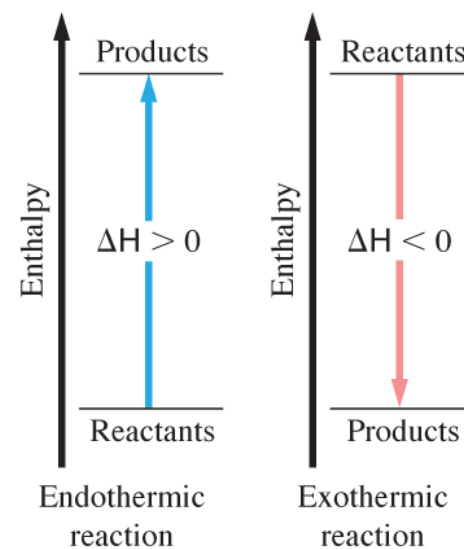
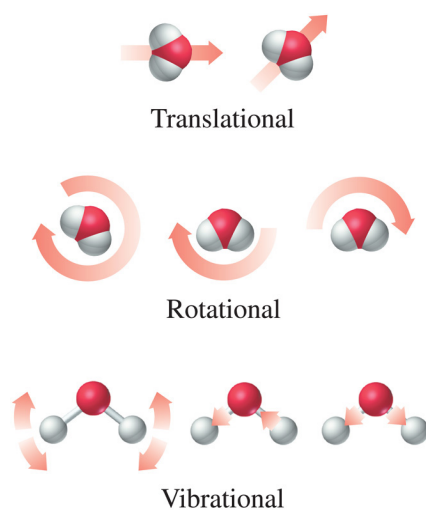
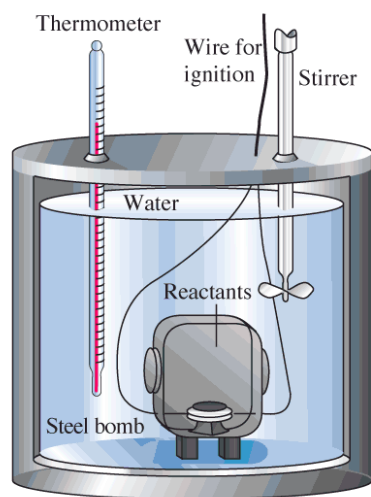


# Chapter 5: Thermochemistry

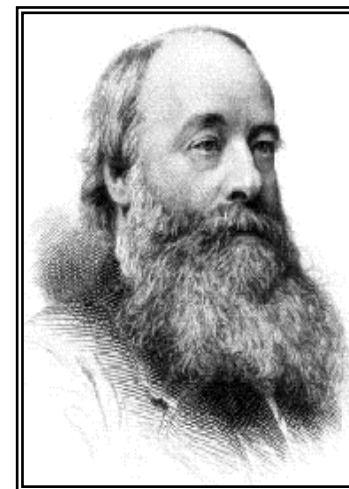


# Conversion of Energy

The capacity to do \_\_\_\_\_ or to produce \_\_\_\_\_.



# Units of Energy

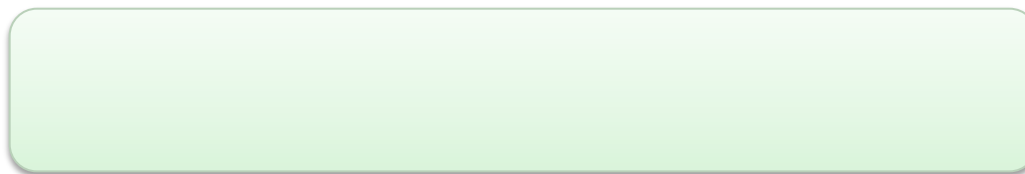


James Joule, 1818-1889

- SI Unit for energy is the **joule, J**:

$$1 \text{ J} = 1 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}$$

- We sometimes use the calorie instead of the joule:



- A nutritional Calorie:  $1 \text{ Cal} = 1000 \text{ cal} = 1 \text{ kcal}$
- New units for R:  **$R = 8.3145 \text{ J/mol} \cdot \text{K}$**



# Some Terminology in Thermochemistry

- **System:** part of the universe under observation
- **Surroundings:** the rest of the universe

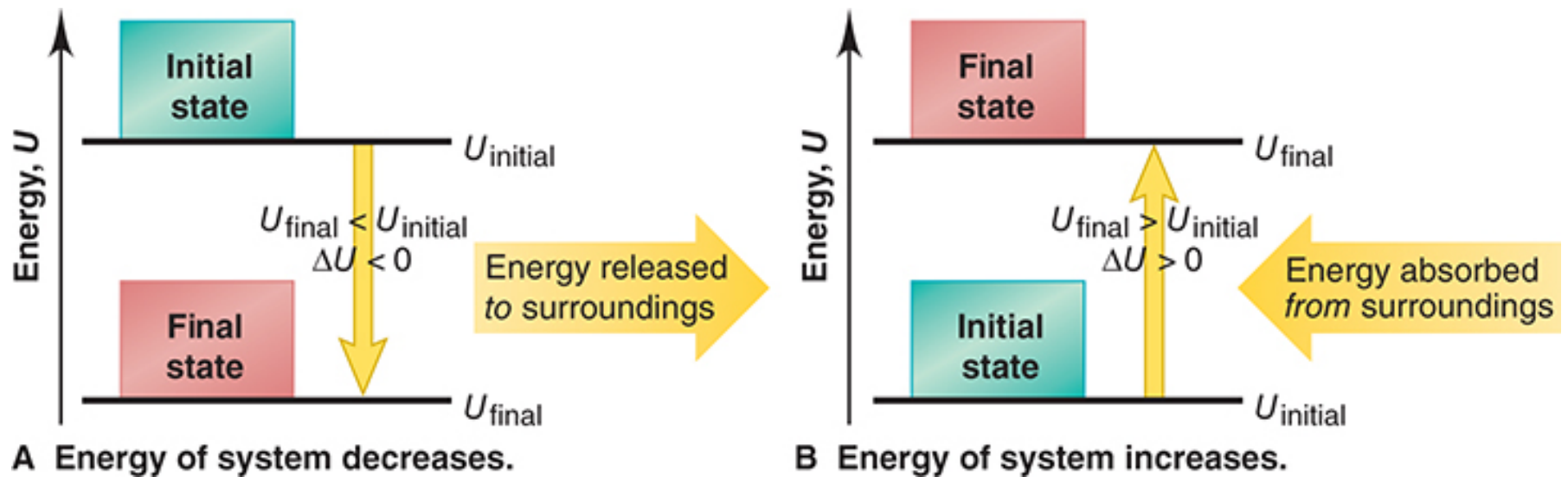
Universe = System + Surroundings



# More terminology...

- **INTERNAL ENERGY, U:** the sum of all microscopic energies of a thermodynamic system

$$\Delta U =$$



# Energy Transfer

## 1. HEAT ( $q$ )

- transfer of thermal energy from a hot object to a cold object
- during this transfer, the temperature or the phase of the system (or both) may change

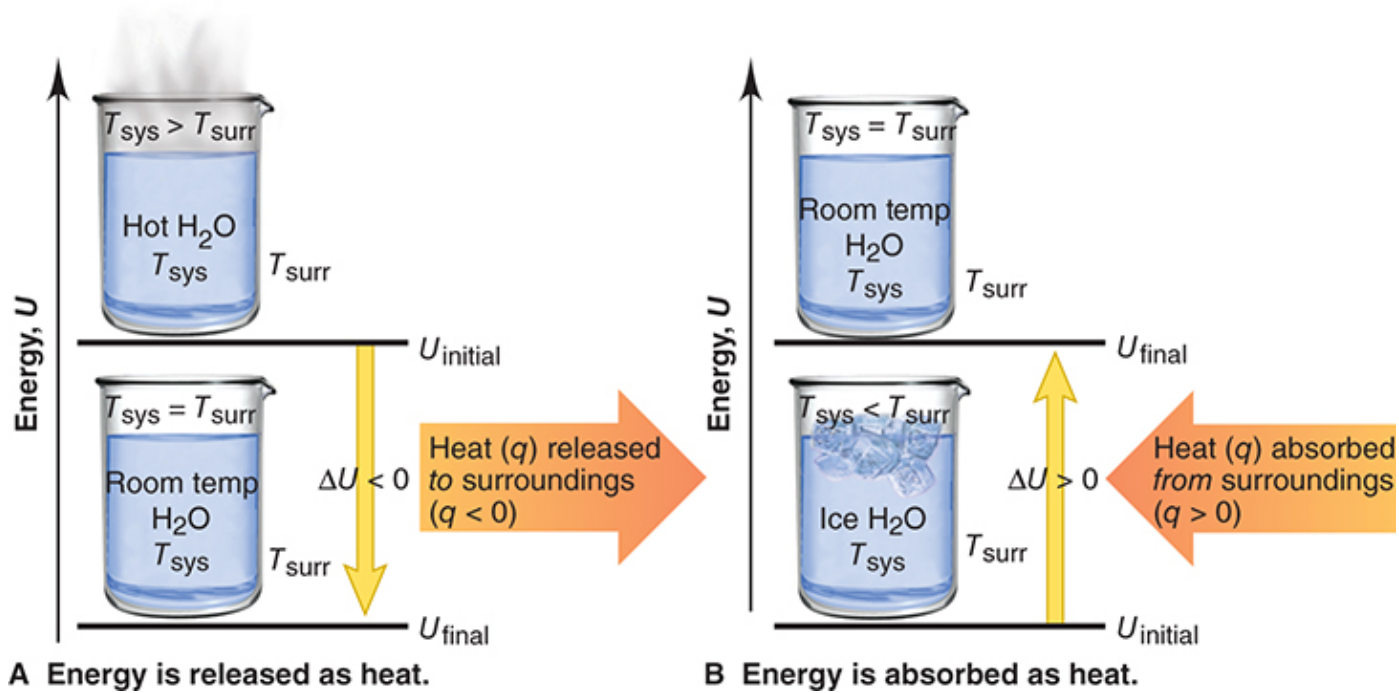
If the system *absorbs* heat, then  $q$  is \_\_\_\_\_

If the system *loses* heat, then  $q$  is \_\_\_\_\_



# Energy Transfer

## 1. HEAT ( $q$ )



# Transfer of energy

## 2. WORK, $W$ :

- a force acting on a given distance
- chemical reactions: changes in volume (gas expansion/contraction)

If the surroundings do work on the system,  $W$  is \_\_\_\_\_

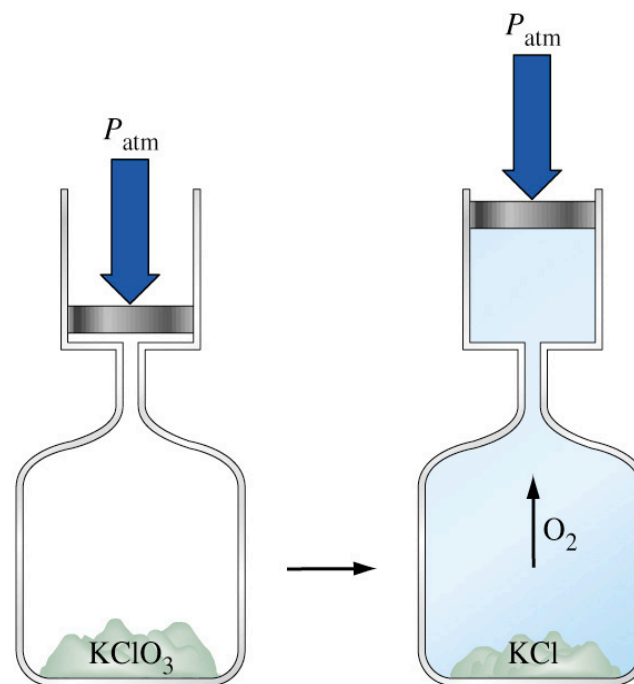
If the system does work on the surroundings,  $W$  is \_\_\_\_\_



