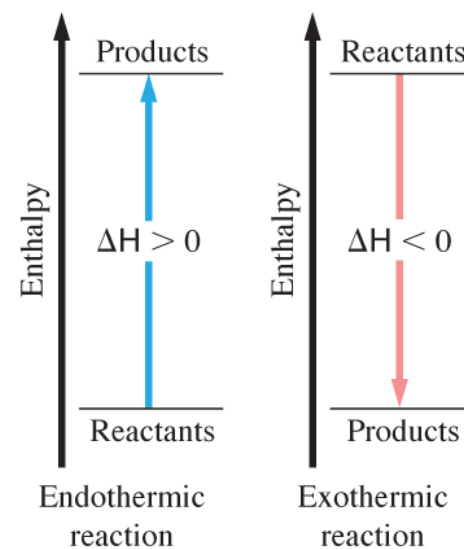
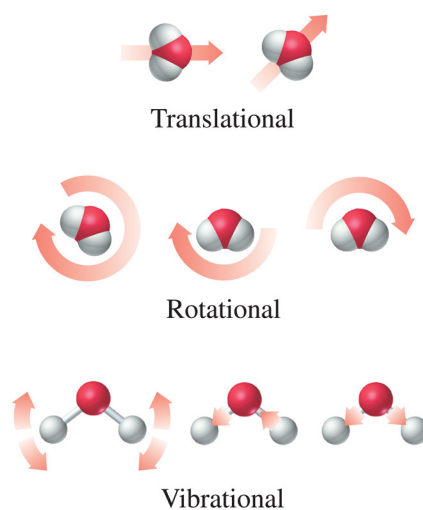
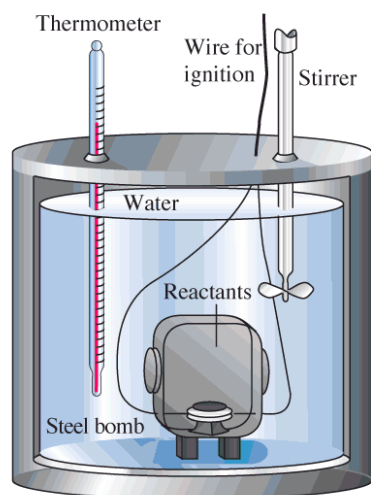


Chapter 7: Thermochemistry



The Nature of Energy

The capacity to do *work* or to produce *heat*.



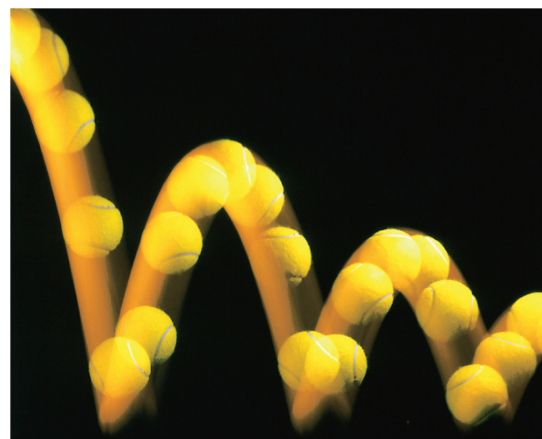
The thermite reaction is so vigorous that the iron that is formed is molten!



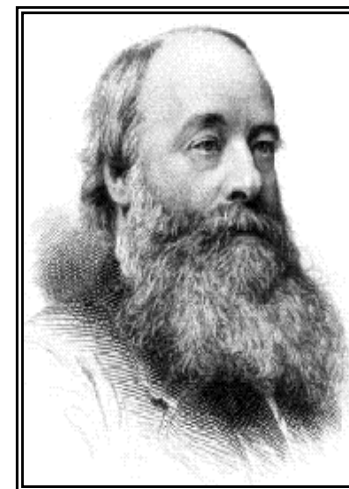
The Nature of Energy

- the forms of energy most relevant in chemistry are:
 - **thermal energy** (kinetic energy) associated with the random motion of molecules
 - **chemical energy** (potential energy) stored in the structural units of chemical substances, i.e. covalent bonds, ionic bonds, hydrogen bonds, etc.

- We can interchange these



Units of Energy



James Joule, 1818-1889

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

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

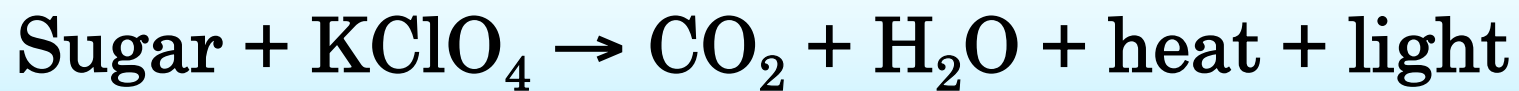
- We sometimes use the calorie instead of the joule:

$$1 \text{ calorie} = 4.184 \text{ J}$$

- A nutritional Calorie: $1 \text{ Cal} = 1000 \text{ cal} = 1 \text{ kcal}$



Conversion of Energy



Some Terminology in Thermochemistry

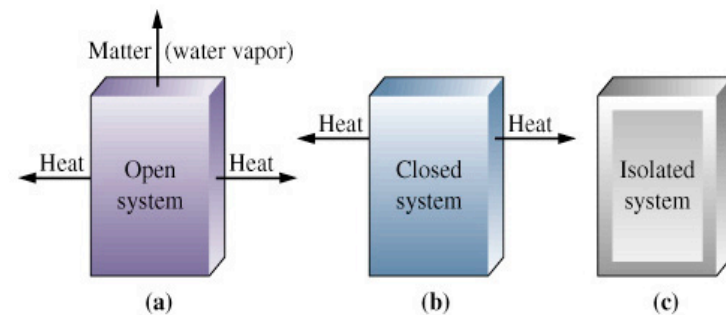
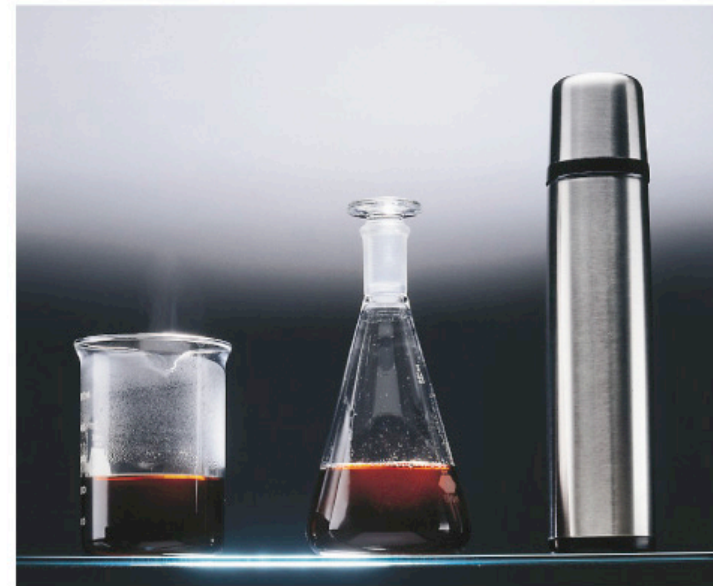
- **System:** part of the universe under observation
- **Surroundings:** the rest of the universe

Universe = System + Surroundings



Three Systems

- open system:
exchanges matter and energy with the surroundings
- closed system:
exchanges only energy with the surroundings
- isolated system:
neither energy nor matter shared with the surroundings



More terminology...

- **ENERGY, E_x** : the capacity to do work
- **INTERNAL ENERGY, U** : the sum of all microscopic energies of a thermodynamic system
- **WORK, W** : a force acting on a given distance

$U \uparrow$ when the surroundings work on the system

$U \downarrow$ when the system works on the surroundings



More terminology...

- **HEAT** (q) is the 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
- the internal energy of the system changes during the energy transfer:

$$\Delta U = U_2 - U_1$$

If the system *absorbs* heat, then q is POSITIVE

If the system *loses* heat, then q is NEGATIVE



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

$$\frac{\text{J}}{\text{g} \cdot \text{C}}$$

or

$$\frac{\text{J}}{\text{gK}}$$

$$\Delta T = 1 \text{ degree celcius} \\ = 1 \text{ K}$$

- an object with a high specific heat will require lots of heat to raise its temperature, and will consequently liberate lots of heat upon cooling



Objects

Heat Capacities

- **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)

$$C = m \cdot s$$

$$\frac{\text{J}}{^{\circ}\text{C}} \quad \text{or} \quad \frac{\text{J}}{\text{K}}$$



Heat Capacity

- the heat capacity relates the change in temperature, ΔT , with the quantity of heat, q , absorbed or released during a thermodynamic process

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

$$s = q/m\Delta T$$

or

$$q = ms\Delta T$$

$$q = m c \Delta T$$

$$q = C\Delta T$$

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



Principle of Conservation of Energy

First Law

“Energy is neither created nor destroyed, only transferred”

- the total energy of the universe is constant:

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

$$q_{\text{system}} + q_{\text{surroundings}} = 0$$

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



Example: Heat capacity

The specific heat capacity of iron is $0.444 \text{ J}/(\text{g K})$. A 869 g block of iron cools from 94°C to 5°C . Calculate the amount of heat lost by the metal.

