■ **Theme Music:**
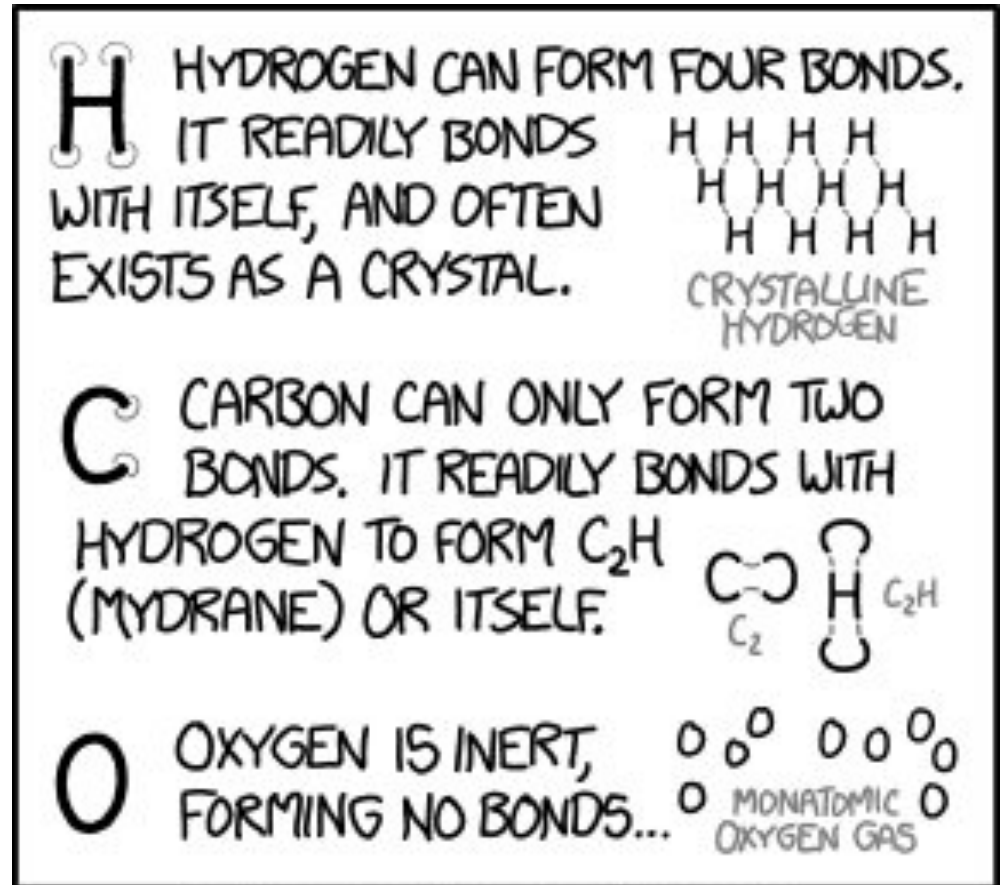**Phish**
   I am hydrogen