# Your Turn...

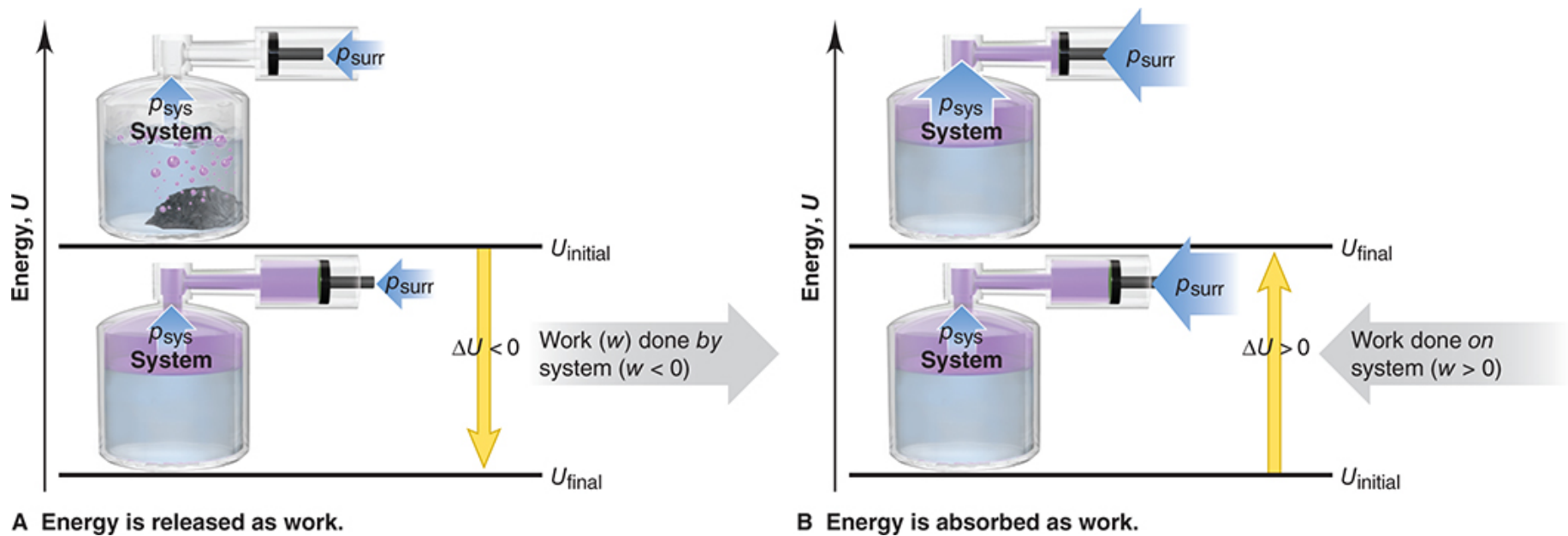
When potassium chlorate decomposes it produces oxygen gas. From the system's point of view (which is the convention),  $W$  is

- A. Positive
- B. Negative
- C. Zero
- D. I'm not sure



# Transfer of energy

## 2. WORK, $w$ :



# The First Law of Thermodynamics

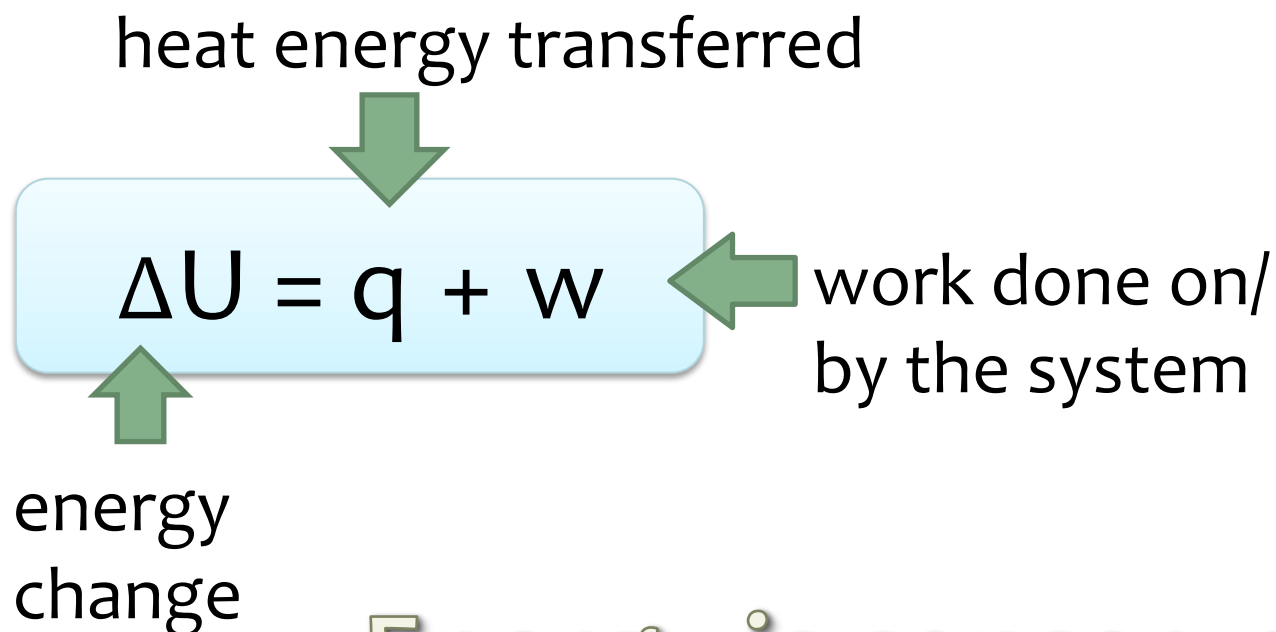
- A system contains only internal energy
- The transfer of heat or work are only observed during a change in the system ( $\Delta U$ )

**“Energy is neither created nor destroyed, only transferred”**

$$\Delta U_{\text{universe}} = \Delta U_{\text{sys}} + \Delta U_{\text{surr}}$$



# The First Law of Thermodynamics



Energy is conserved!