$$\begin{aligned}q &= m s \Delta T \\&= (869 \text{ g})(0.444 \text{ J}/\text{g}\cdot\text{K})(-89 \text{ K}) \\&= -34.3 \times 10^4 \text{ J} \\&= -34.3 \text{ kJ}\end{aligned}$$

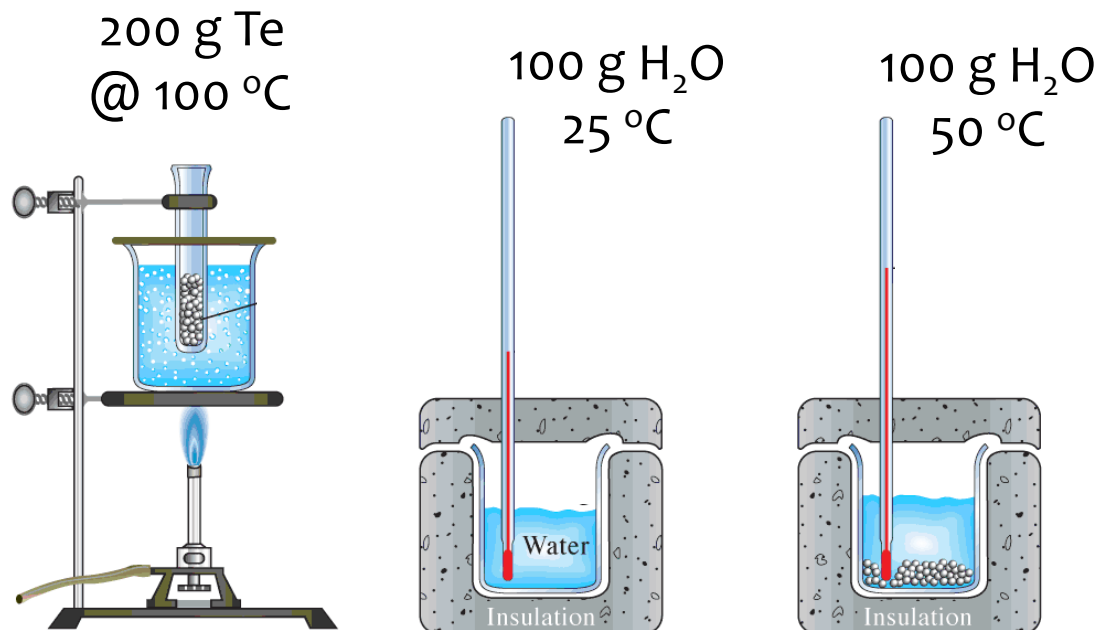


Your Turn...

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. Not sure



$$q_{\text{H}_2\text{O}} = (100\text{g}) (4\text{J/g}\cdot\text{c})(+25) = +10\,000\text{ J}$$

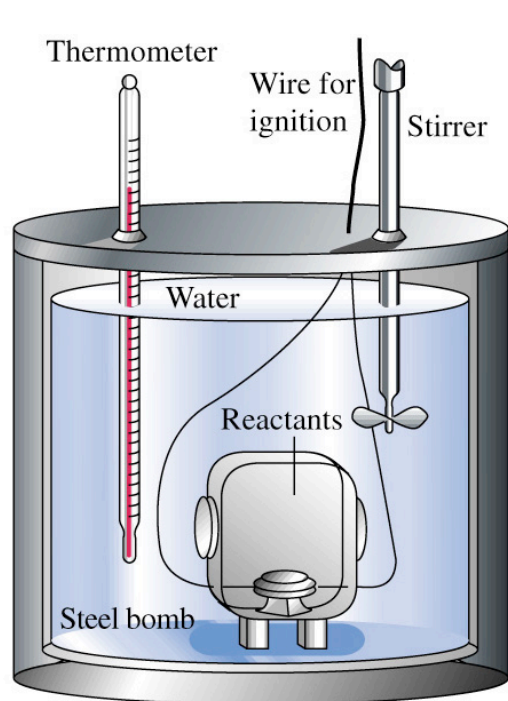
$$q_{\text{Te}} = -10\,000\text{ J} = (200\text{g})(5)(-50)$$

$$s =$$



Heats of Reaction and Calorimetry

- calorimeter:** isolated system in which one measures ΔT during a chemical reaction



$$q_{\text{rxn}} = -q_{\text{cal}}$$

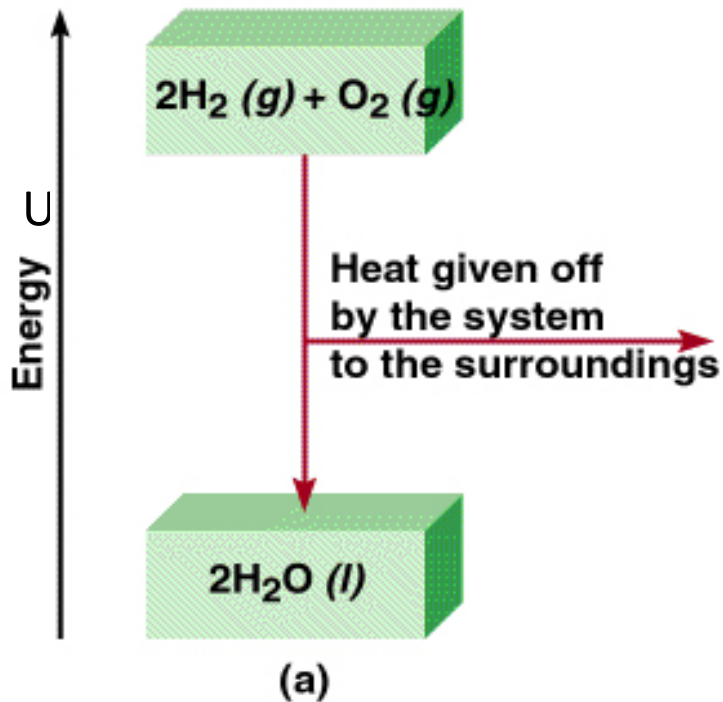


Heats of Reaction and Calorimetry

- When a reaction occurs in the system, heat can be released or absorbed by the system.
- **Heat of reaction, q_{rxn} :**
 - The quantity of heat exchanged between a system and its surroundings when a chemical reaction occurs within the system, at constant temperature.



Exothermic Reactions



- a process which *releases* heat to the surroundings is called **EXOTHERMIC**
- for example, the combustion of hydrogen is exothermic because heat is released from the system into the surroundings

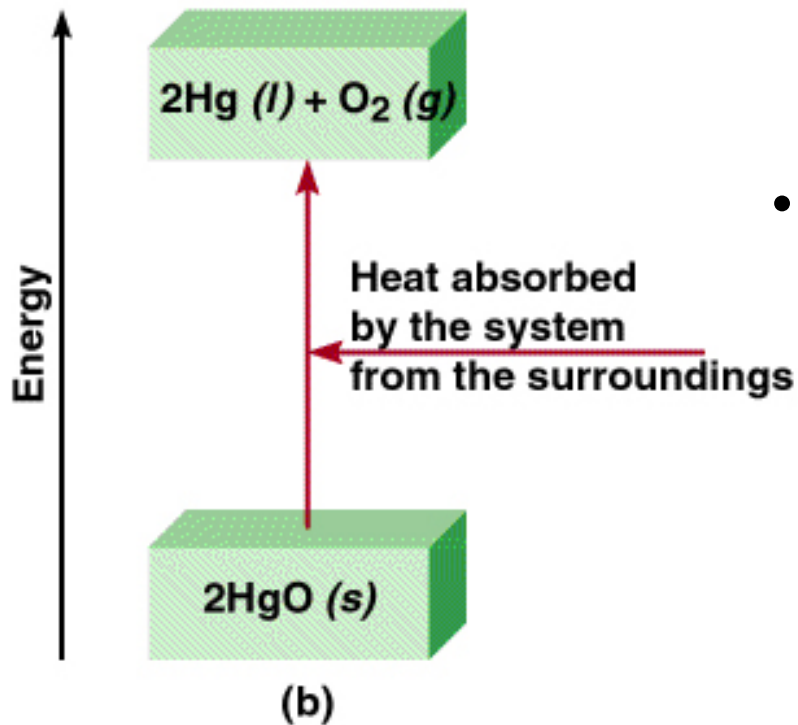
$$U_2 < U_1$$

$$\Delta U = U_2 - U_1 = \text{negative!}$$

$q < 0$  **EXOTHERMIC**



Endothermic Reactions



- a process which *absorbs* heat from the surroundings is called **ENDOTHERMIC**
- for example, the decomposition of $\text{HgO}(s)$ is endothermic because heat must be supplied to the system to release $\text{O}_2(g)$