■ **Cartoon:**
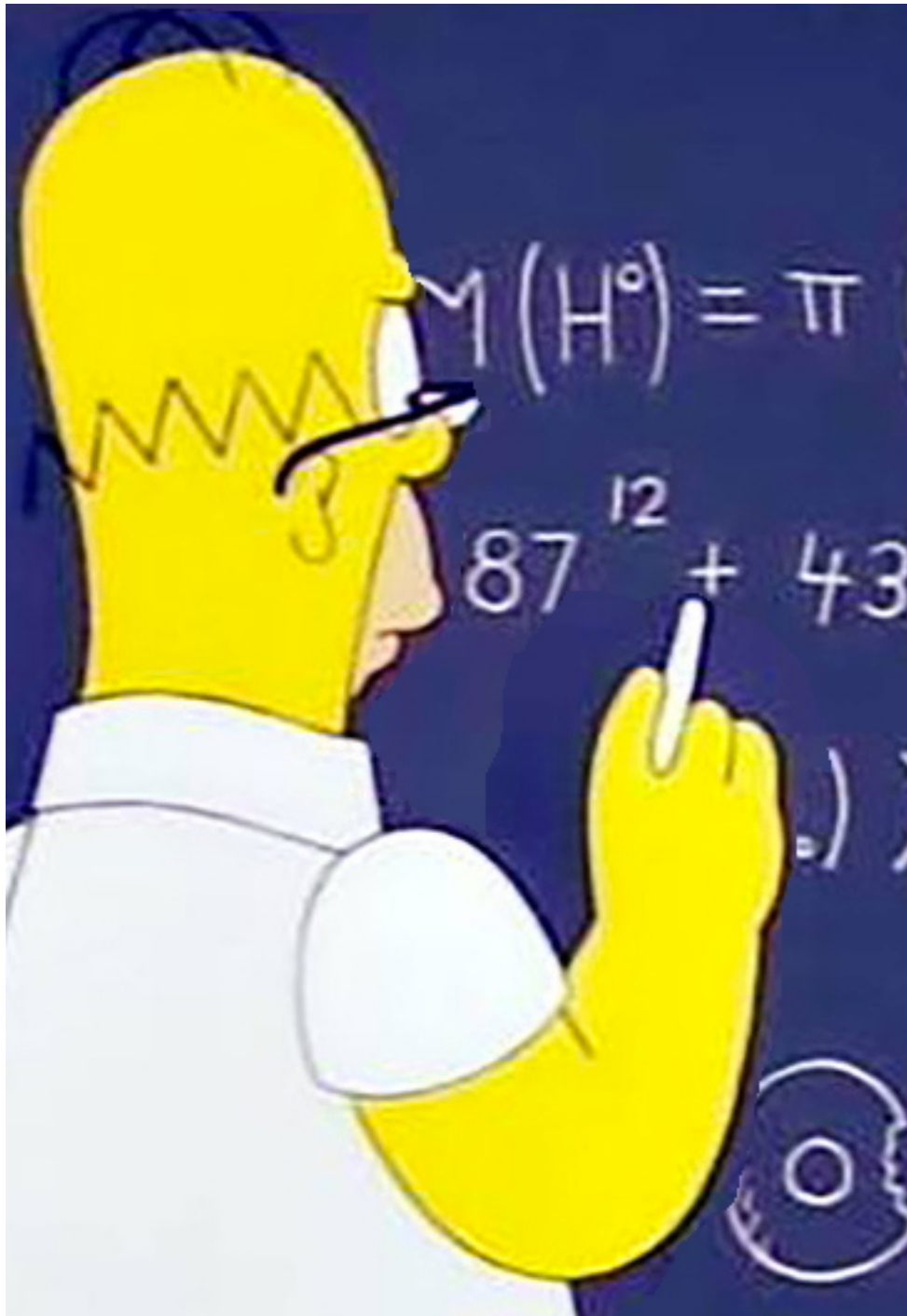**Randall Munroe**
   xkcd

Outline

■ Quiz 1

■ Energy conservation with chemical and thermal terms

■ Enthalpy

■ Examples

Clickers still not registered correctly

- Fish
- Hoang
- Saravia

How many have not yet done the paper survey?

Do it in Course Center this week!

Energy conservation with chemical reactions

$$\Delta U_{\text{internal}} = \Delta U_{\text{thermal}} + \Delta U_{\text{chemical}}$$

Physics 132

Energy conservation with chemical reactions: 1

■ Consider the collision of two molecules in isolation $A + B \rightarrow A + B$

$$K_A + K_B + U_{AB} = \text{constant}$$

■ If the initial and final states both have the two molecules far apart, $U_{AB} \sim 0$.

$$K_A + K_B = \text{constant}$$

We have to refine our definition of "internal energy"

■ When we talked about molecular motion last term, we ignored the possibility of chemical reactions.

■ "Internal energy" was the sum of the KE of the molecules (for a gas) or the sum of the KE and (interaction) PE of the molecules (for a liquid or solid).

■ If chemical reactions can take place, we have to take changes in binding energy into account.