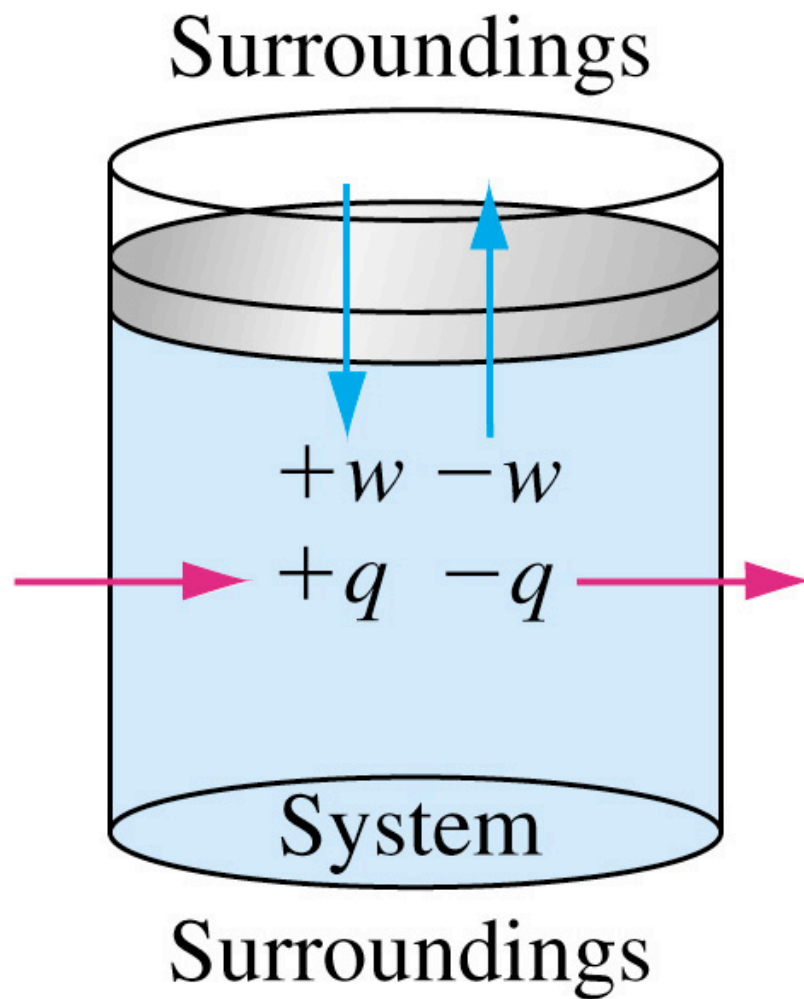


# The First Law of Thermodynamics

Reactants  $\rightarrow$  Products

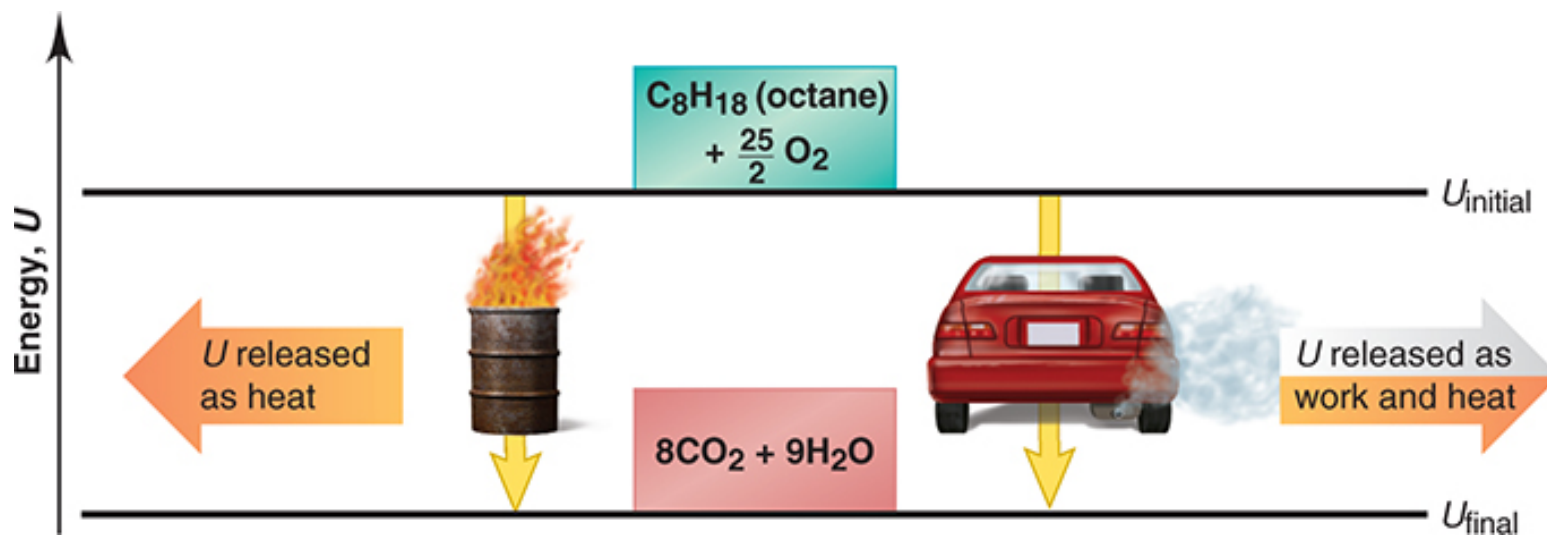
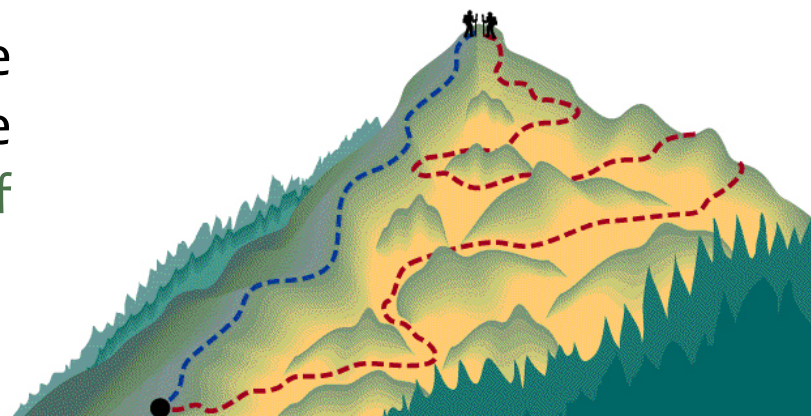
$$\Delta U = U_2 - U_1$$

$$\Delta U = q + W$$



# State Functions

- a **state function** is a property of the system that is determined by the state of the system, independent of how the system got to that state.



# Work, W

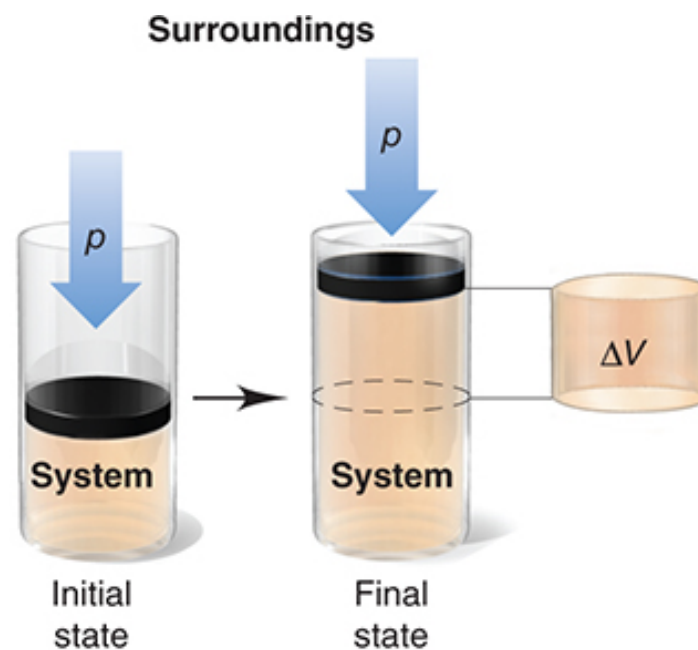
- chemical reactions can also carry out work:
  - electrochemical work by redox chemistry (next year!)
  - PV work by expansion/contraction of a gas

$$W = F \times d \quad \text{and} \quad P = \frac{F}{A}$$

$$W = P \times A \times d$$

$$W = P \times V$$

$$W_{\text{system}} = -P\Delta V$$

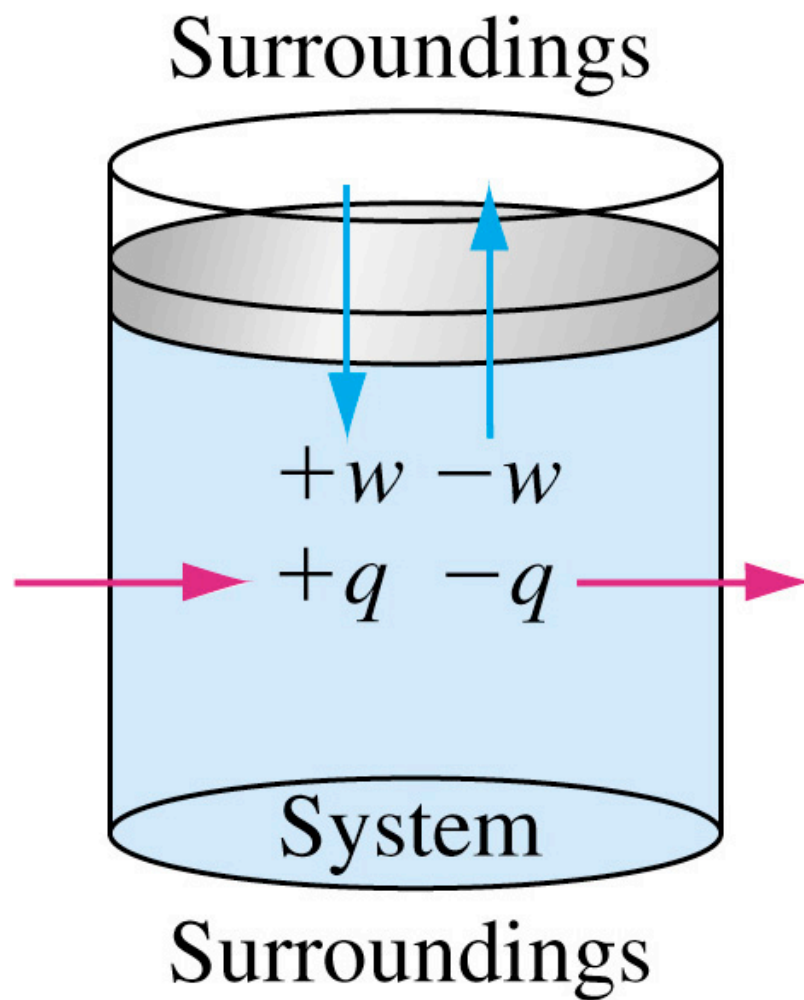


# The First Law of Thermodynamics

Reactants  $\rightarrow$  Products

$$\Delta U = U_2 - U_1$$

$$\Delta U = q + W$$



# Example: PV Work

The volume of a gas changes from 264 mL to 971 mL at constant temperature. Calculate the amount of work done by the gas (in joules) if it expands (a) against a vacuum, and (b) against a constant pressure of 4.00 atm.



# Work and Heat

- in the previous example, the quantity of work *depended on the path taken* to the final state; thus **work is not a state function**
- because  $\Delta U = q + W$ , and we know that  $U$  is a state function but  $W$  isn't, that means that  **$q$  is also not a state function**
- the value of  $W$  is dependent on the pathway taken, but the **value of  $\Delta U$  is path independent**, therefore the value of  $q$  must depend on the path taken.



# A New Function: Enthalpy

- the majority of chemical reactions and processes are carried out under constant pressure conditions:

$$\Delta U = q_p - P\Delta V$$

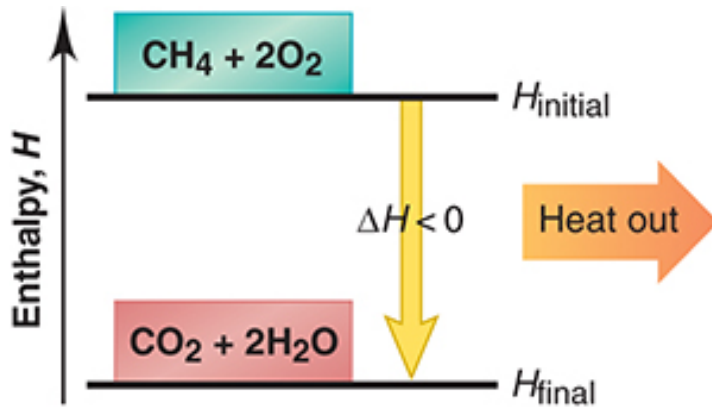
- Enthalpy, H: amount of heat transferred under constant pressure conditions

$$H = U + PV$$

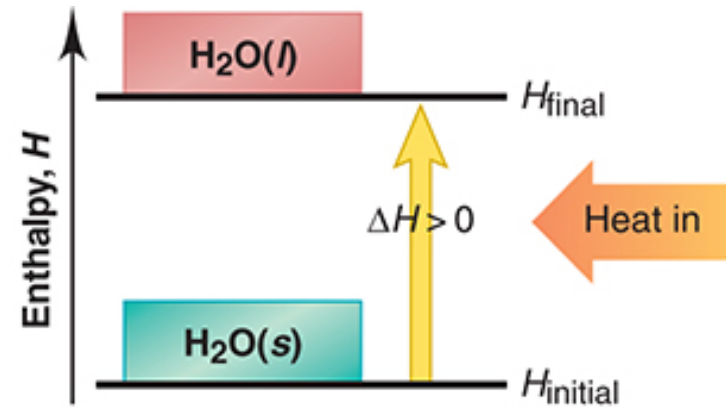
$$q_p = \Delta H = \Delta U + P\Delta V$$