$$U_2 > U_1$$

$$\Delta U = U_2 - U_1 = \text{positive!}$$

$$q > 0$$



ENDOTHERMIC



EXOTHERMIC

Bomb Calorimeter

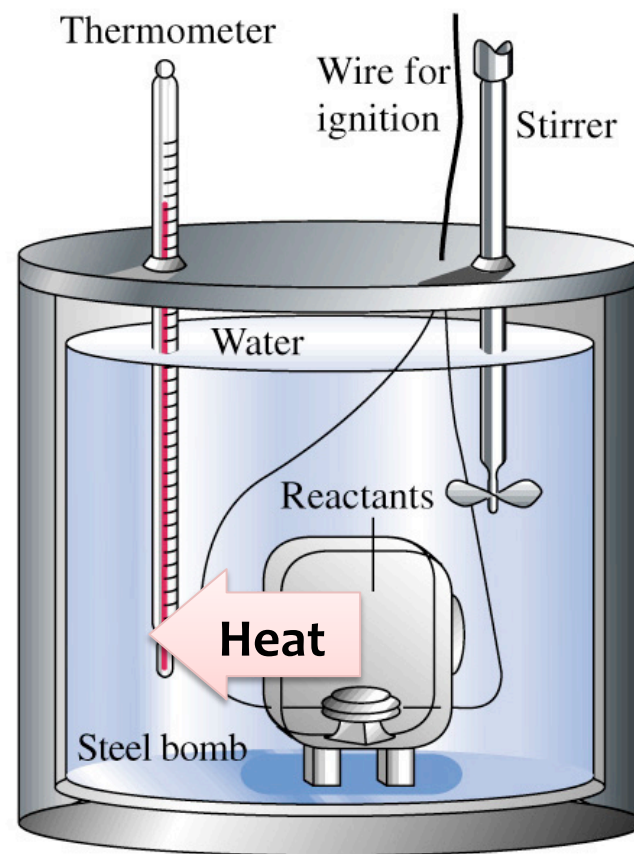
Constant Volume Condition

$$q_{\text{rxn}} = -q_{\text{cal}}$$

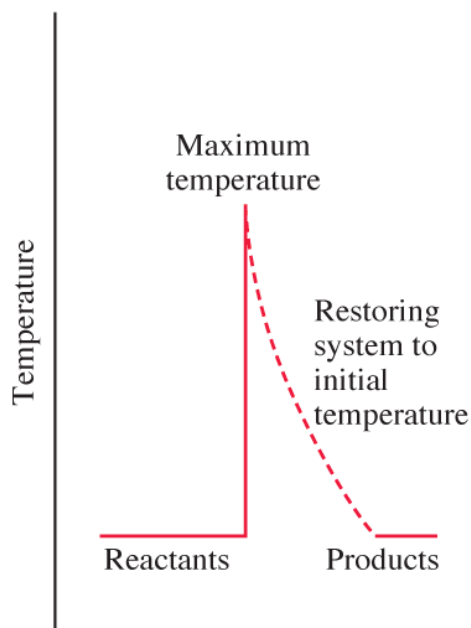
$$q_{\text{cal}} = q_{\text{bomb}} + q_{\text{water}} + q_{\text{wires}} + \dots$$

We can define the heat capacity of the calorimeter:

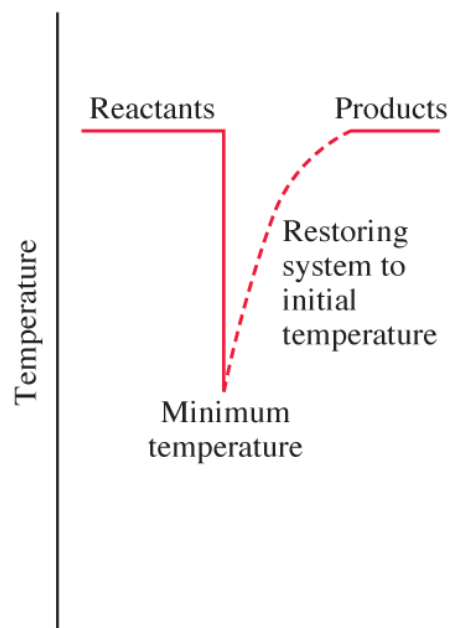
$$q_{\text{cal}} = \sum m_i c_i \Delta T = C_{\text{cal}} \Delta T$$



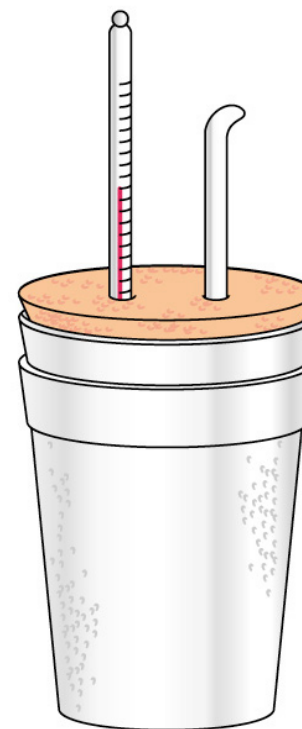
Coffee Cup Calorimeter



(a) Exothermic reaction



(b) Endothermic reaction



See Example 7-4 for a sample calculation.

$$q_{\text{rxn}} = -q_{\text{cal}}$$



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.



Example: Bomb Calorimetry

1.010 g of sucrose, T: 24.92 to 28.33°C. $C_{\text{cal}} = 4.90 \text{ kJ/}^\circ\text{C}$.

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

STEP 1: Calculate $q_{\text{calorimeter}}$:

$$q_{\text{cal}} = C\Delta T = (4.90 \text{ kJ/}^\circ\text{C})(28.33 - 24.92)^\circ\text{C}$$
$$= 16.7 \text{ kJ}$$



Example: Bomb Calorimetry

1.010 g of sucrose, T: 24.92 to 28.33°C. $C_{\text{cal}} = 4.90 \text{ kJ/}^\circ\text{C}$.

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

STEP 2: Calculate q_{rxn} :

$$q_{\text{rxn}} = -q_{\text{cal}} = -16.7 \text{ kJ per } 1.010 \text{ g}$$



Example: Bomb Calorimetry

1.010 g of sucrose, T: 24.92 to 28.33°C. $C_{\text{cal}} = 4.90 \text{ kJ/}^\circ\text{C}$.

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

STEP 3: Calculate q_{rxn} in the requested units:

$$q_{\text{rxn}} = \frac{-16.7 \text{ kJ}}{1.010 \text{ g sucrose}} \cdot \frac{343.3 \text{ g sucrose}}{\text{mol sucrose}}$$
$$= -5.65 \times 10^3 \text{ kJ/mol}$$



Example: Bomb Calorimetry

1.010 g of sucrose, T: 24.92 to 28.33°C. $C_{\text{cal}} = 4.90 \text{ kJ/}^\circ\text{C}$.

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

STEP 4: Convert this value to Calories:

$$q_{\text{rxn}} = \frac{-16\,700 \text{ J}}{1.010 \text{ g sucrose}} \cdot \frac{4.8 \text{ g}}{1 \text{ tsp}} \cdot \frac{1 \text{ cal}}{4.184 \text{ J}} \cdot \frac{1 \text{ Cal}}{1000 \text{ cal}} = -19 \text{ Cal/tsp}$$



Work, W

- chemical reactions can also carry out work on their surroundings
- How? Via changes in volume: expansion/contraction of a gas

$W = \text{force} \cdot \text{distance}$

$\text{Pressure} = \text{force}/\text{area}$

$W = \text{pressure} \cdot \text{area} \cdot \text{distance}$

$W = \text{pressure} \cdot \text{volume}$

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

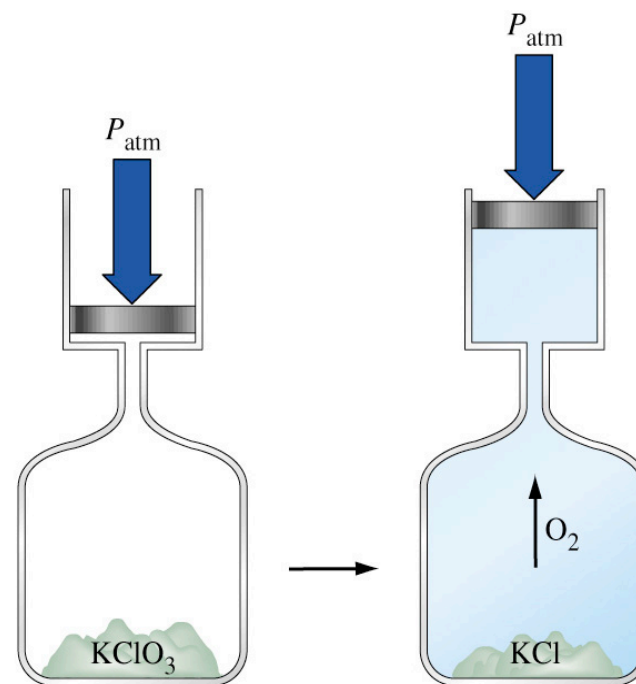
Work of
Gas Expansion



Your Turn...

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

1. positive.
2. negative.
3. zero.