■ Define: U_{thermal} = sum of KE (and PE) of molecules
U_{chemical} = sum of BEs of molecules
$U_{\text{internal}} = U_{\text{thermal}} + U_{\text{chemical}}$

Energy conservation with chemical reactions: 2

■ Consider the reaction of two molecules in isolation $A + B \rightarrow C + D$

$$\left(K_A + E_A\right) + \left(K_B + E_B\right) + U_{AB} = \left(K_C + E_C\right) + \left(K_D + E_D\right) + U_{CD}$$

■ If the initial and final states both have the two molecules far apart, $U_{AB} \sim U_{CD} \sim 0$.

$$\left(K_A + E_A\right) + \left(K_B + E_B\right) = \left(K_C + E_C\right) + \left(K_D + E_D\right)$$

Note: The "E"'s here are **molecular internal energies** and are <u>negative</u> since the molecules are bound. The (positive) **bond energies** from chemistry are given by $\mathcal{E} = -E > 0$.

2/1

Energy conservation
with chemical reactions: 3

■ Consider as gas consisting of a mixture of two molecules A, and B that are colliding with each other but not reacting.

■ In a gas, most of the time any two molecules are far enough apart that their mutual PE, U_{AB}, can be neglected.

$$\sum_{\text{all A mols.}} K_A + \sum_{\text{all B mols.}} K_B = \text{constant}$$

■ This is the thermal energy of the gas, U_{thermal}

Energy conservation with chemical reactions: 4

■ Consider the reaction of a gas of A and B molecules that react (fully) to C and D molecules $A + B \rightarrow C + D$

– If the initial and final states both have the two molecules far apart, $U_{AB} \sim U_{CD} \sim 0$.

$$\sum_A \left(K_A + E_A \right) + \sum_B \left(K_B + E_B \right) = \sum_C \left(K_C + E_C \right) + \sum_D \left(K_D + E_D \right)$$

■ Let's make sense of this (and connect back to chemistry) by rearranging.

Let's do the math!

$$\sum_A \left(K_A + E_A\right) + \sum_B \left(K_B + E_B\right) = \sum_C \left(K_C + E_C\right) + \sum_D \left(K_D + E_D\right)$$

$$\left(\sum_{AB}\left(K_A + K_B\right)\right) + \left(\sum_{AB}\left(E_A + E_B\right)\right) = \left(\sum_{CD}\left(K_C + K_D\right)\right) + \left(\sum_{CD}\left(E_C + E_D\right)\right)$$

$$U^i_{thermal} + U^i_{chemical} = U^f_{thermal} + U^f_{chemical}$$

$$U^i_{chemical} - U^f_{chemical} = U^f_{thermal} - U^i_{thermal}$$

$$-\Delta U_{chemical} = \Delta U_{thermal}$$

$$\Delta U_{thermal} + \Delta U_{chemical} = 0$$

Reading questions

■ Is it a good idea to always correlate a positive change in enthalpy to be a endothermic reaction, and a negative change in enthalpy to be a exothermic reaction, or is this idea specific to only chemical reactions, not physics?

■ I often find myself confusing enthalpy with entropy. Are there any "tricks" to keep them separate?

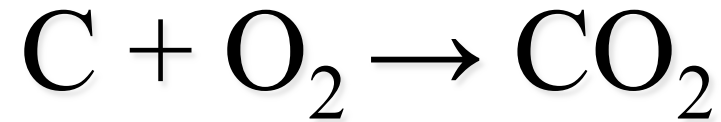■ Is an exothermic reaction always spontaneous?

Consider the reaction
$C + O_2 \rightarrow CO_2$
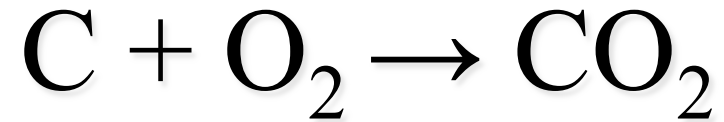
What is the **magnitude** of the change in the chemical energy for this reaction (per reaction)?
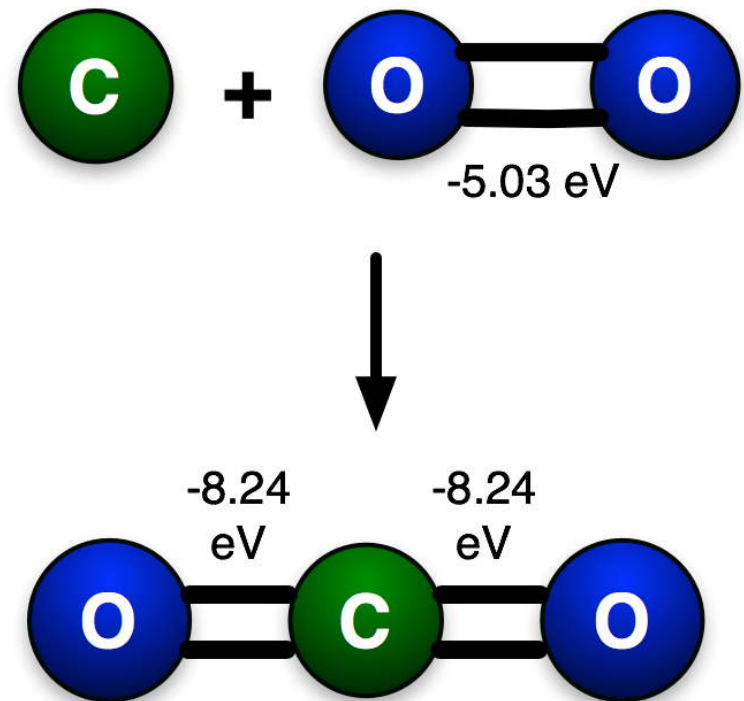
A. 8.24 eV