# Enthalpy is a State Function

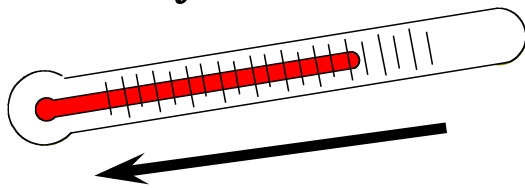


A Exothermic process



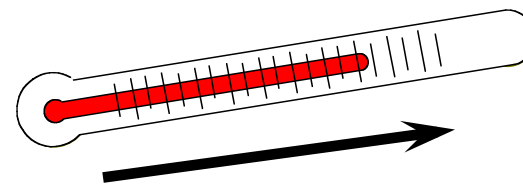
B Endothermic process

$$q_{\text{system}} < 0$$



**EXOTHERMIC**

$$q_{\text{system}} > 0$$



**ENDOTHERMIC**

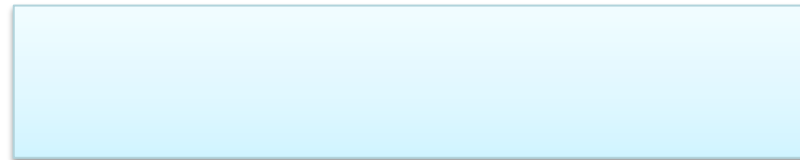


# Comparing $\Delta U$ and $\Delta H$

$$\Delta U = q + W$$

$$\Delta U = \Delta H - P\Delta V$$

1. Reactions with NO GASES:



2. Reactions WITH GASES:

$$PV = nRT$$

*P and T are constant*

$$P\Delta V = \Delta n_{\text{gas}}RT$$

$$P\Delta V = (n_{\text{products}} - n_{\text{reactants}})RT$$



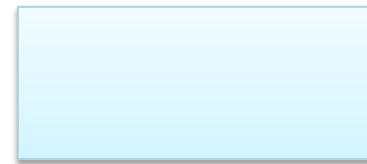
# Comparing $\Delta U$ and $\Delta H$

$$\Delta U = q + W$$

$$\Delta U = \Delta H - P\Delta V$$

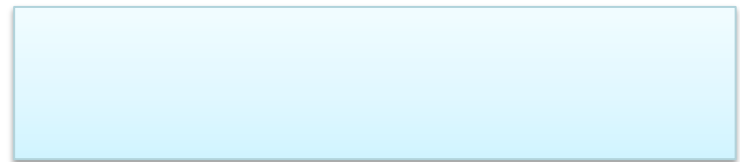
2. a) Reactions where  $\Delta n_{\text{gas}} = 0$

$$P\Delta V = \Delta n_{\text{gas}}RT = 0$$

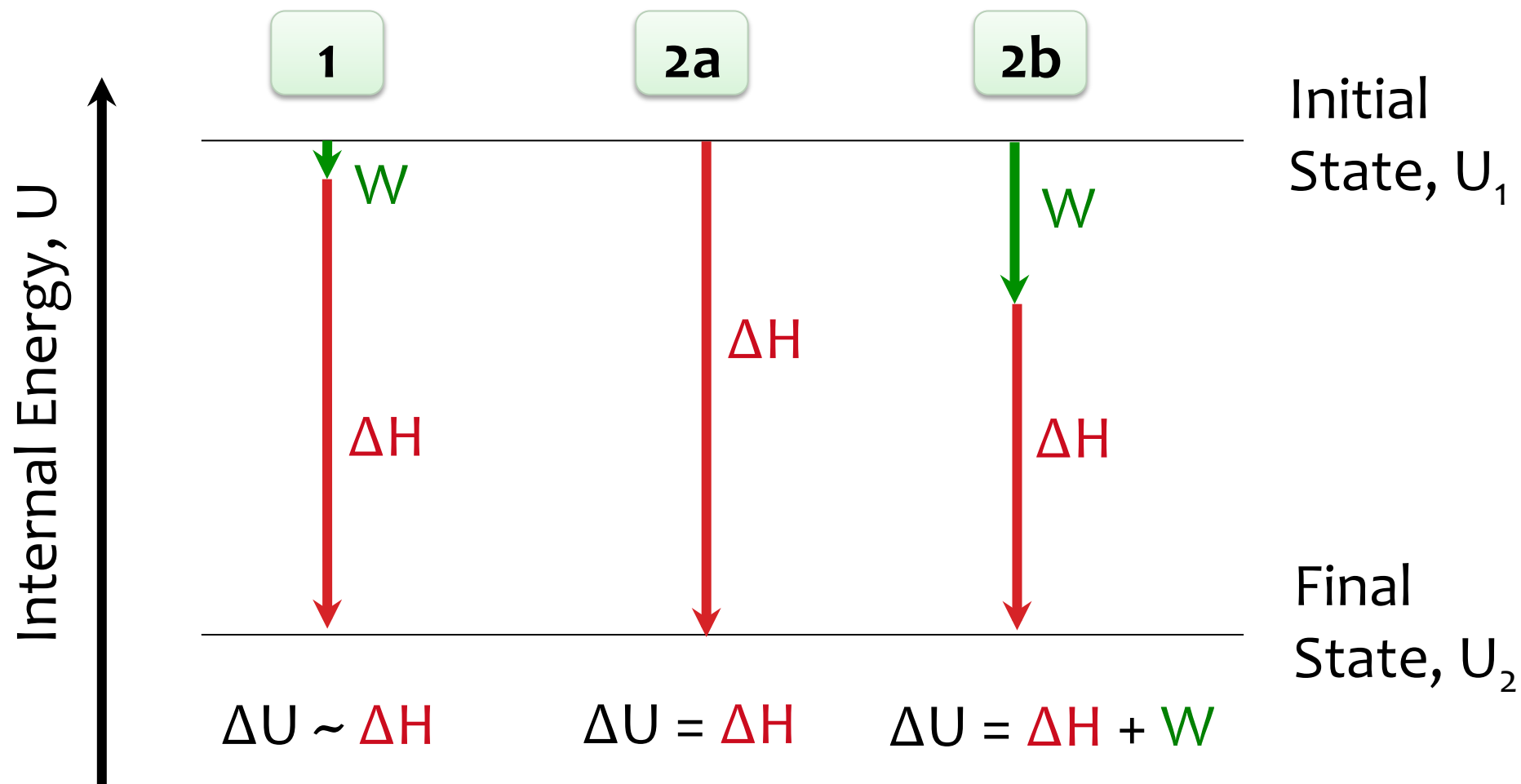


2. b) Reactions where  $\Delta n_{\text{gas}} \neq 0$

$$P\Delta V = \Delta n_{\text{gas}}RT \neq 0$$

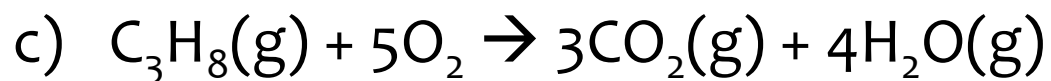
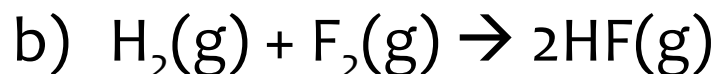
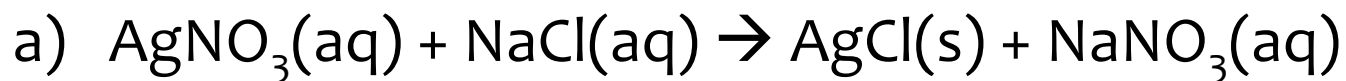


# Energy Diagram



# Example: Constant P reactions

Qualitatively compare  $\Delta H$  and  $\Delta U$  for each of the following reactions.



# Calorimetry

“Energy is neither created nor destroyed, only transferred”

- measure heat transferred to/from a reaction

$$\Delta E_{\text{universe}} = 0$$

$$q_{\text{system}} = -q_{\text{surroundings}}$$



# Heat Capacities

- **SPECIFIC HEAT CAPACITY (*s* or *c*)** of a substance is the quantity of heat necessary to change one gram of that substance by one degree
- **HEAT CAPACITY (*C*)** of a substance is the quantity of heat necessary to change the temperature of a system by one degree (Kelvin or Celsius)

$$C = m \cdot c$$



# Heat Transfer

specific heat capacity =  $\frac{\text{heat transferred to/from a substance (J)}}{\text{mass of object (g)} \cdot \text{change in temp (}^\circ\text{C)}}$

$$c = q/m\Delta T \quad \text{or}$$

$$q = mc\Delta T$$

$$q = C\Delta T$$

- if  $\Delta T > 0$ ,  $q$  is \_\_\_\_\_
- if  $\Delta T < 0$ ,  $q$  is \_\_\_\_\_



# Example: Heat transfer

How much energy (in joules) is needed to raise the temperature of UCU AUD by one degree? (Say, 20°C to 21°C)

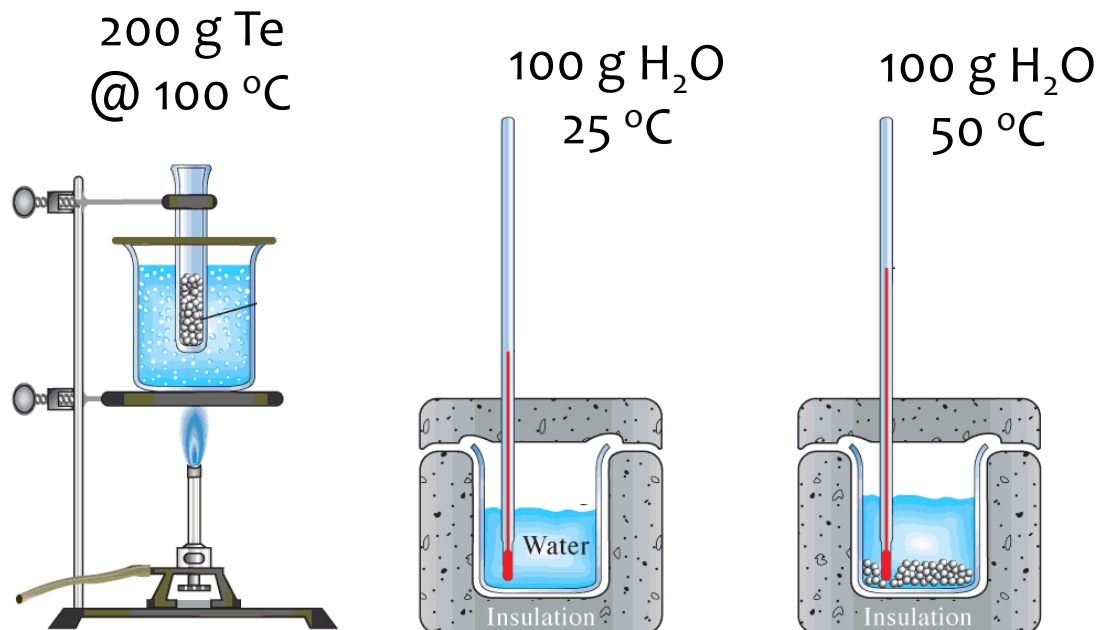


# Your Turn...

What is the specific heat capacity of tellurium? Use 4 J/g°C for the heat capacity of water.