The First Law of Thermodynamics



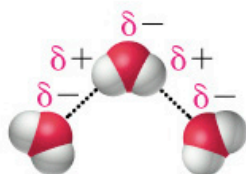
Translational



Rotational



Vibrational



Electrostatic
(Intermolecular attractions)

- **Internal Energy, U** = total energy (potential and kinetic) in a system
 - Translational kinetic energy
 - Molecular rotation
 - Bond vibration
 - Intermolecular attractions
 - Chemical bonds
 - Electrons



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 (ΔU)

“Energy is neither created nor destroyed, only transferred”

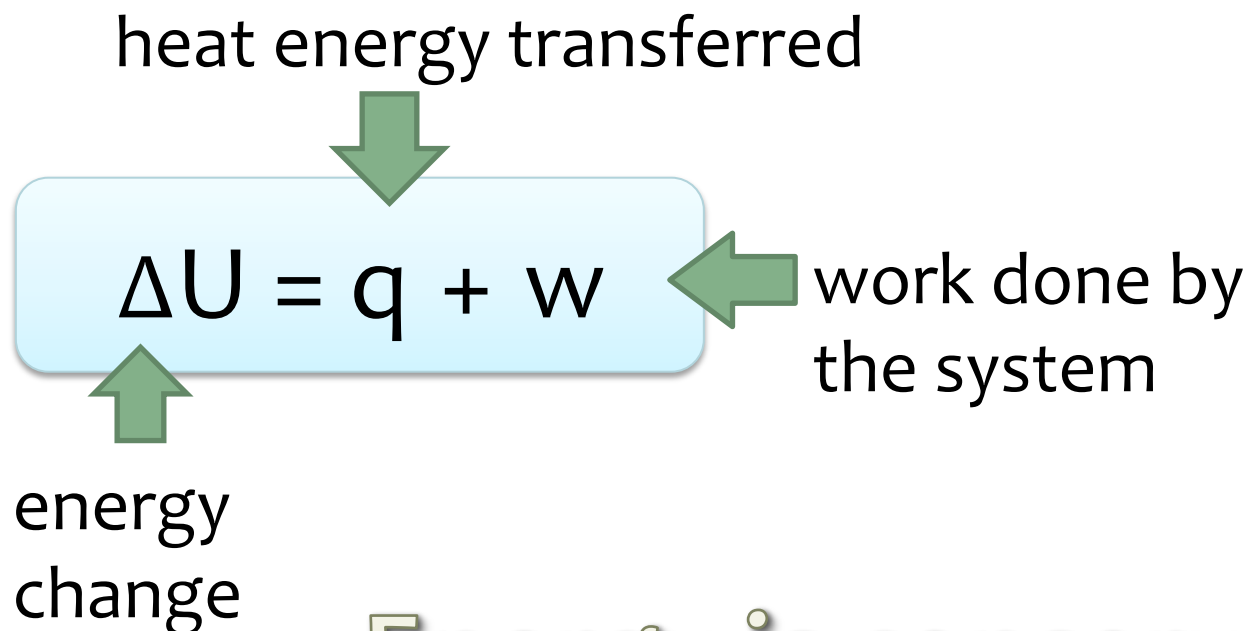
- the internal energy of an isolated system (no transfer of heat or matter) is constant, or:

$$\Delta U_{\text{isolated}} = 0$$



The First Law of Thermodynamics

- for an open system: heat and matter can be transferred



Energy is conserved!



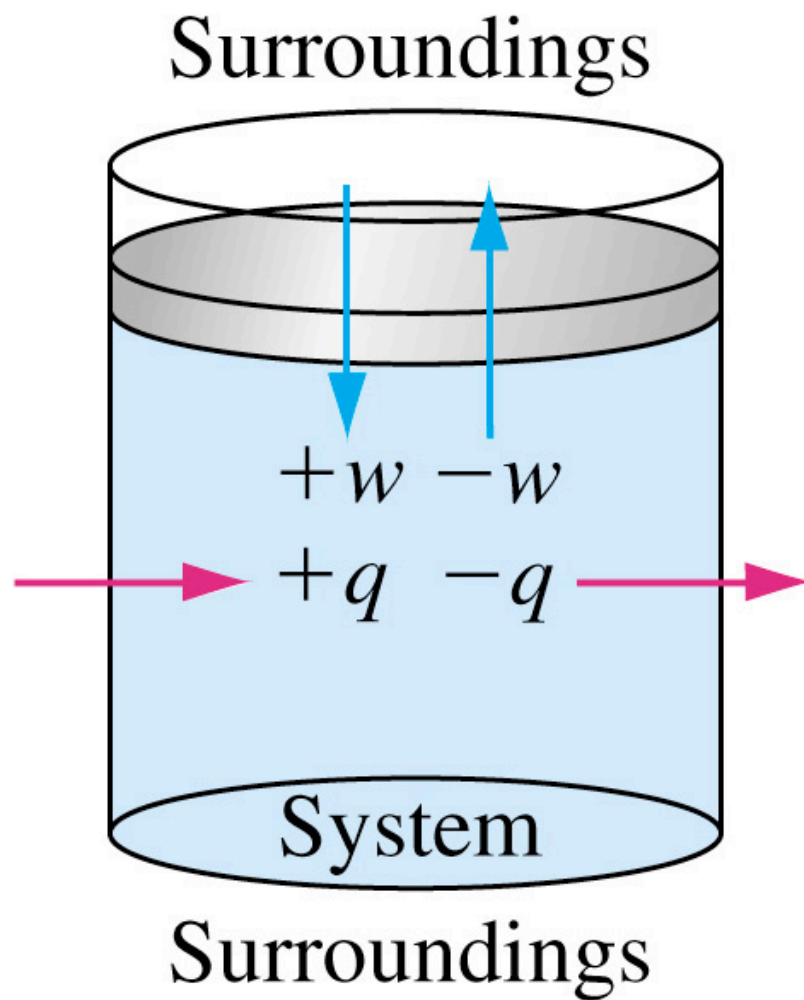
The First Law of Thermodynamics

Reactants \rightarrow Products

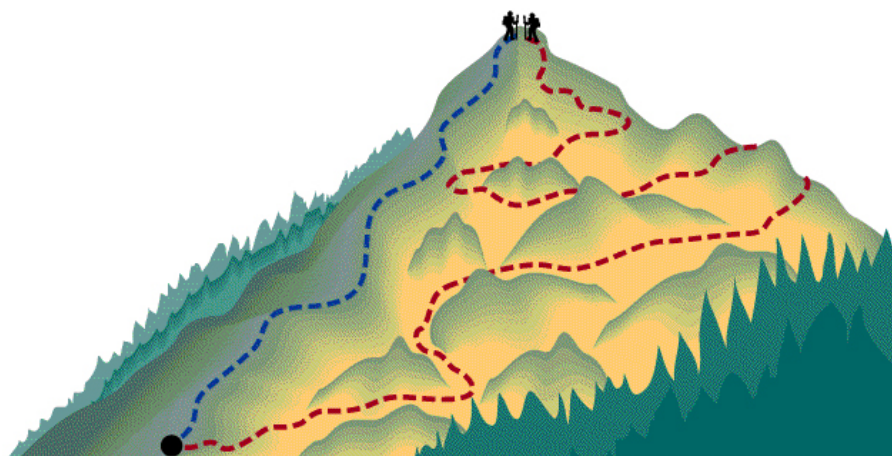
$$\Delta U = U_2 - U_1$$

$$\Delta U = q_{\text{rxn}} + W$$

$$\Delta U = q_{\text{rxn}} - P\Delta V$$



State Functions



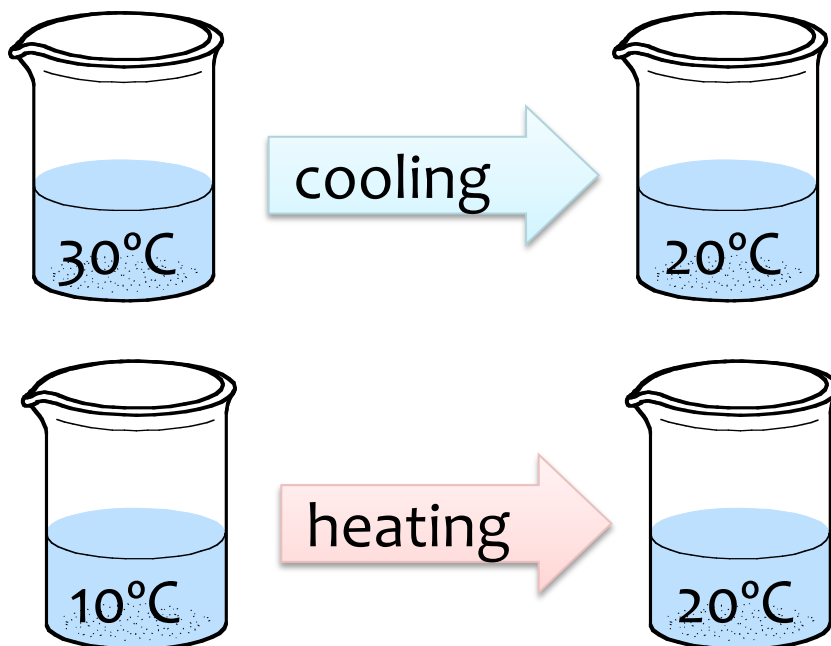
Potential Energy – A state function

- the state of a system is defined by all of its microscopic variables, such as composition, temperature, pressure, volume, etc.
- 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.

