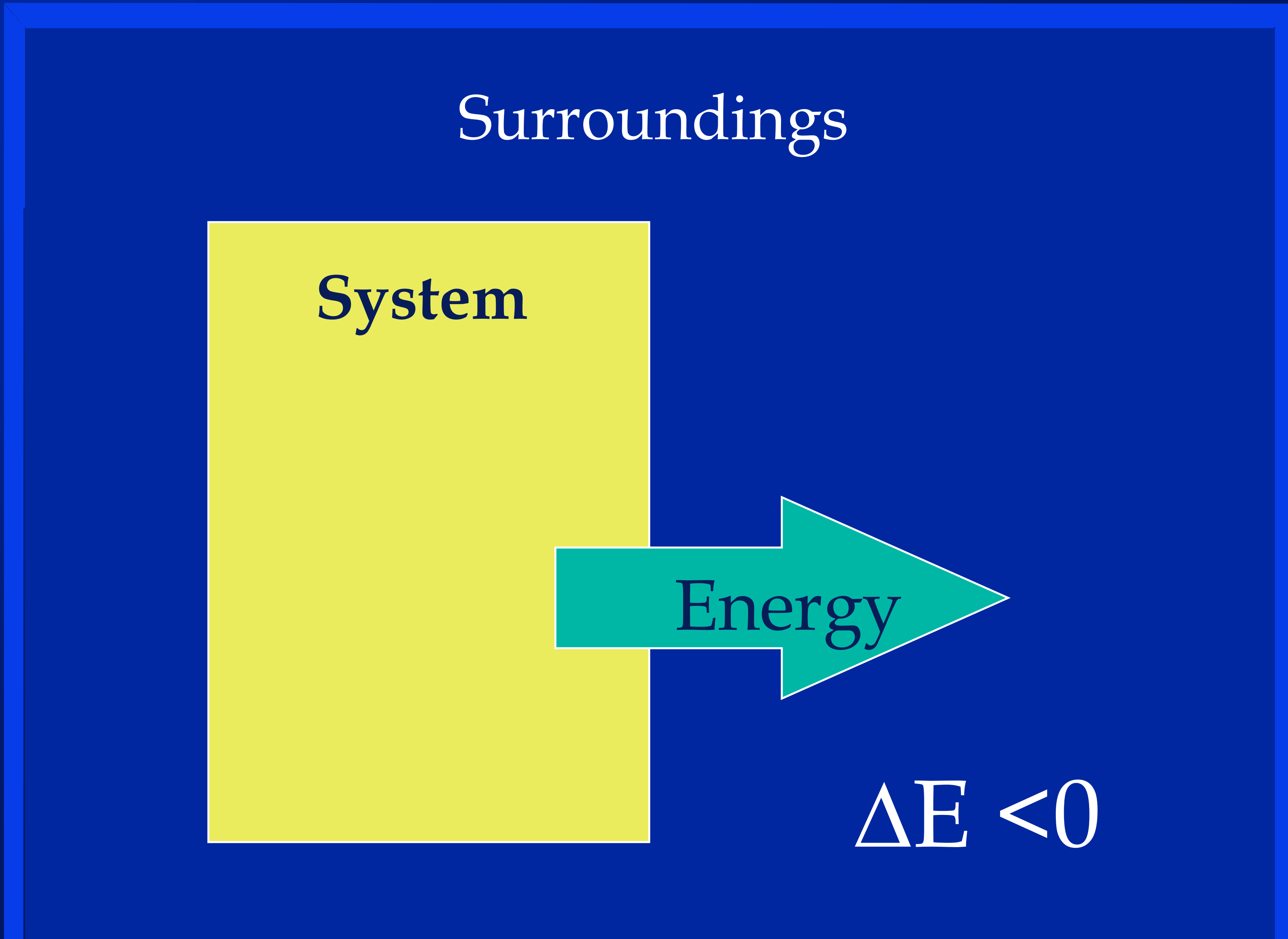


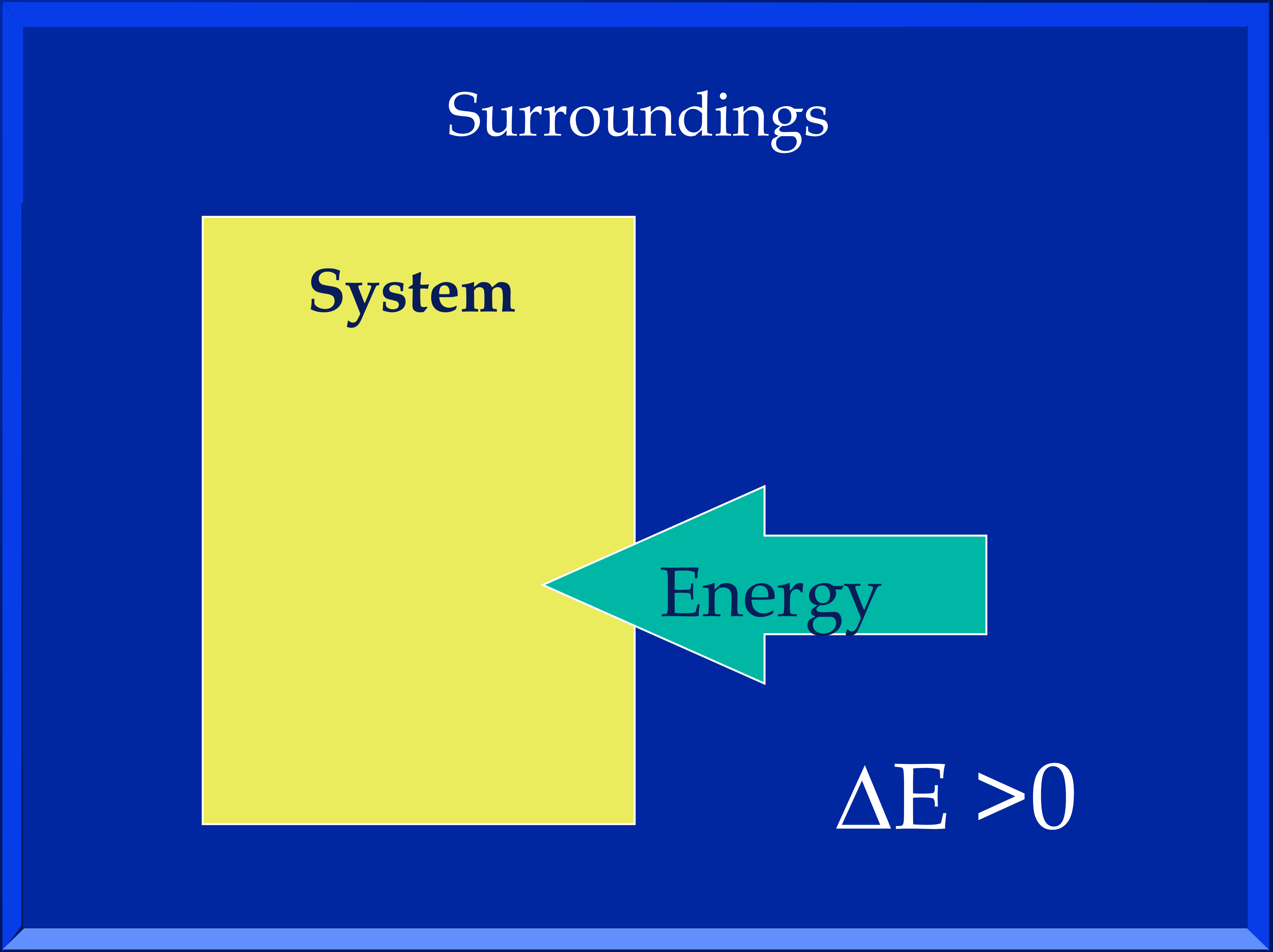
Direction

- Every energy measurement has three parts.

1. A unit (Joules of calories).
2. A number how many.
3. and a sign to tell direction.

- negative - exothermic
- positive- endothermic


Surroundings
System
Energy
ΔE <0


Surroundings
System
Energy
ΔE >0

Same rules for heat and work

- Heat given off is negative.
- Heat absorbed is positive.
- Work done by system on surroundings is positive.
- Work done on system by surroundings is negative.
- Thermodynamics- The study of energy and the changes it undergoes.

First Law of Thermodynamics

- The energy of the universe is constant.
- Law of conservation of energy.
- q = heat
- w = work
- $\Delta E = q + w$
- Take the systems point of view to decide signs.