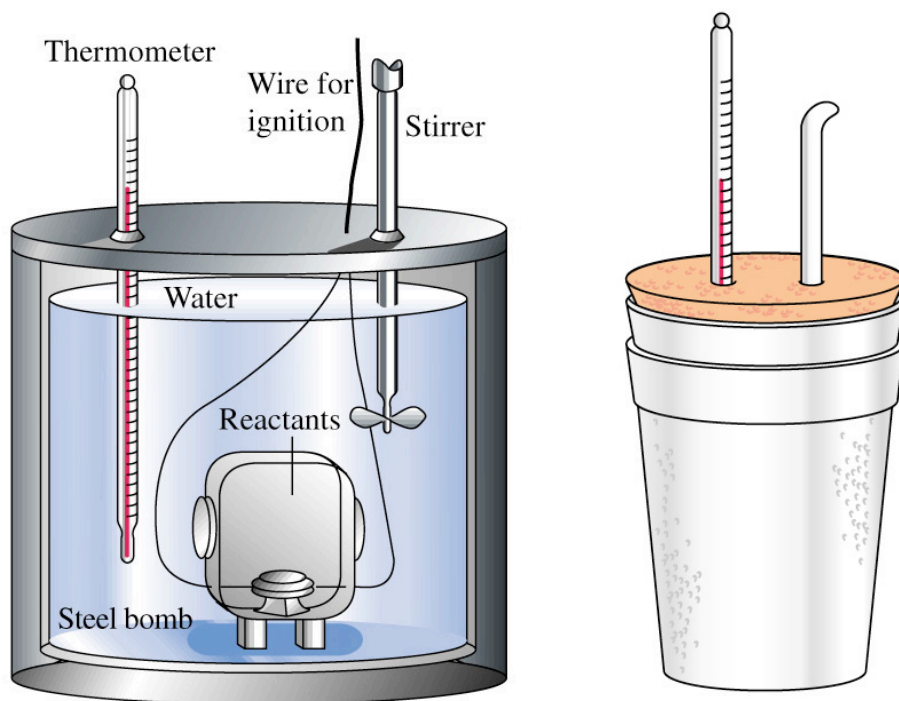
$$-q_{\text{Te}} = q_{\text{H}_2\text{O}}$$

- A. 0.5 J/g °C
- B. 1 J/g °C
- C. 2 J/g °C
- D. 10 J/g °C
- E. I'm not sure



# Heats and Calorimetry

- **calorimeter:** isolated system in which one measures  $\Delta T$  during a chemical reaction



# Heat of \_\_\_\_\_

- quantity of heat transferred during a process, usually expressed in **J/mol** or **kJ/mol**

Reaction	Example	Enthalpy
heat of combustion	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-802 kJ/mol
heat of solution	$\text{NH}_4\text{NO}_3 (\text{s}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq})$	+25.69 kJ/mol
heat of neutralization	$\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	-57 kJ/mol
heat of vapourization	$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$	+40.7 kJ/mol

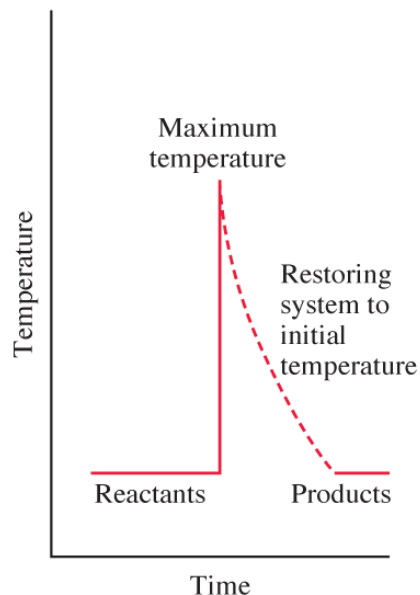
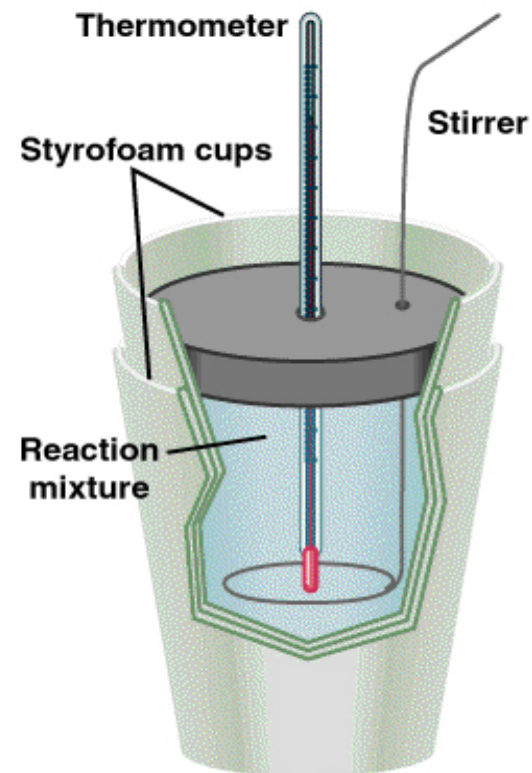


# Constant Pressure Calorimetry

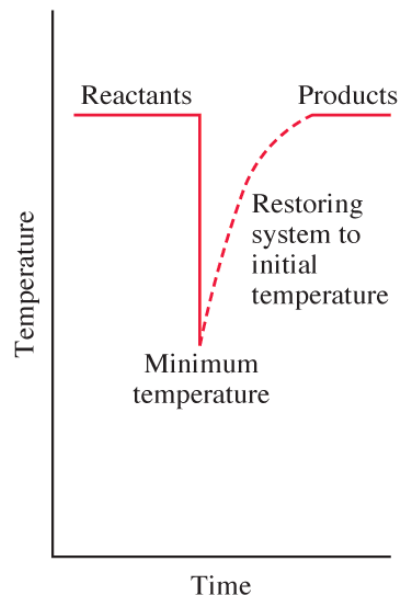
For most reactions (i.e. endothermic or mildly exothermic reactions), constant pressure conditions suffice:

$$q_{\text{reaction}} = -(q_{\text{H}_2\text{O}} + q_{\text{calorimeter}})$$

where  $q_{\text{cal}}$  must be determined in advance using a standard reaction.



(a) Exothermic reaction



(b) Endothermic reaction



CHM1311



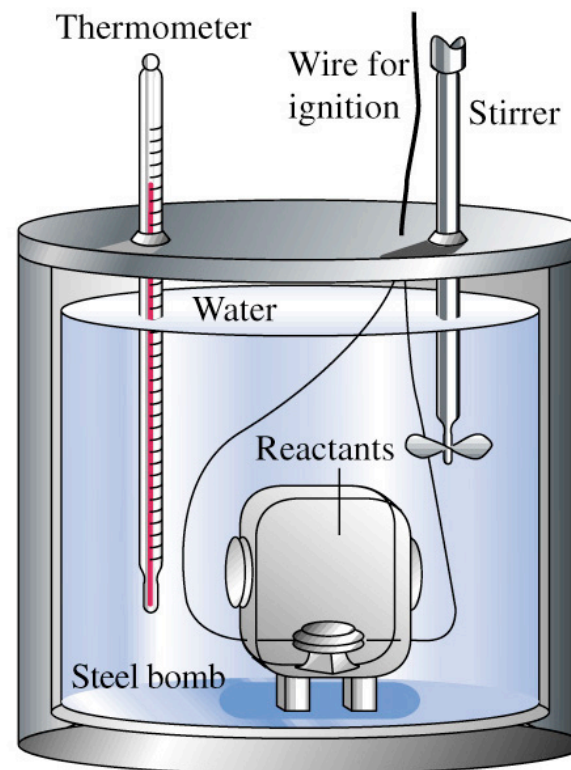
Thermochemistry

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# Constant Volume Calorimetry

- used for more **vigorous** reactions (like combustions)
- the heat released by the reaction is absorbed by the bomb

$$q_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}} c_{\text{H}_2\text{O}} \Delta T$$
$$q_{\text{bomb}} = C_{\text{bomb}} \Delta T$$



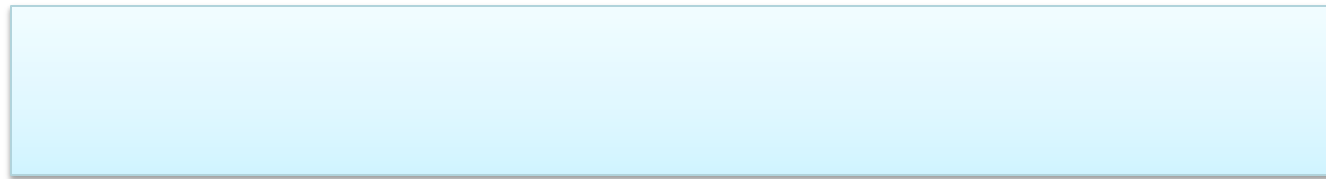
# Constant Volume Calorimetry

- Note: constant volume conditions!

$$\Delta V = 0$$

$$W = -P\Delta V = 0$$

$$\therefore \Delta U = q + W$$



# Example: Bomb Calorimetry

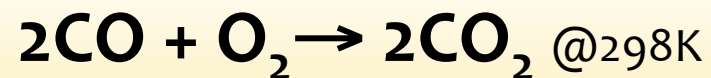
The combustion of 1.010 g sucrose, in a bomb calorimeter, causes the temperature to rise from 24.92 to 28.33°C. The heat capacity of the calorimeter assembly is 4.90 kJ/°C.

- (a) What is the heat of combustion of sucrose, expressed in kJ/mol  $C_{12}H_{22}O_{11}$ ?
- (b) Verify the claim of sugar producers that one teaspoon of sugar (about 4.8 g) contains only 19 Calories.



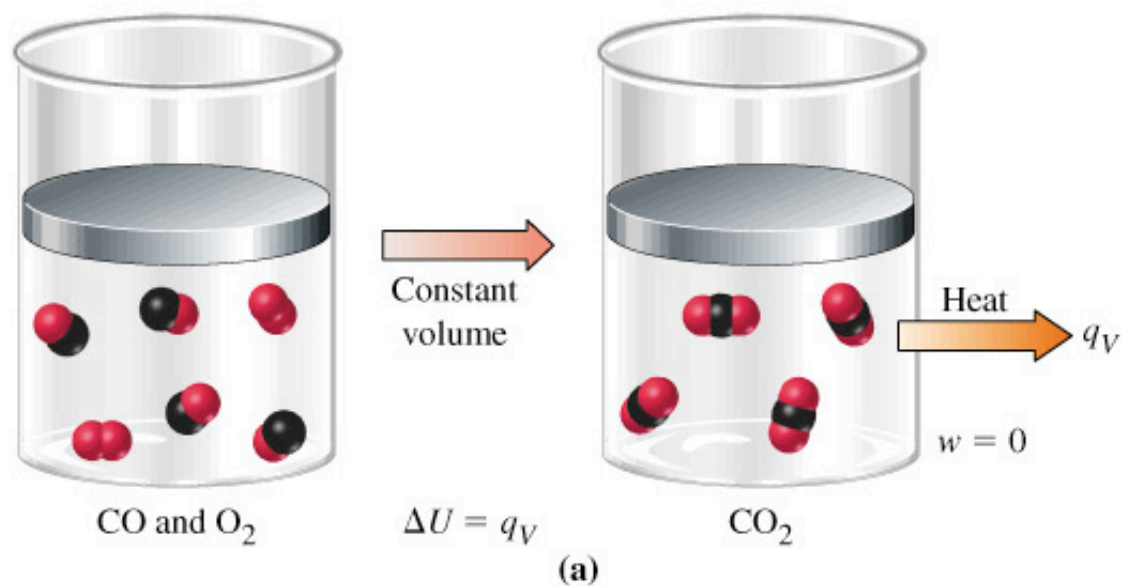
# Constant P vs. Constant V

Consider the following reaction:



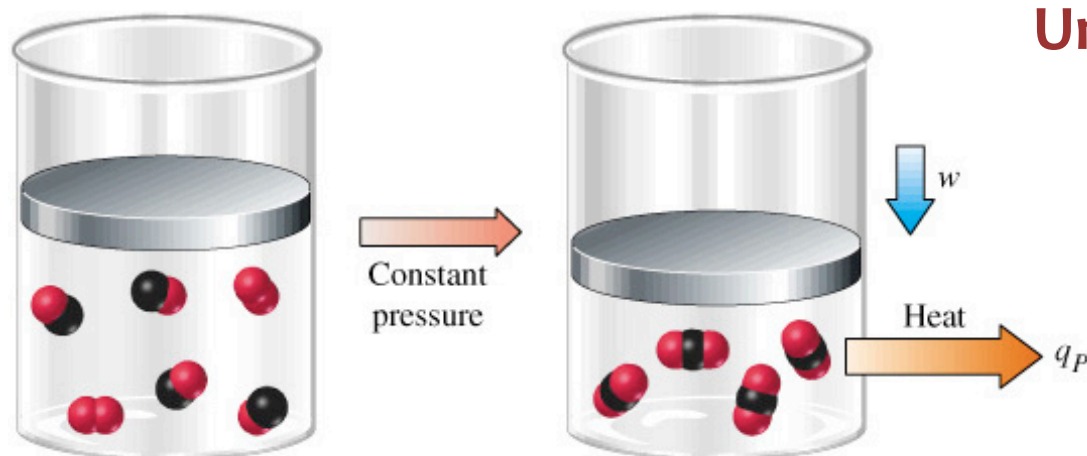
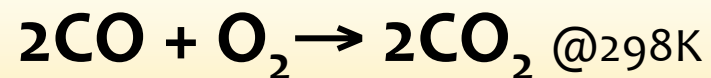
**Under constant V:**

$$\begin{aligned}\Delta U &= q_V \\ &= -563.5 \text{ kJ/mol}\end{aligned}$$



# Constant P vs. Constant V

Consider the following reaction:



**Under constant P:**

$$W = -P\Delta V = -\Delta nRT$$

$$= -(n_f - n_i)RT$$

$$= +2.5 \text{ kJ/mol (small!)}$$

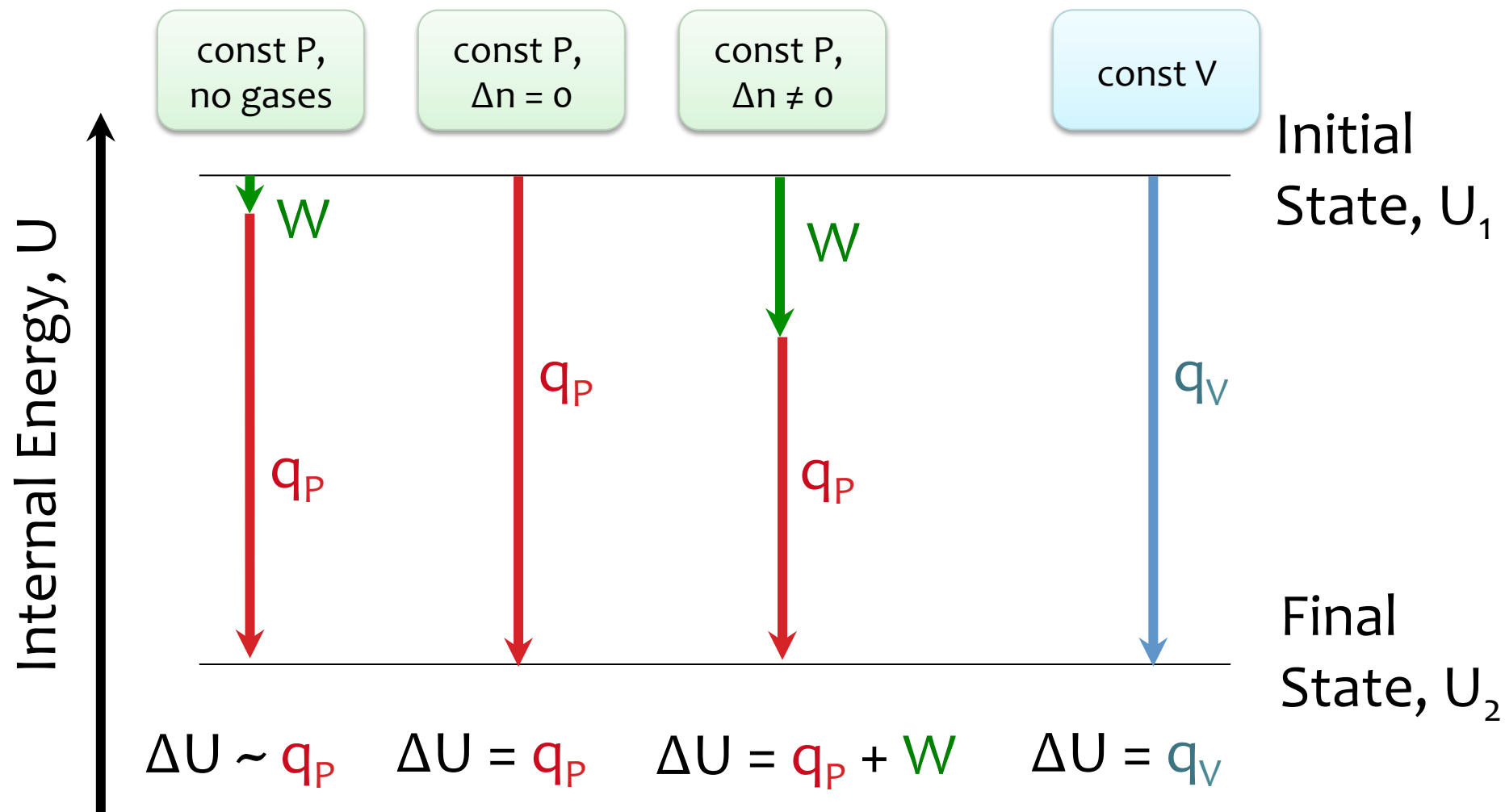
$$\Delta U = q_p - P\Delta V$$

$$q_v = q_p - P\Delta V$$

(b)



# Constant P vs. Constant V

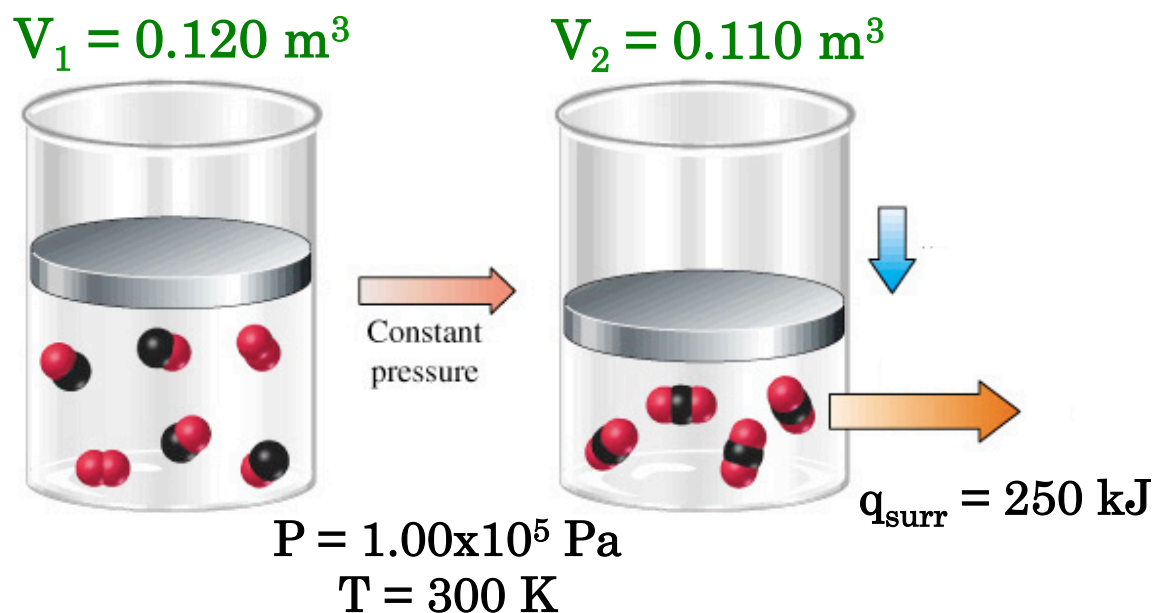


# Your Turn...

Determine  $\Delta H$  and  $\Delta U$  for the process shown below.

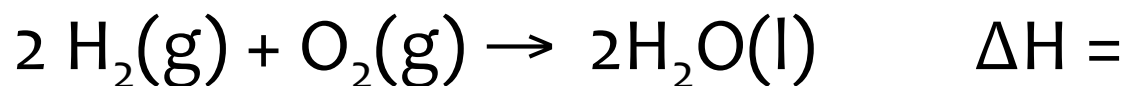
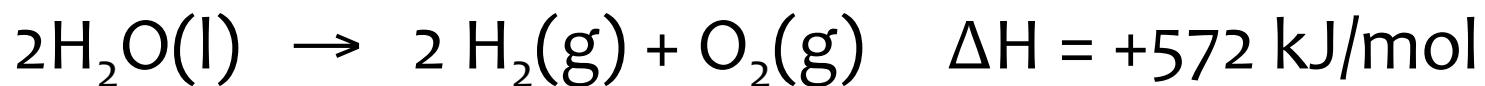
Note:  $1 \text{ Pa} = 1 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$  and  $1 \text{ J} = 1 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-2}$

- |    | $\Delta H$ | $\Delta U$ |
|----|------------|------------|
| A. | -250 kJ    | -249 kJ    |
| B. | -250 kJ    | -251 kJ    |
| C. | 250 kJ     | 251 kJ     |
| D. | 250 kJ     | 249 kJ     |