More calories were burned by those who took a longer path, so they did more work



State Functions



these two samples of water will have the same pressure, volume, temperature, mass, energy, enthalpy, heat capacity, etc., because these properties are

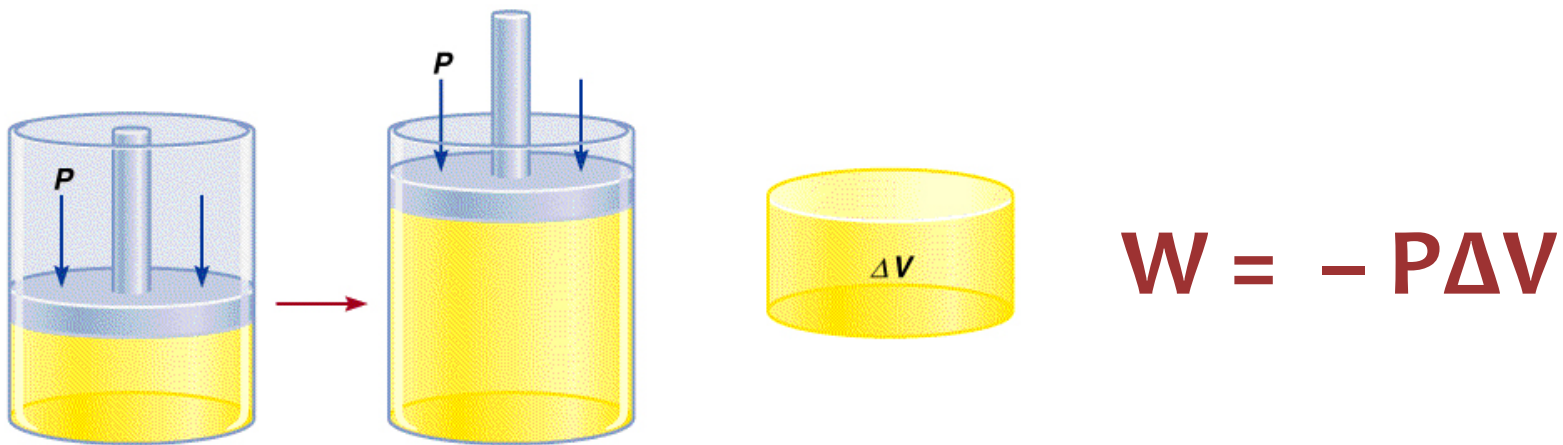
State Functions

- A state equation links state functions together
 - $PV = nRT$ is a state equation because it calculates the value of a fourth parameter when three of the other values are known (P , V , n , T)



Back to Work...

- the mechanical work produced by the expansion or contraction of a gas is known as PV work



- Expansion of gas, therefore ΔV is positive, and the work done by the system is negative
- If the system does work, work is negative



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.

Converting to SI units:

$$1 \text{ atm} = 101\,325 \text{ Pa} \quad \text{and} \quad 1 \text{ mL} = 1 \times 10^{-6} \text{ m}^3$$

(a) $P = 0$ therefore $W = 0$

$$(b) \quad W = -P\Delta V = -(4.00 \text{ atm}) \cdot \left(\frac{101325 \text{ Pa}}{1 \text{ atm}}\right) \cdot (971 \text{ mL} - 264 \text{ mL}) \cdot \left(\frac{10^{-6} \text{ m}^3}{1 \text{ mL}}\right)$$
$$W = -287 \text{ J}$$



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 ΔU is path independent**, therefore the value of q must depend on the path taken.



Internal Energy, Heat, and Work

$$\Delta U = q_{\text{rxn}} - P\Delta V$$

When **pressure** is constant
(as in most cases):

-99% of the time, pressure is constant
-P= constant Δv does not equal 0

$$\begin{aligned}\Delta u &= q + w \\ &= q - P\Delta v \\ &= q_p - P\Delta v\end{aligned}$$

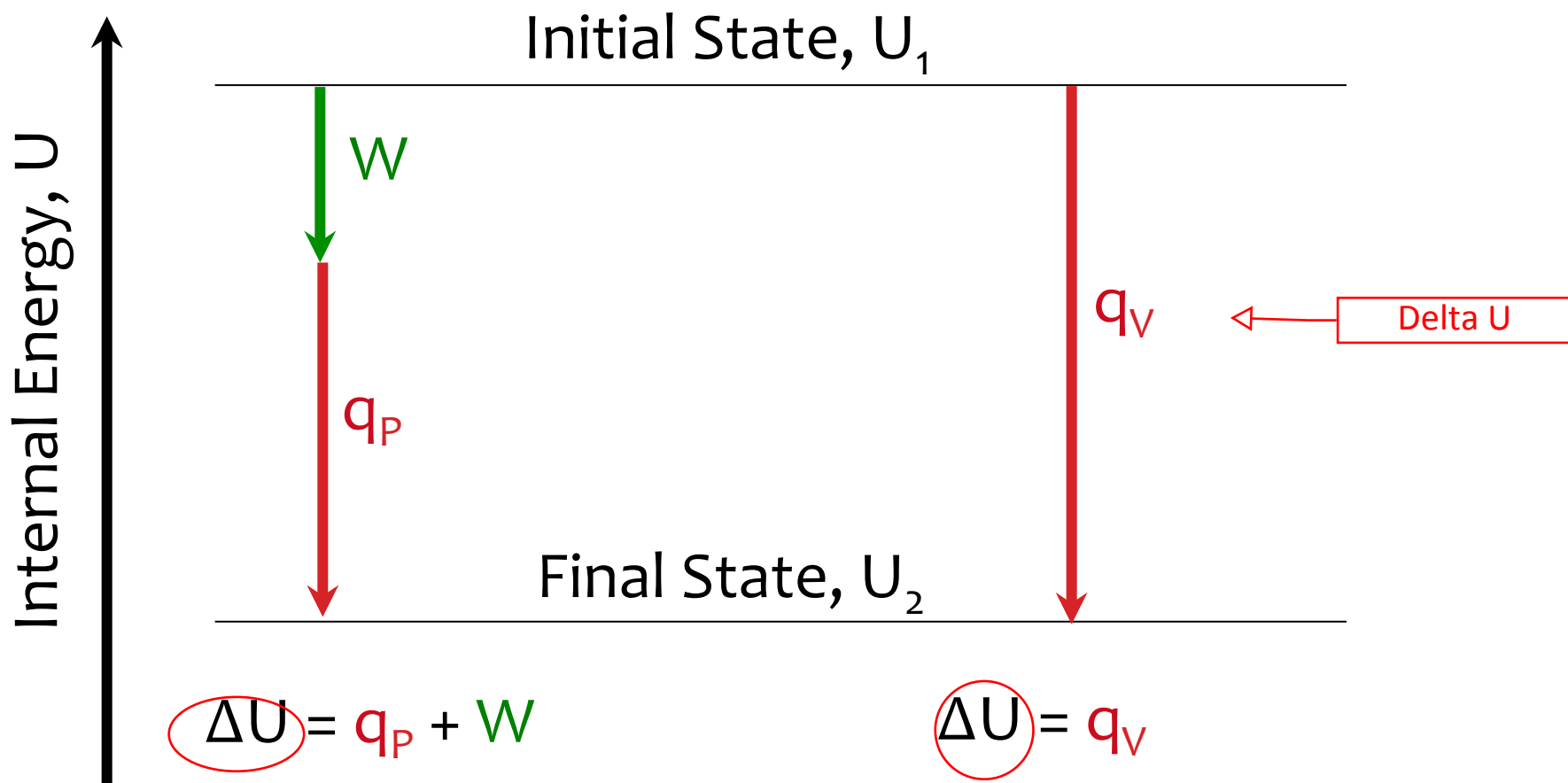
When **volume** is constant
(i.e. bomb calorimeter):

-1% of the time, volume is constant
-V=constant $\Delta v = 0$

$$\Delta u = q_v$$



Constant P. vs. Constant V.



Delta U is the same for both



A New Function: Enthalpy

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

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

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

- Enthalpy, H , is thus defined as:

$$H = U + PV$$

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



Enthalpy $\rightarrow q_p$

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

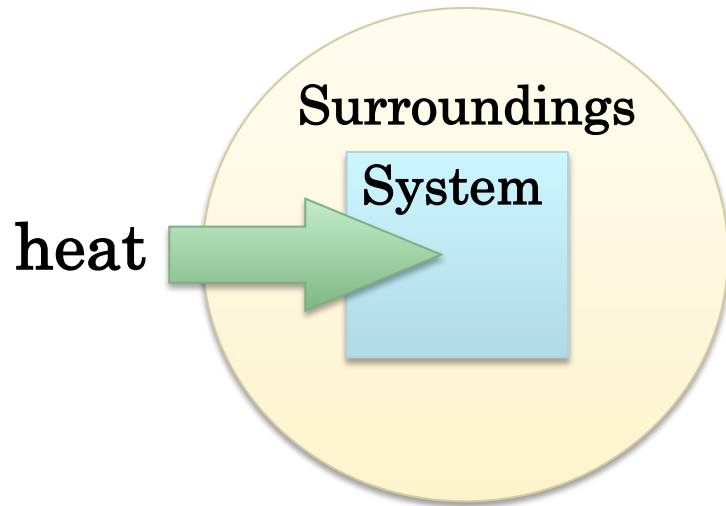
- during a reaction under constant pressure conditions, the enthalpy of the reaction, ΔH , is the amount of heat gained or lost
- enthalpy is a state function

$$\Delta H = H_{\text{final}} - H_{\text{initial}} = H_{\text{products}} - H_{\text{reactants}}$$

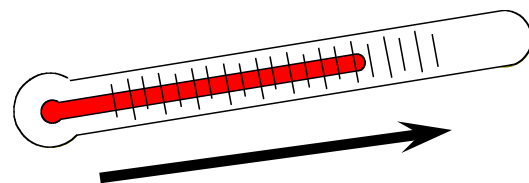
- if $\Delta H > 0$, the reaction is endothermic
- if $\Delta H < 0$, the reaction is exothermic