What is work?

- Work is a force acting over a distance.
- $w = F \times \Delta d$
- $P = F / \text{area}$
- $d = V / \text{area}$
- $w = (P \times \text{area}) \times \Delta (V / \text{area}) = P\Delta V$
- Work can be calculated by multiplying pressure by the change in volume at constant pressure.
- units of liter - atm   L-atm

Work needs a sign

- If the volume of a gas increases, the system has done work on the surroundings.
- work is negative
- $w = - P\Delta V$
- Expanding work is negative.
- Contracting, surroundings do work on the system w is positive.
- 1 L atm = 101.3 J

Examples

- What amount of work is done when 15 L of gas is expanded to 25 L at 2.4 atm pressure?
- If 2.36 J of heat are absorbed by the gas above. what is the change in energy?
- How much heat would it take to change the gas without changing the internal energy of the gas?

Enthalpy

- abbreviated H
- $H = E + PV$ (that's the definition)
- at constant pressure.
- $\Delta H = \Delta E + P\Delta V$
- the heat at constant pressure q_p can be calculated from
- $\Delta E = q_p + w = q_p - P\Delta V$
- $q_p = \Delta E + P \Delta V = \Delta H$

Calorimetry

- Measuring heat.
- Use a calorimeter.
- Two kinds
- Constant pressure calorimeter (called a coffee cup calorimeter)
- heat capacity for a material, C is calculated
- C= heat absorbed/ $\Delta T = \Delta H / \Delta T$
- specific heat capacity = C/mass

Calorimetry

- molar heat capacity = C/moles
- heat = specific heat x m x ΔT
- heat = molar heat x moles x ΔT
- Make the units work and you've done the problem right.
- A coffee cup calorimeter measures ΔH.
- An insulated cup, full of water.
- The specific heat of water is 1 cal/g^{o}C
- Heat of reaction= ΔH = sh x mass x ΔT

Examples

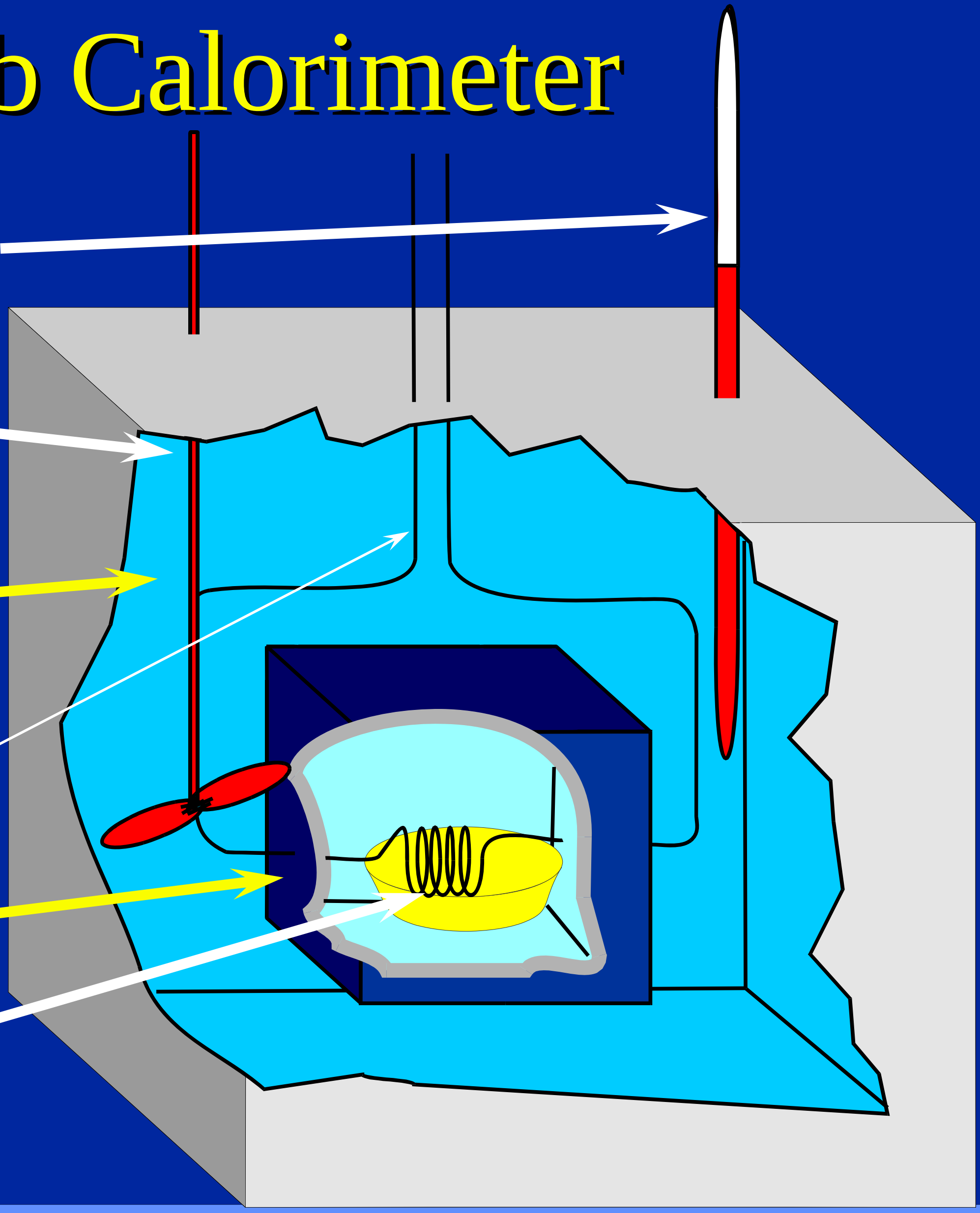
- The specific heat of graphite is 0.71 J/g°C. Calculate the energy needed to raise the temperature of 75 kg of graphite from 294 K to 348 K.
- A 46.2 g sample of copper is heated to 95.4°C and then placed in a calorimeter containing 75.0 g of water at 19.6°C. The final temperature of both the water and the copper is 21.8°C. What is the specific heat of copper?