# Enthalpy: A State Function

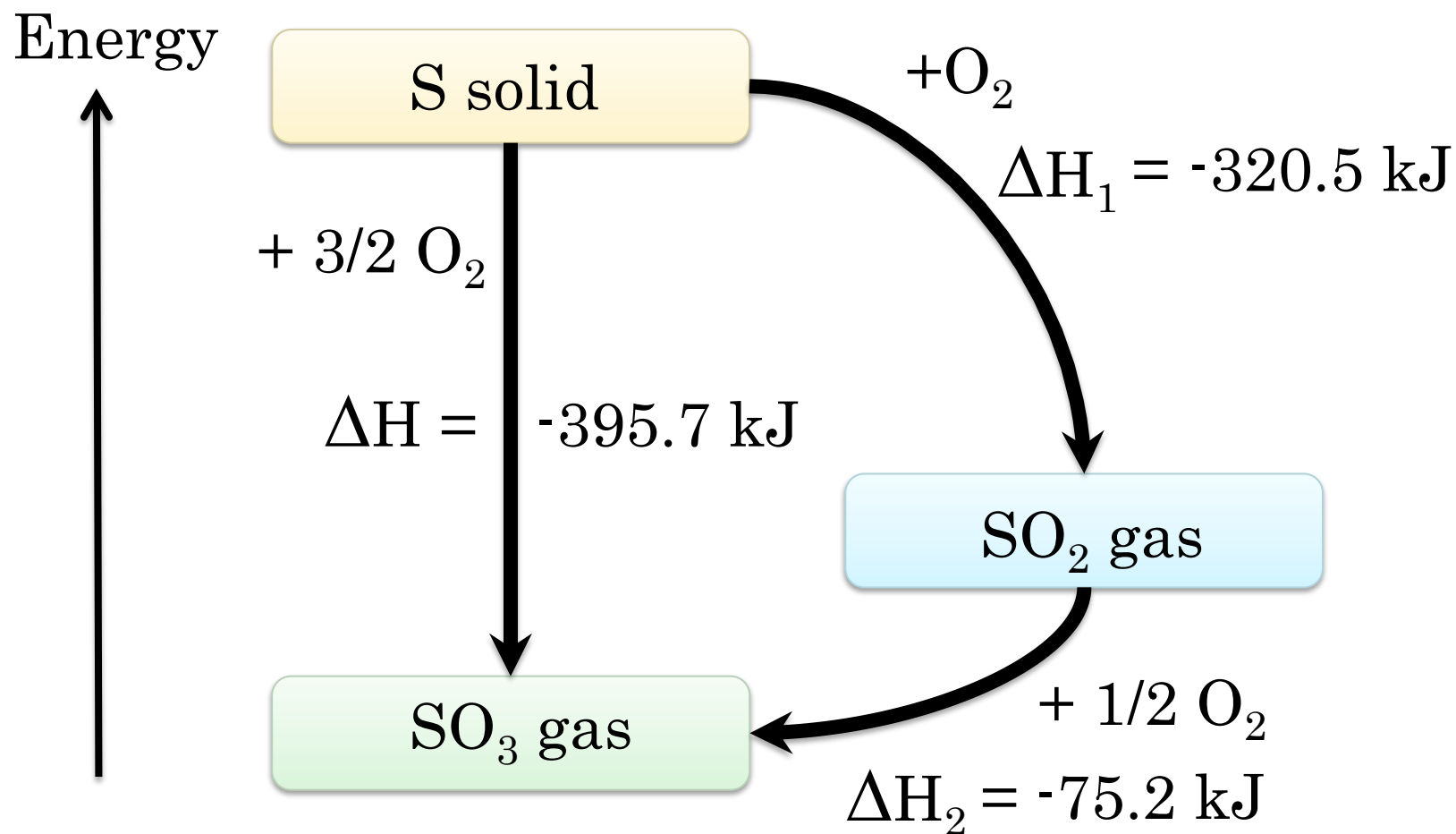
1. **SIGN:** If a reaction is **reversed**,  $\Delta H$  is also **reversed**.



2. **MAGNITUDE:** The **magnitude** of  $\Delta H$  is proportional to the **amount** of substance.

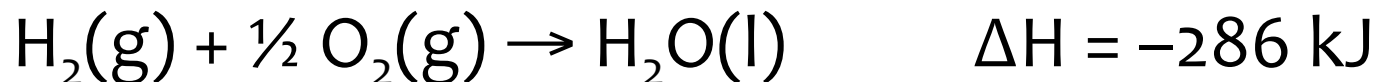
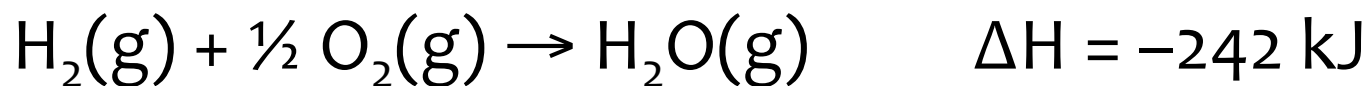


# $\Delta H$ : A State Function = Independent of Path



# Hess's Law

Our example involves two steps: (1 mole reaction)



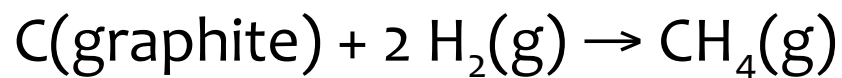
Example of **HESS'S LAW**:

The net  $\Delta H$  is the **sum of the  $\Delta H$ 's** of the individual steps

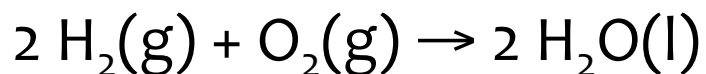


# Example : Hess's Law

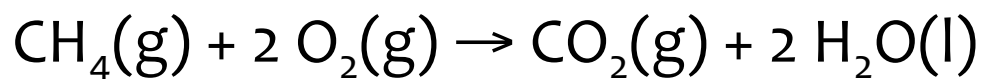
Using the thermochemical data below, calculate the enthalpy of the following reaction:



$$\Delta H^\circ_{\text{rxn}} = -393.5 \text{ kJ}$$



$$\Delta H^\circ_{\text{rxn}} = -571.6 \text{ kJ}$$



$$\Delta H^\circ_{\text{rxn}} = -890.4 \text{ kJ}$$



# Standard Enthalpy Values: An “anchor point”

- Measure the enthalpy change under standard conditions
  - $\Delta H$  values are labeled  $\Delta H^\circ$
- Define a **standard state** (at the temperature of interest – often 298.15K):
  - **Compounds:**
    - For a gas, pressure is exactly 1 bar
    - For a solution, concentration is exactly 1 molar
    - Pure substance (liquid or solid), it is the pure liquid or solid
  - **Elements:**
    - The form  $[\text{N}_2(\text{g}), \text{K}(\text{s})]$  in which it exists at 1 bar



# Standard Enthalpy Values

- NIST (Nat'l Institute for Standards and Technology) gives values of

$\Delta H^{\circ}_f$  = standard molar enthalpy of formation

- This is the enthalpy change when **1 mol** of **compound** is formed from the reference form of the **elements** under standard conditions.
- The standard enthalpy of formation of a pure element in its reference state is: \_\_\_\_\_



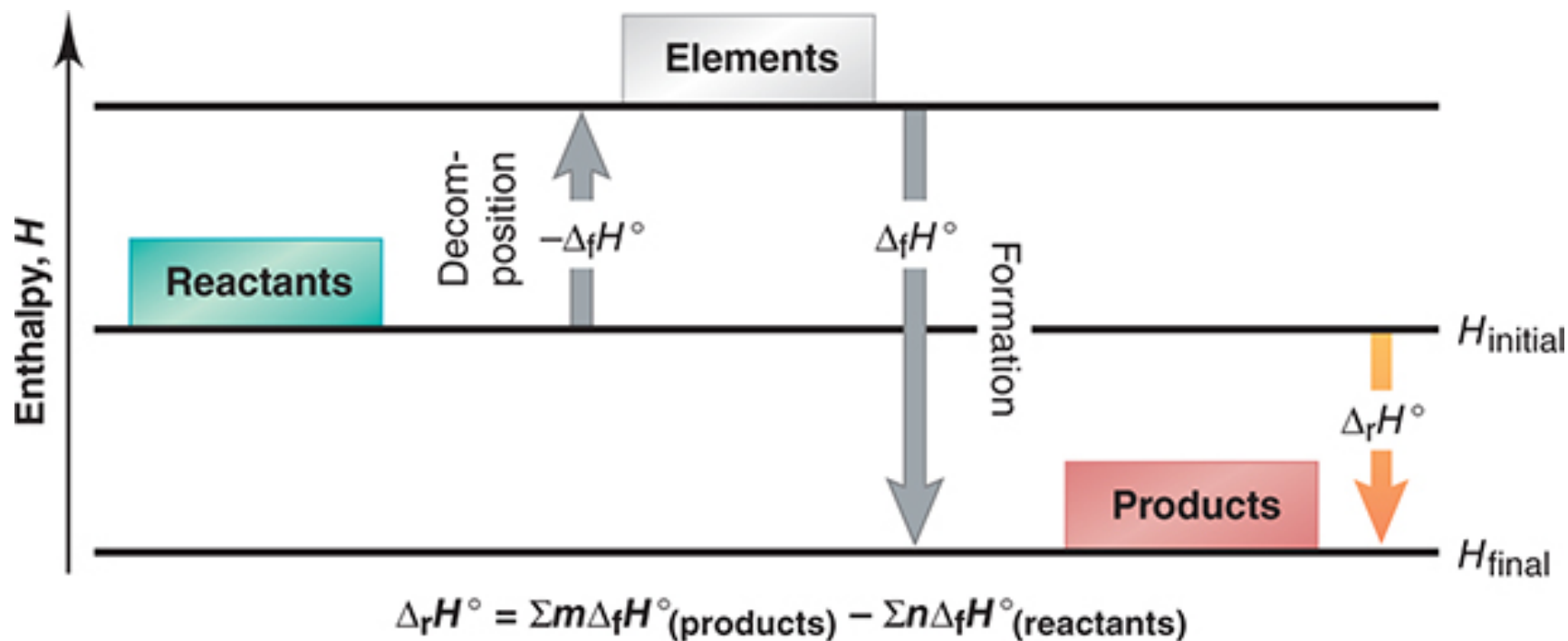
# Your Turn...

Which of the following equations represents the  $\Delta H_f^\circ$  of ammonium nitrate,  $\text{NH}_4\text{NO}_3$ ?

- A.  $\text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \rightarrow \text{NH}_4\text{NO}_3(\text{s})$
- B.  $\text{NH}_3(\text{g}) + \text{HNO}_3(\text{l}) \rightarrow \text{NH}_4\text{NO}_3(\text{s})$
- C.  $\text{N}_2(\text{g}) + \text{O}_3(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{NH}_4\text{NO}_3(\text{s})$
- D.  $\text{N}_2(\text{g}) + \frac{3}{2} \text{O}_2(\text{g}) + 2 \text{H}_2(\text{g}) \rightarrow \text{NH}_4\text{NO}_3(\text{s})$
- E.  $2\text{N}_2(\text{g}) + 3 \text{O}_2(\text{g}) + 4 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_4\text{NO}_3(\text{s})$

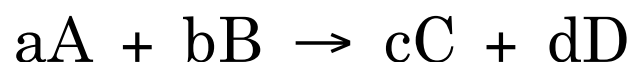


# Standard Enthalpies of Formation



# Changes in Enthalpy

- using standard enthalpies of formation,  $\Delta H_f^\circ$ , we can calculate standard enthalpies of reaction,  $\Delta H_{\text{rxn}}^\circ$ , i.e., for a general reaction:



$$\Delta H_{\text{rxn}}^\circ = [c \Delta H_f^\circ(C) + d \Delta H_f^\circ(D)] - [a \Delta H_f^\circ(A) + b \Delta H_f^\circ(B)]$$

- the general formula is:

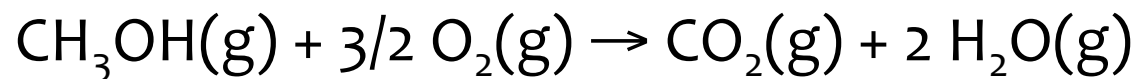
$$\Delta H_{\text{rxn}}^\circ = \sum n \Delta H_f^\circ(\text{products}) - \sum m \Delta H_f^\circ(\text{reactants})$$

- where **n** and **m** are the stoichiometric coefficients for the reactants and products.