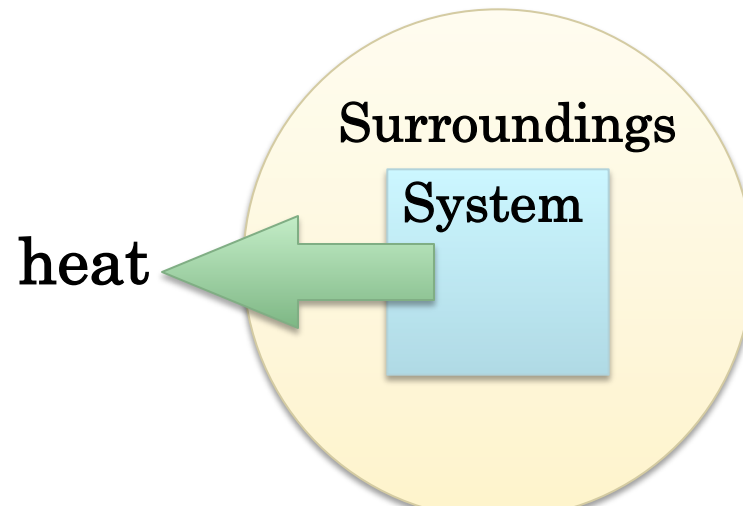
ΔH and Reactions



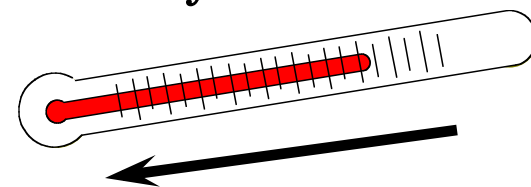
$$q_{\text{system}} > 0$$



ENDOTHERMIC



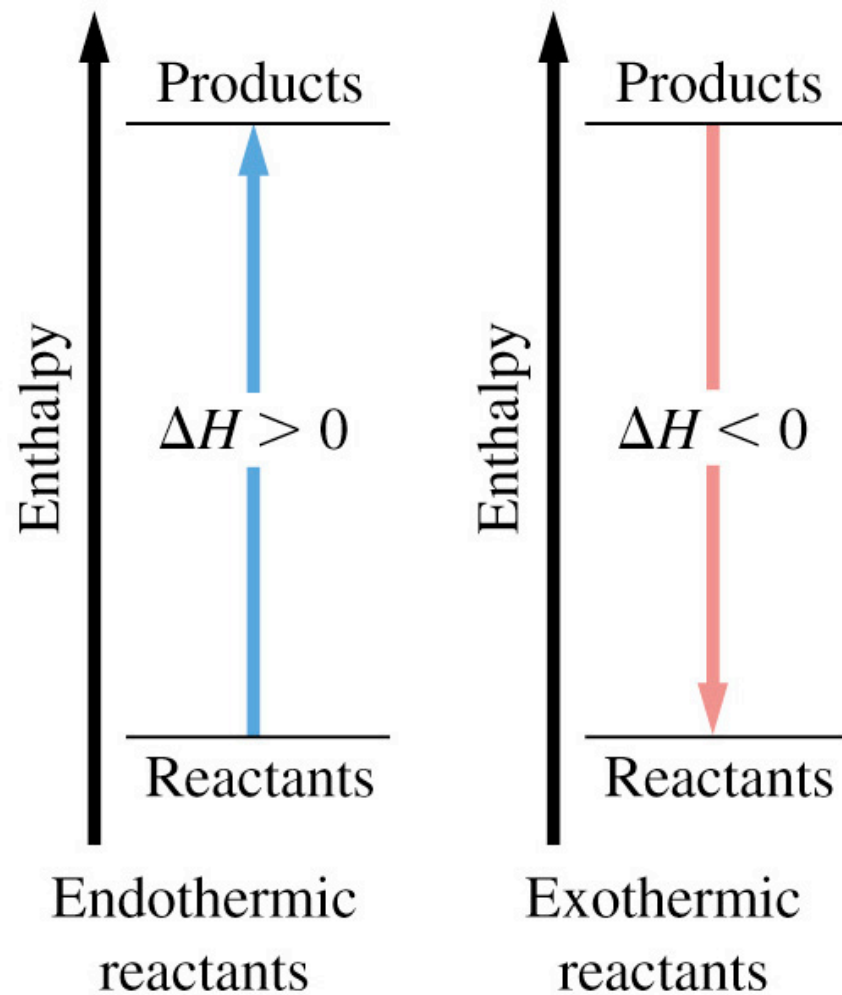
$$q_{\text{system}} < 0$$



EXOTHERMIC



Enthalpy Diagrams – Another way to see it



Constant Volume Calorimetry

- heats of combustion are measured in constant volume bomb calorimeters
- the bomb is an isolated system, so there is no heat or matter transfer to the exterior

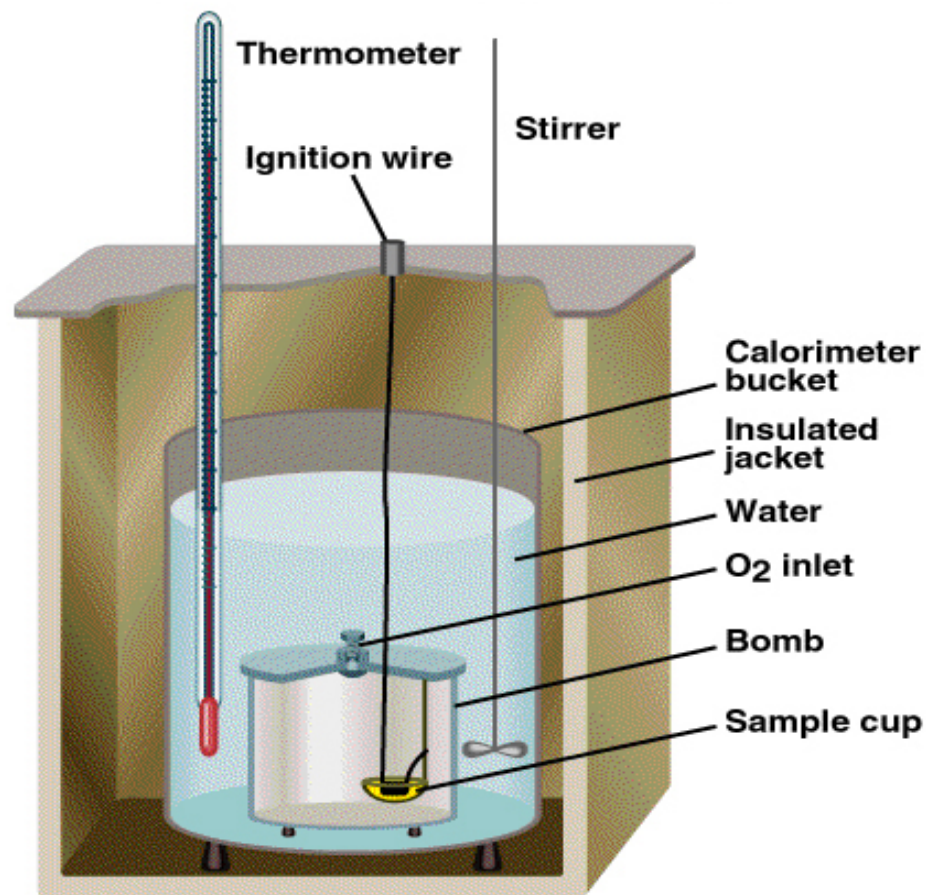
$$q_{\text{system}} = 0$$

$$q_{\text{bomb}} + q_{\text{reaction}} = 0$$

- Therefore:

$$q \text{ of reaction} = -q \text{ of the bomb}$$

$$q_{\text{bomb}} = -q_V$$



Constant Volume Calorimetry

- the heat released by the reaction is absorbed by the water inside the bomb

$$q_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}} s_{\text{H}_2\text{O}} \Delta T$$

$$q_{\text{bomb}} = C_{\text{bomb}} \Delta T$$

where C_{bomb} must be determined in advance using a standard combustion reaction



Constant Volume Calorimetry

- N.B. constant volume conditions!

$$\Delta V = 0$$

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

$$\therefore \cancel{\Delta H}^{qv} = \Delta U - P\Delta V = q_{\text{rxn}}$$

No work is done!!