Calorimetry

- Constant volume calorimeter is called a bomb calorimeter.
- Material is put in a container with pure oxygen. Wires are used to start the combustion. The container is put into a container of water.
- The heat capacity of the calorimeter is known and tested.
- Since $\Delta V = 0$, $P\Delta V = 0$, $\Delta E = q$

Bomb Calorimeter

- thermometer
- stirrer
- full of water
- ignition wire
- Steel bomb
- sample

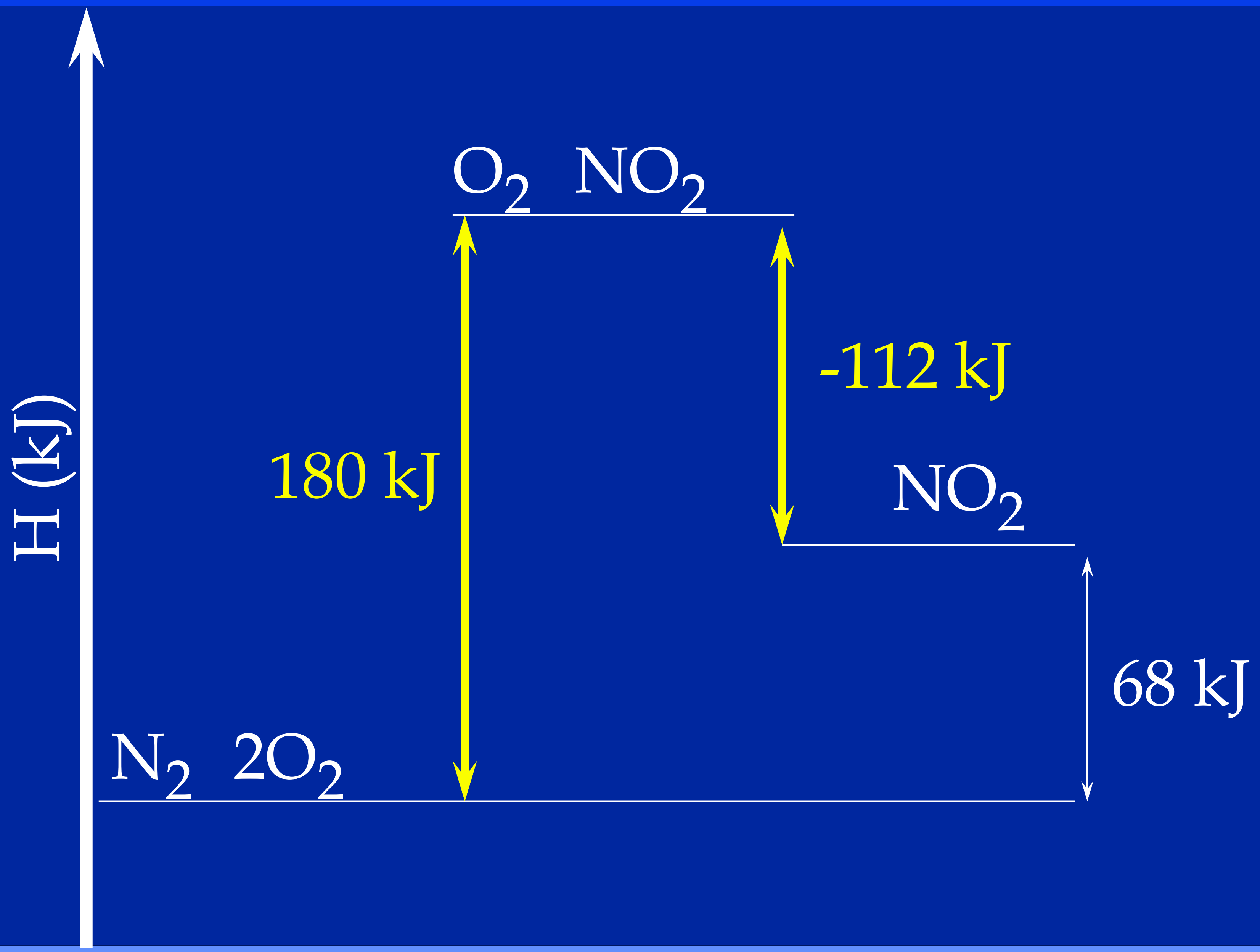


Properties

- intensive properties not related to the amount of substance.
- density, specific heat, temperature.
- Extensive property - does depend on the amount of stuff.
- Heat capacity, mass, heat from a reaction.

Hess's Law

- Enthalpy is a state function.
- It is independent of the path.
- We can add equations to to come up with the desired final product, and add the ΔH
- Two rules
- If the reaction is reversed the sign of ΔH is changed
- If the reaction is multiplied, so is ΔH



H (kJ)
O2 NO2
180 kJ
-112 kJ
NO2
68 kJ
N2 2O2

Standard Enthalpy

- The enthalpy change for a reaction at standard conditions (25^{o}C, 1 atm , 1 M solutions)
- Symbol ΔH^o
- When using Hess's Law, work by adding the equations up to make it look like the answer.
- The other parts will cancel out.

Example

- Given

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$$

ΔH^o= -1300. kJ