# Example: Using $\Delta H_f^\circ$ Values

Calculate the heat of combustion of methanol, i.e.,  $\Delta H_{\text{rxn}}^\circ$  for:



$$\Delta H_{\text{rxn}}^\circ = \sum \Delta H_f^\circ(\text{prod}) - \sum \Delta H_f^\circ(\text{react})$$

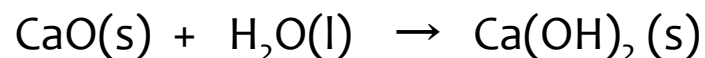
$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \{\Delta H_f^\circ(\text{CO}_2) + 2 \Delta H_f^\circ(\text{H}_2\text{O})\} - \{3/2 \Delta H_f^\circ(\text{O}_2) + \Delta H_f^\circ(\text{CH}_3\text{OH})\} \\ &= \{(-393.5 \text{ kJ}) + 2(-241.8 \text{ kJ})\} - \{0 + (-201.5 \text{ kJ})\} \\ &= -675.6 \text{ kJ / mol of methanol}\end{aligned}$$



# Example: Integrative Question

## 2012 Exam

In the Marion lab, you mix 25.0 g of CaO with exactly 80 mL of water at 25.0°C and you observe the following reaction, as well as the release of some steam:

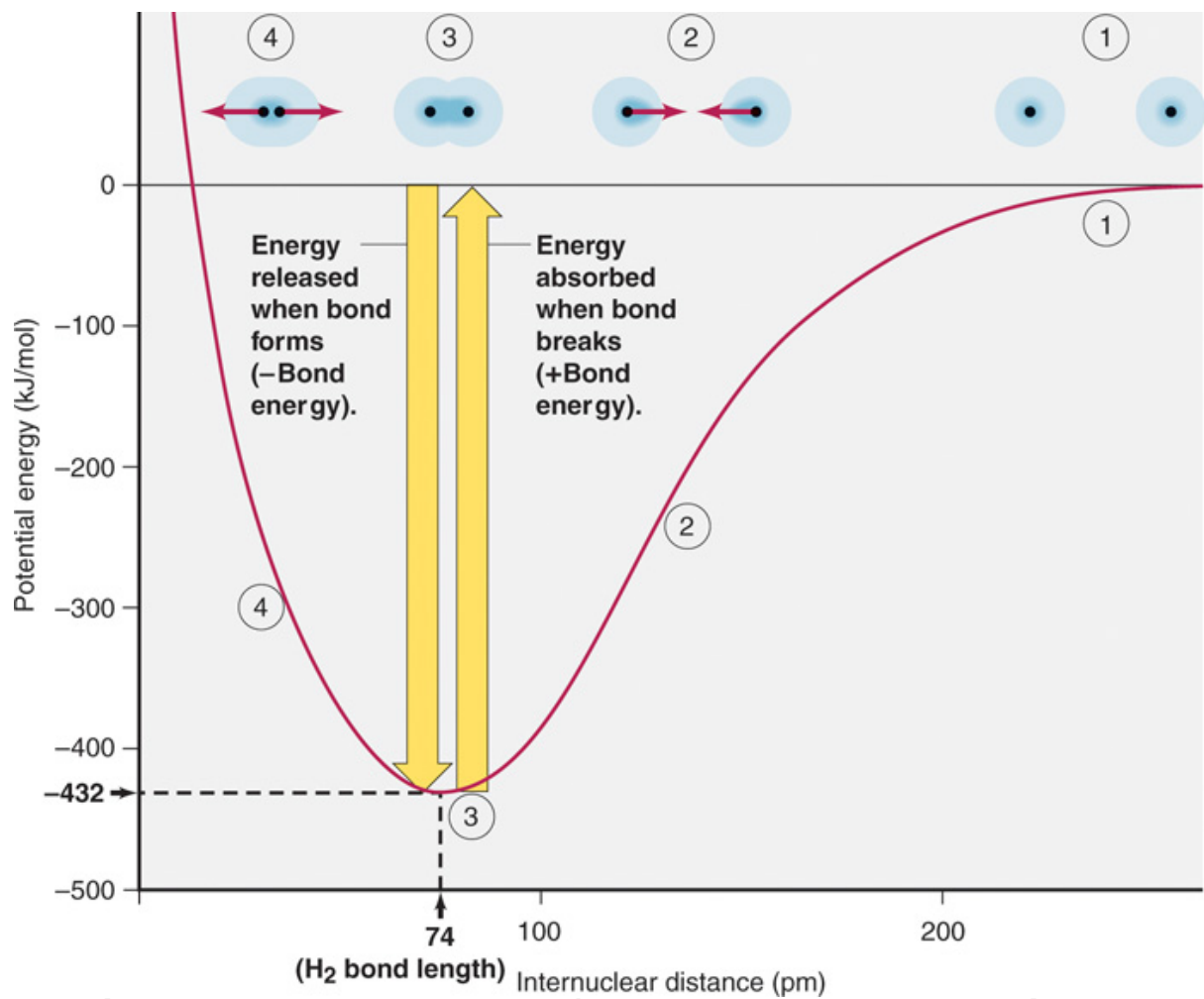


- a) What is the reagent in excess and how many grams of it will be left at the end of the reaction?
- b) Using the data in the table below and from the data sheets, calculate the mass of the steam that escaped during the reaction.

	$\Delta H^\circ_f$ (kJ/mol)
CaO (s)	-635
H <sub>2</sub> O (l)	-286
Ca(OH) <sub>2</sub> (s)	-987

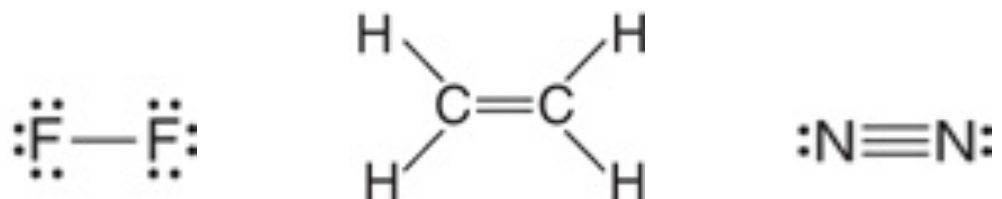


# Where does the energy come from?



# Properties of Covalent Bonds

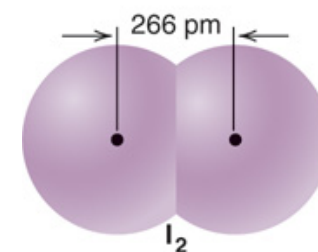
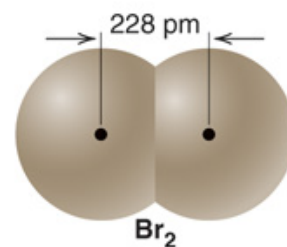
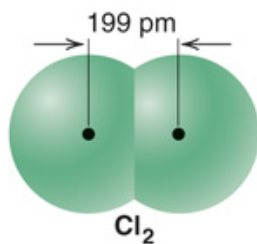
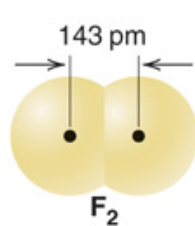
- Bond Order



- Bond Energy



- Bond Length





# Trends in the Data...

**TABLE 8.3** The Relation of Bond Order, Bond Length, and Bond Energy

Bond	Bond Order	Average Bond Length (pm)	Average Bond Energy (kJ/mol)
C—O	1	143	358
C=O	2	123	745
C≡O	3	113	1070
C—C	1	154	347
C=C	2	134	614
C≡C	3	121	839
N—N	1	146	160
N=N	2	122	418
N≡N	3	110	945



# Bond Energy and $\Delta H_{\text{rxn}}$



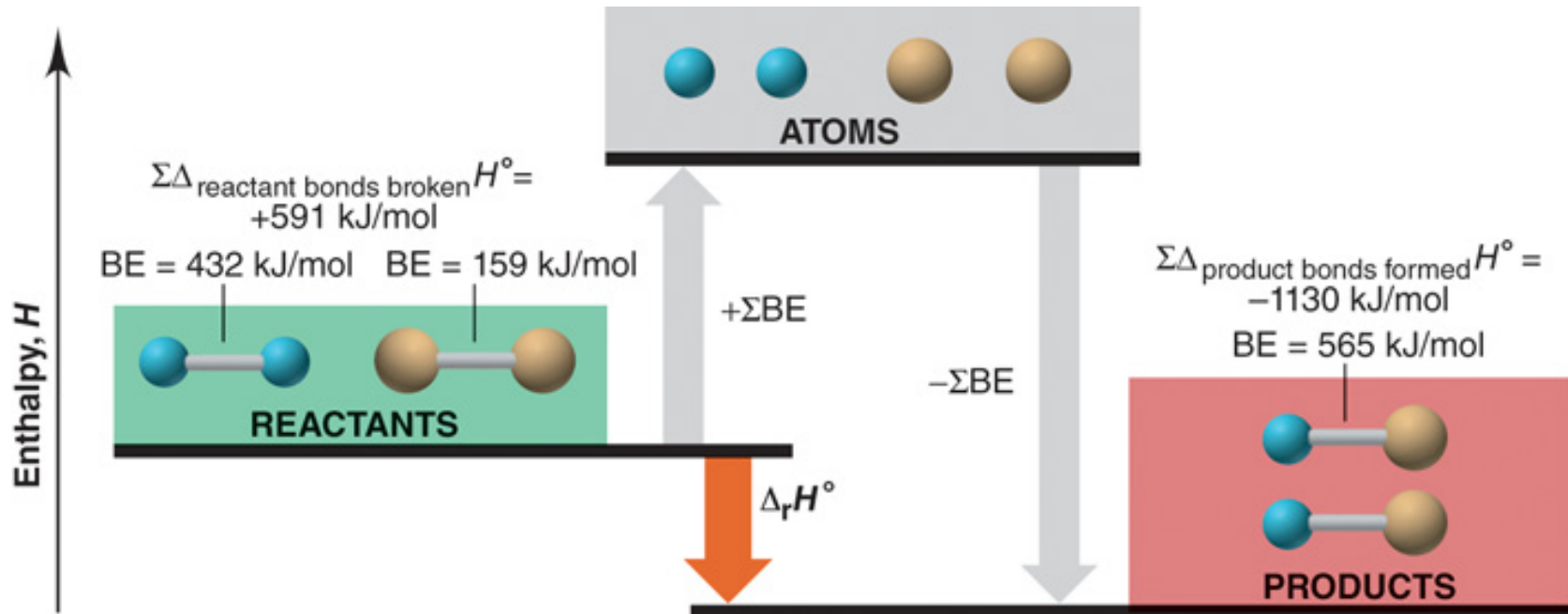
breaking:

making:



# Predicting $\Delta H_{\text{rxn}}$

$$\Delta H_{\text{rxn}} = \sum(\text{BE}_{\text{bonds broken}}) - \sum(\text{BE}_{\text{bonds formed}})$$



# Chapter 5: Key Concepts

1. Thermodynamic terminology
2. Internal energy ( $U$ ), heat ( $q$ ), work ( $W$ ), and enthalpy ( $H$ )
3. First Law of Thermodynamics
4. Const.  $V$  vs const.  $P$  calorimetry
5. Hess's Law
6. Enthalpies of Formation
7. (8.3/8.4) Bond Energies



# Chapter 5: Suggested Problems

5.8, 5.15, 5.19, 5.26, 5.28, 5.33, 5.37, 5.41,  
5.43, 5.47, 5.50, 5.54, 5.56, 5.65, 5.71, 5.74,  
5.75, 5.81, 5.82, 5.84, 5.89, 5.93, 5.103

**Section 8.4: 8.45, 8.47, 8.49, 8.50**