B. 3.21 eV

C. 11.45 eV

D. 16.48 eV
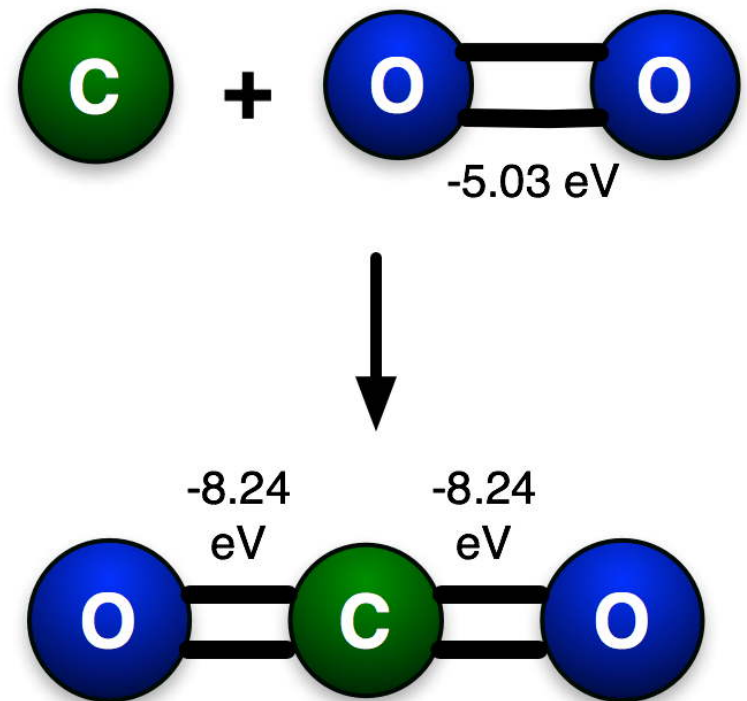
C + O O
-5.03 eV

-8.24 eV   -8.24 eV

O   C   O
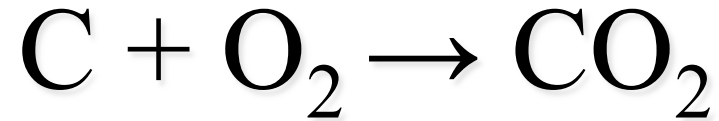
Consider the reaction
$C + O_2 \rightarrow CO_2$

What is the **sign** of the change in the chemical energy for this reaction (per reaction)?