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

ΔH^o= -394 kJ

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$

ΔH^o= -286 kJ

calculate ΔH^o for this reaction

$$2C(s) + H_2(g) \rightarrow C_2H_2(g)$$

Example

Given

$O_2(g) + H_2(g) \rightarrow 2OH(g)$ $\Delta H^o = +77.9kJ$

$O_2(g) \rightarrow 2O(g)$ $\Delta H^o = +495\ kJ$

$H_2(g) \rightarrow 2H(g)$ $\Delta H^o = +435.9kJ$

Calculate ΔH^o for this reaction

$O(g) + H(g) \rightarrow OH(g)$

Standard Enthalpies of Formation

- Hess's Law is much more useful if you know lots of reactions.
- Made a table of standard heats of formation. The amount of heat needed to for 1 mole of a compound from its elements in their standard states.
- Standard states are 1 atm, 1M and 25ºC
- For an element it is 0
- There is a table in Appendix 4 (pg A22)

Standard Enthalpies of Formation

- Need to be able to write the equations.
- What is the equation for the formation of NO_2 ?
- $\frac{1}{2}N_2\,(g) + O_2\,(g) \rightarrow NO_2\,(g)$
- Have to make one mole to meet the definition.
- Write the equation for the formation of methanol CH_3OH.

Since we can manipulate the equations

- We can use heats of formation to figure out the heat of reaction.
- Lets do it with this equation.
- $C_2H_5OH + 3O_2(g) \rightarrow 2CO_2 + 3H_2O$
- which leads us to this rule.

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