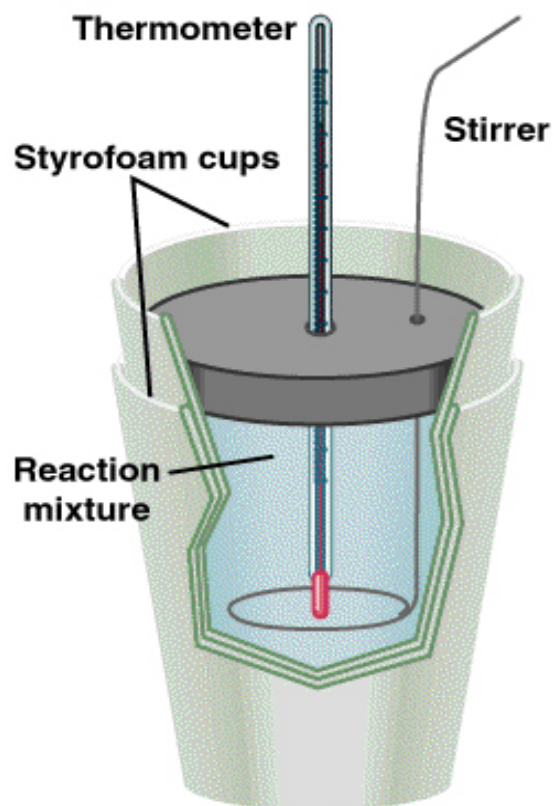


Constant Pressure Calorimetry

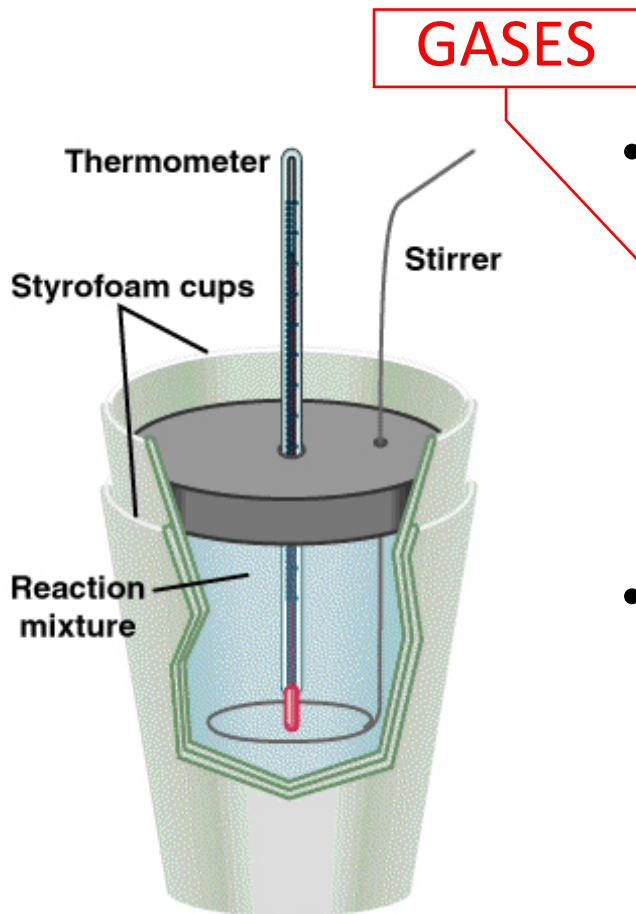
For reactions other than combustions (i.e. endothermic or mildly exothermic reactions), constant pressure conditions are sufficient:

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

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



Constant Pressure Calorimetry



- $\Delta V \neq 0$, so a small amount of internal energy will be transformed into work:

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

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

Extremely small value

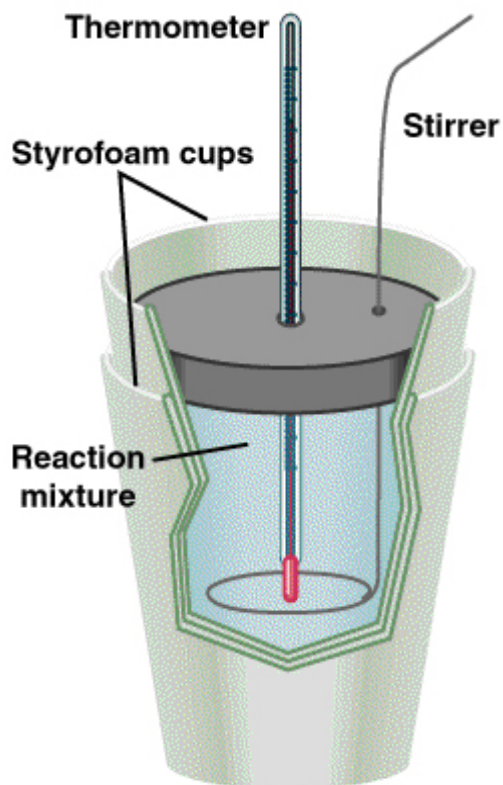
- ***BUT*** for reactions in the solid or liquid phase, ΔV is very small, thus:

$$\Delta H \approx \Delta U = q_P$$

NO GASSES



Constant Pressure Calorimetry



- for reactions in the gas phase ΔV is no longer negligible:

$$PV = nRT$$

P and T are constant

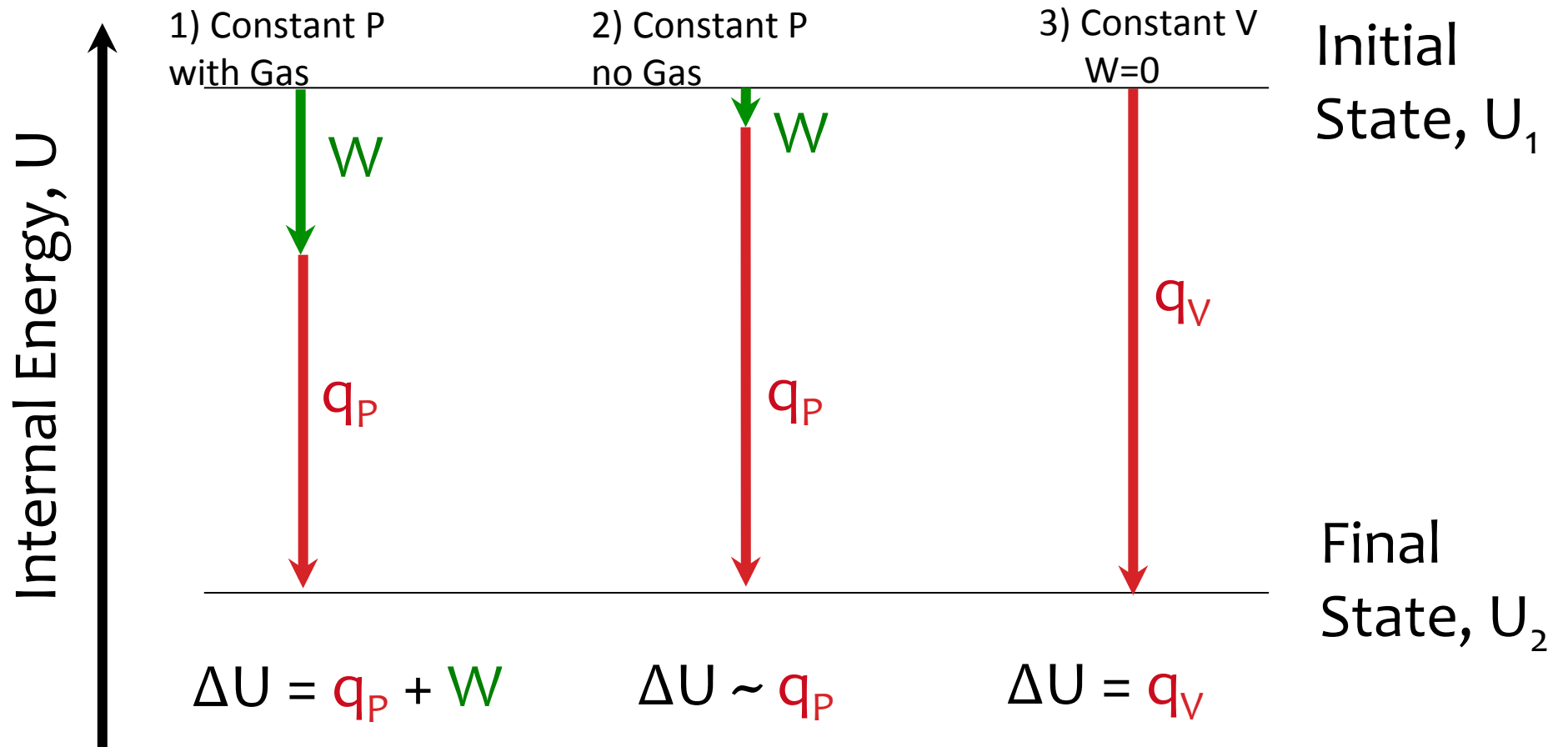
$$P\Delta V = \Delta nRT$$

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

Δn_{gas}

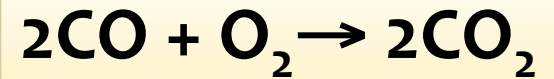


Modified ΔU diagram...