A. Positive

B. Negative

C. Cannot be determined
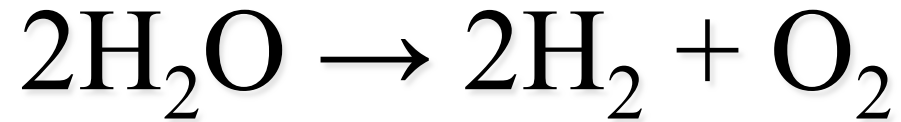
Consider the reaction
$$C + O_2 \rightarrow CO_2$$

If a mixture of carbon and oxygen gas undergoes the reaction at the right, what is the **sign** of the change in the **thermal** energy?
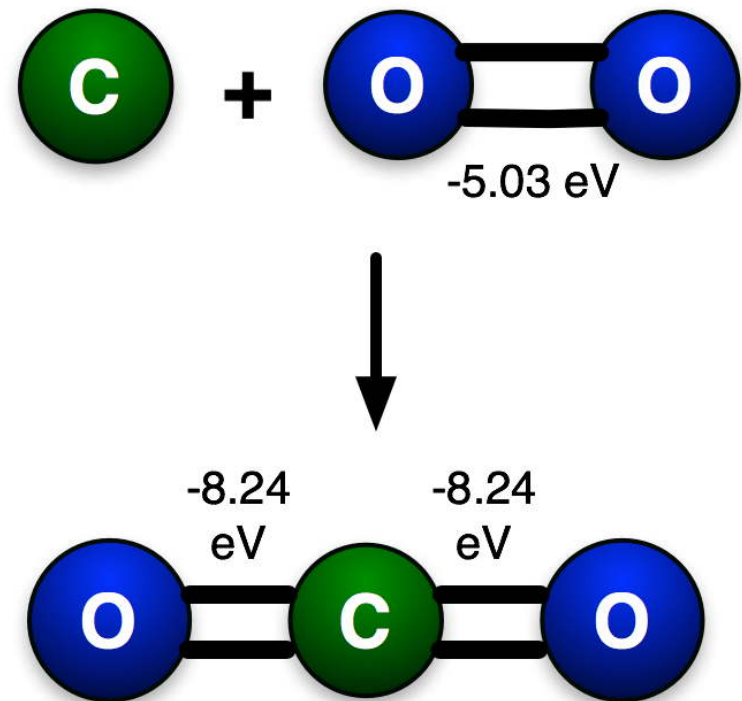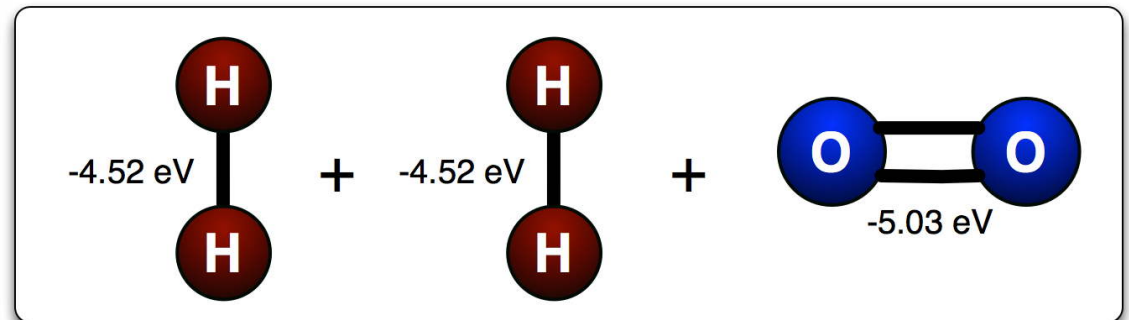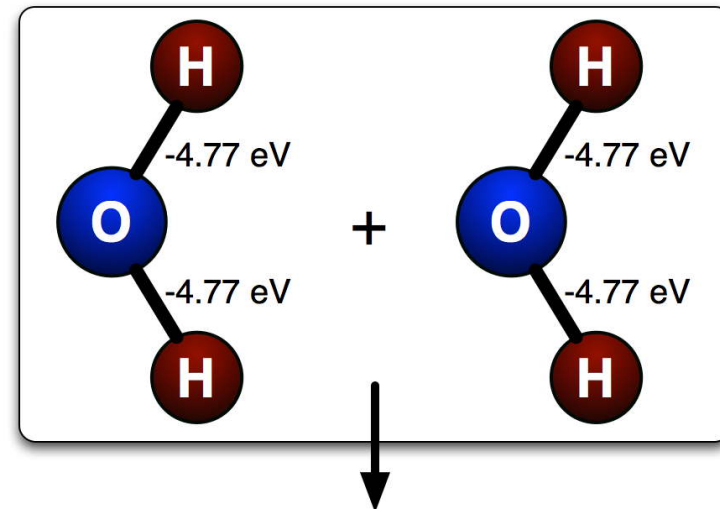
A. Positive

B. Negative

C. Cannot be determined

-5.03 eV

-8.24 eV   -8.24 eV

Does this make sense with your everyday experiences?
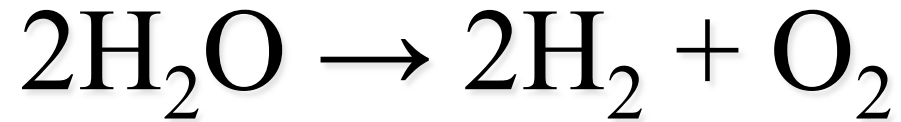
Consider the reaction
$2H_2O \rightarrow 2H_2 + O_2$

What is the **sign** of the change in the chemical energy for this reaction (per reaction)?
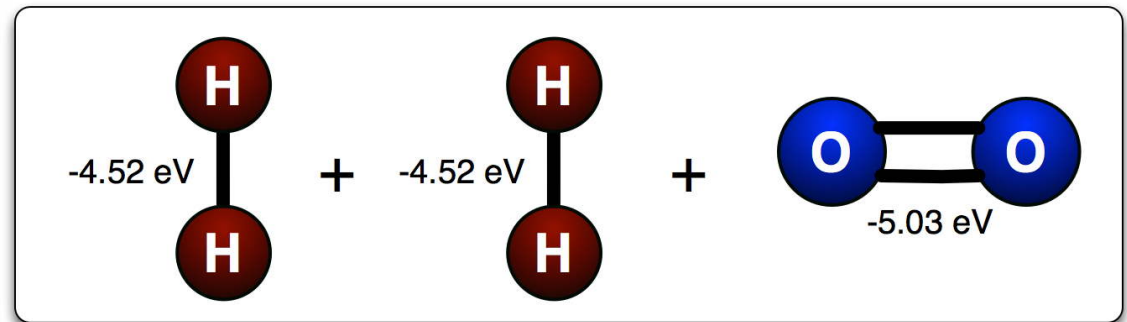
A. Positive

B. Negative

C. Cannot be determined

H   -4.77 eV   H   -4.77 eV
O   +   O
-4.77 eV   -4.77 eV
H   H

H   -4.52 eV   +   H   -4.52 eV   +   O   O
                                            -5.03 eV
H   H

2/1/16   Physic

Does this make sense with your everyday experiences?

Consider the reaction
$2H_2O \rightarrow 2H_2 + O_2$

What is the **magnitude** of the change in the chemical energy for this reaction (per reaction)?
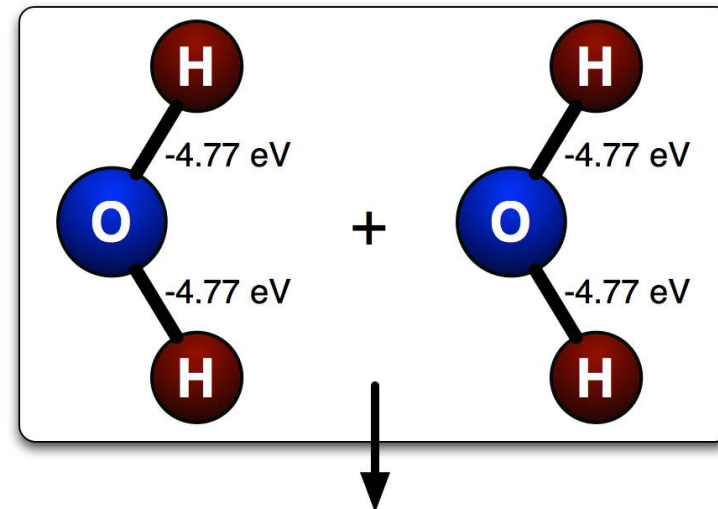
Changing our assumptions

■ In each of our examples above,
we imagined a gas (or two gases) reacting
in a closed container.

■ While this is plausible – and relevant for many
mechanical engineering example (the piston
in the engine of an automobile, for example)
in most biological situations,
reactions occur at a constant pressure
(in the open), not at a constant volume.

■ What does that do to our energy conservation?

Why we need enthalpy

■ When chemicals react in the open, they do so in a pressurized environment. They will expand or contract in order to maintain their pressure.

■ In so doing, they will either do work on their environment or have work done on them.

■ This will change the energy balance equation.

Recap: Partial pressure

■ In a gas, pressure is produced by molecules hitting any surface introduced into it.

$$pV = Nk_BT \qquad p = nk_BT \qquad n = \frac{N}{V}$$

■ If T is constant, p is directly proportional to n – the number density.

■ Mixing many gases together, the pressure just adds the result of each molecule hitting the wall.

■ The total p is the sum of the *partial pressures*.
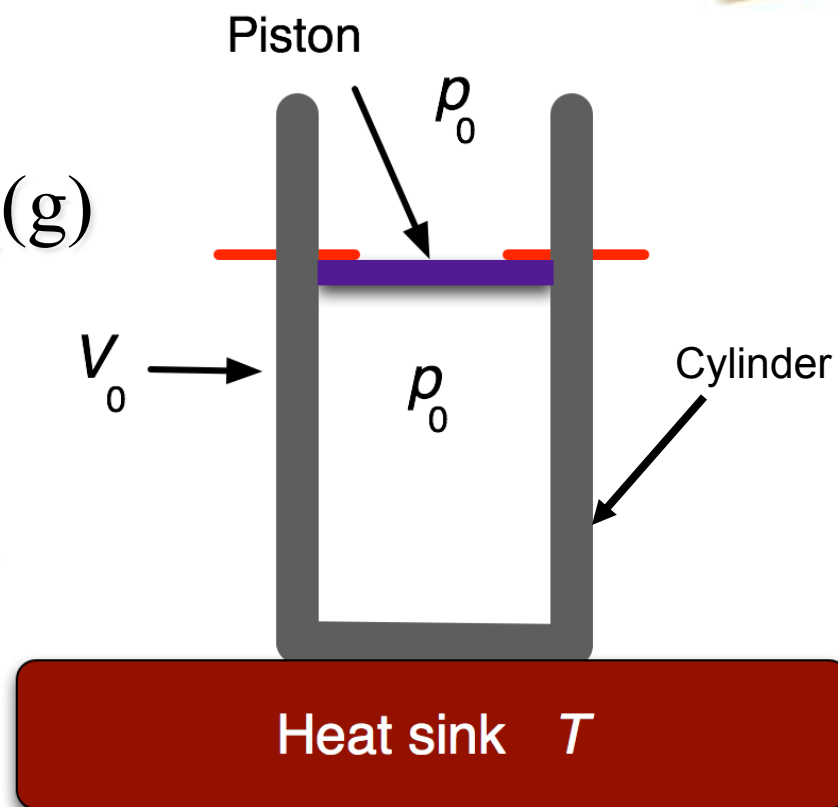
$$p = p_1 + p_2 + ... = (n_1 + n_2 + ...)k_BT$$

Suppose we have a fixed volume, V, containing 1 mole of NO_2 at pressure p.

Piston

p_0

Suppose all the

$$2NO_2(g) \rightarrow N_2(g) + 2O_2(g)$$

If T remains the same, what would happen to p?

$V_0 \longrightarrow$

p_0

Cylinder

A. It would remain the same.

B. It would be 1.5 X as big.

C. It would double.

Heat sink T

D. It would decrease but not by half.

E. It would increase but not double.

If we pull the pins holding the piston in place, the gases would expand until the pressures are equal. What would the new volume be?
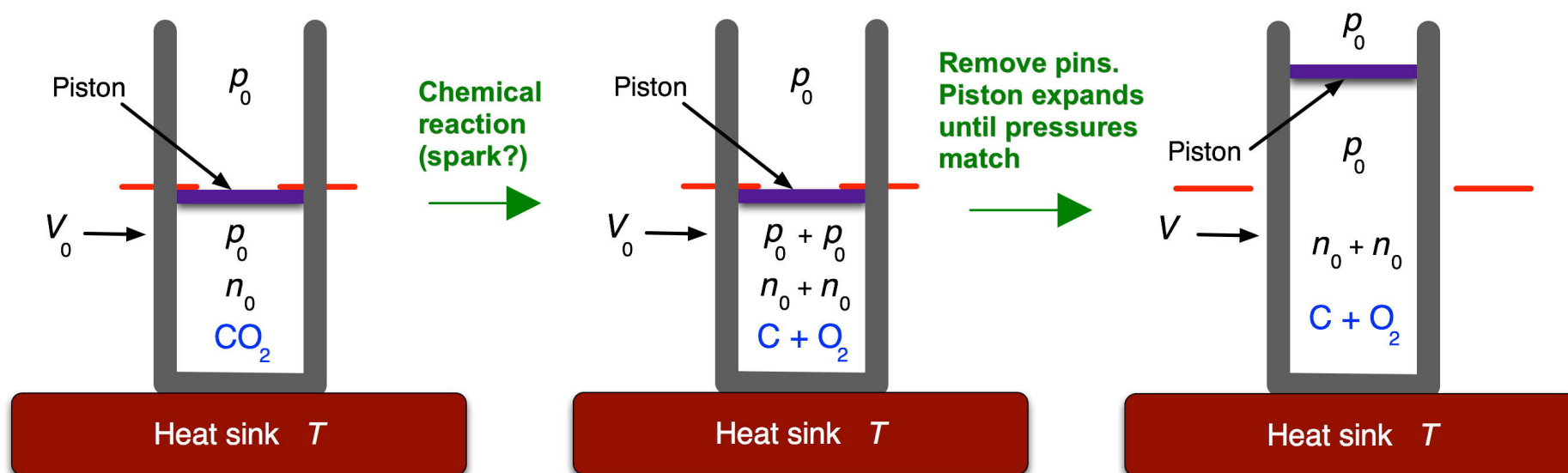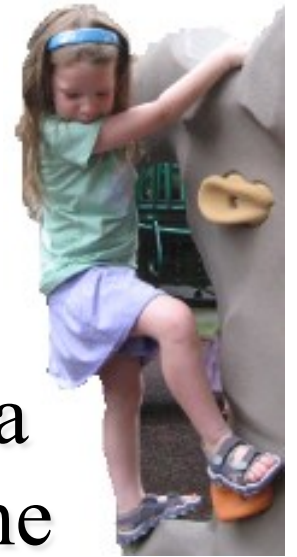
A. V_0

B. $2/3\ V_0$

C. $3/2\ V_0$

D. Between A and B

E. Between A and C
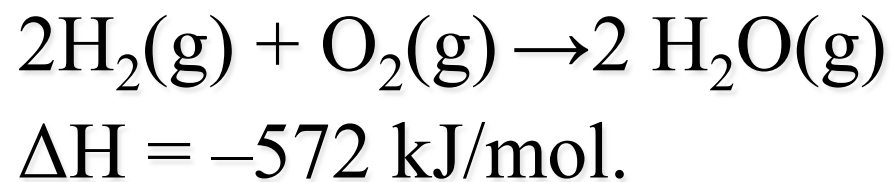
Foothold ideas: Enthalpy

■ When a chemical reaction takes place at a **constant T and p** (especially in a gas), the gas may have to do work to "make room for itself". This affects the energy balance between the chemical energy change and the thermal energy change.

■ Define *enthalpy, H*

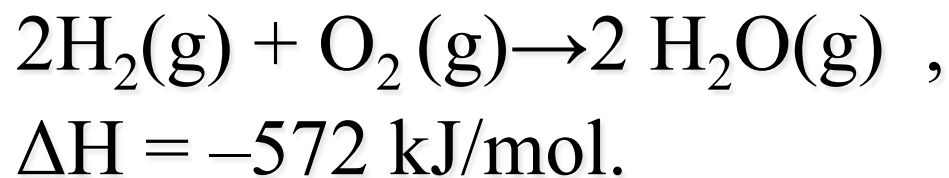$$\Delta H = \Delta U_{thermal} + \Delta U_{chemical} + p\Delta V$$

For this reaction

$$2H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$$
$$\Delta H = -572 \text{ kJ/mol.}$$

is $p\Delta V$

1. positive,
2. negative,
3. zero?

For this reaction (occurring in a vessel at STP)

$$2H_2(g) + O_2(g) \rightarrow 2 H_2O(g) \ ,$$
$$\Delta H = -572 \text{ kJ/mol.}$$

is the magnitude of the internal energy change
($|\Delta U_{int}|$)

1. Greater than 572 kJ/mol?
2. Less than 572 kJ/mol?
3. Equal to 572 kJ/mol?

(Hint: Estimate the value of $p\Delta V$)