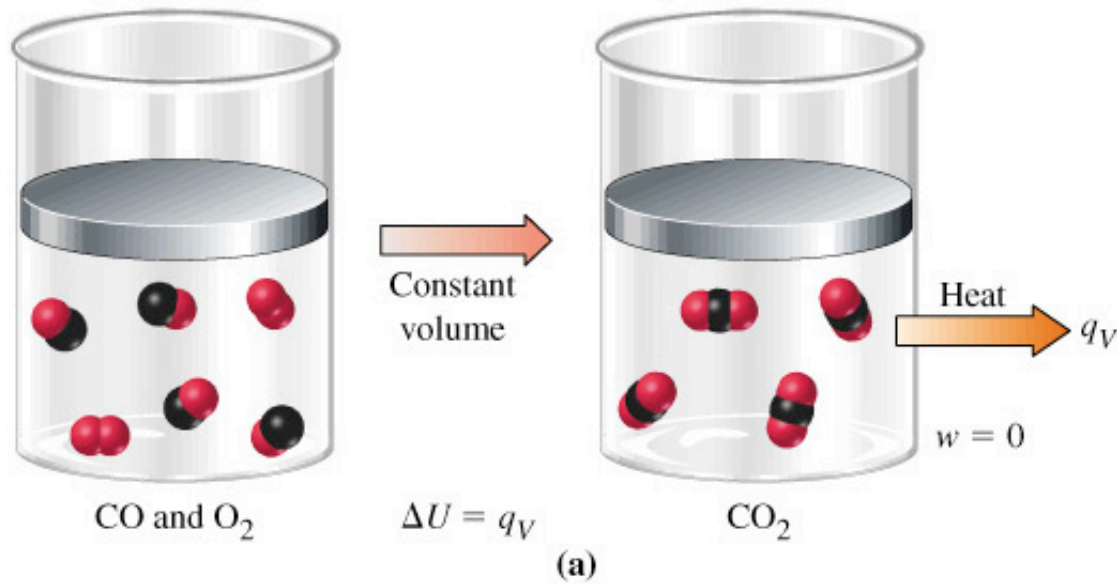
Comparing Heats of Reaction

Consider the following reaction:



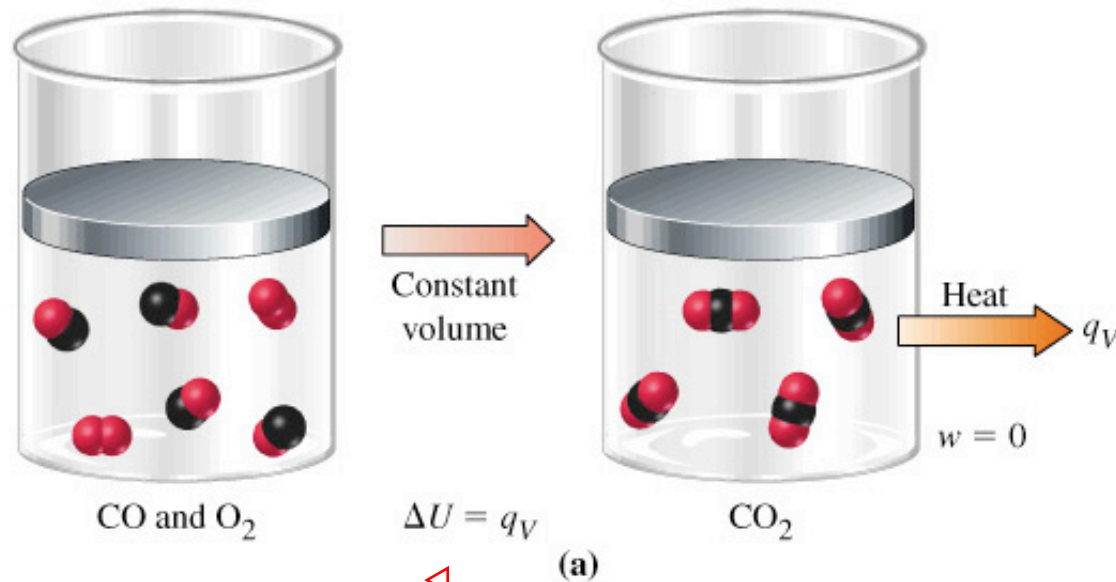
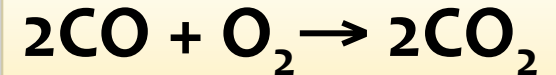
Under constant V:

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



Comparing Heats of Reaction

Consider the following reaction:



Under constant P:

$$P\Delta V = \Delta nRT$$

$$= (n_f - n_i)RT$$

$$= -2.5 \text{ kJ (small!)}$$

$$\text{Work} = -nRT = +2.5 \text{ kJ}$$

Therefore:

$$\Delta U = q_V = q_P - P\Delta V$$

$$q_P = -566 \text{ kJ/mol} = \Delta H$$

Indirect
method of
calculating
enthalpies

See next
figure!

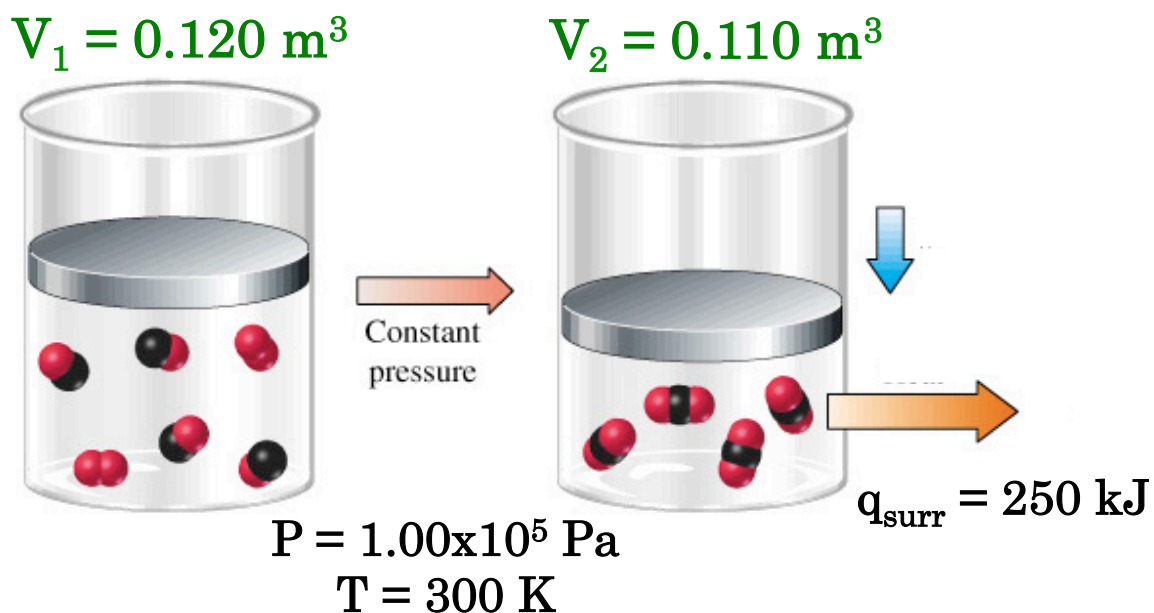


Your Turn...

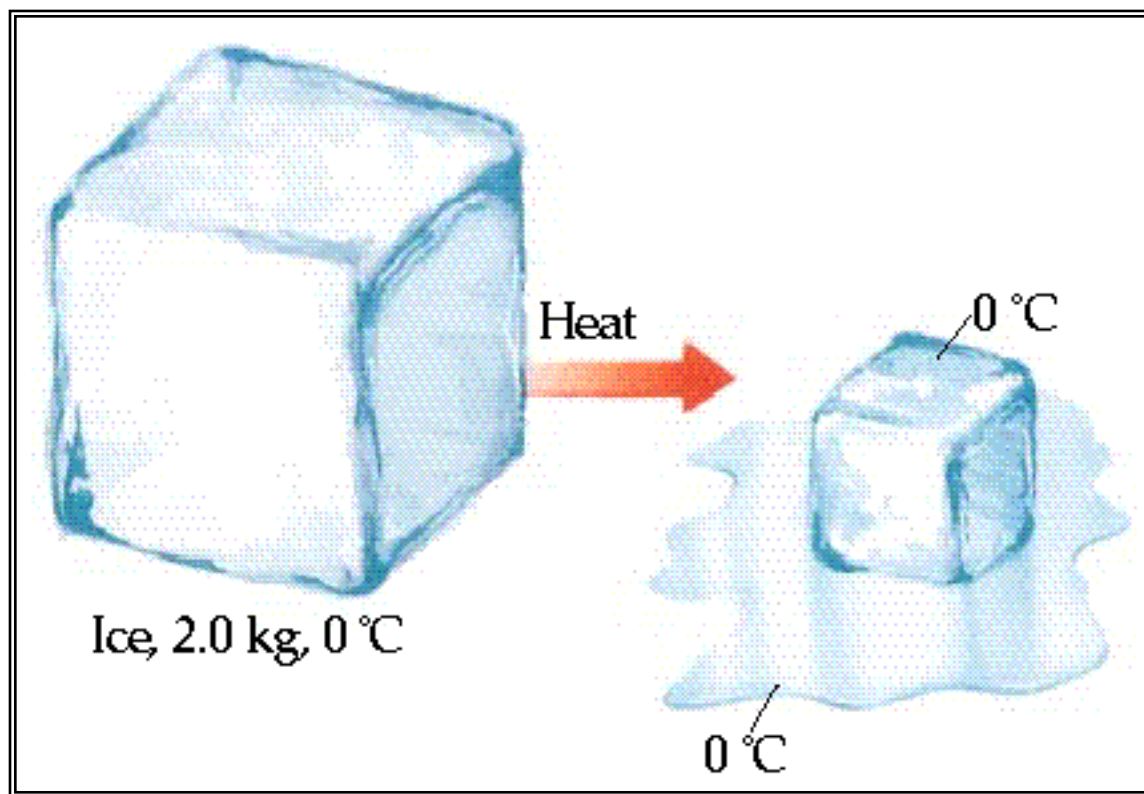
Determine ΔH and ΔU for the process shown below.

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

- | | ΔH | ΔU |
|----|------------|------------|
| A. | -250 kJ | -249 kJ |
| B. | -250 kJ | -251 kJ |
| C. | 250 kJ | 251 kJ |
| D. | 250 kJ | 249 kJ |



Heat Capacity, Enthalpy and Changes of State



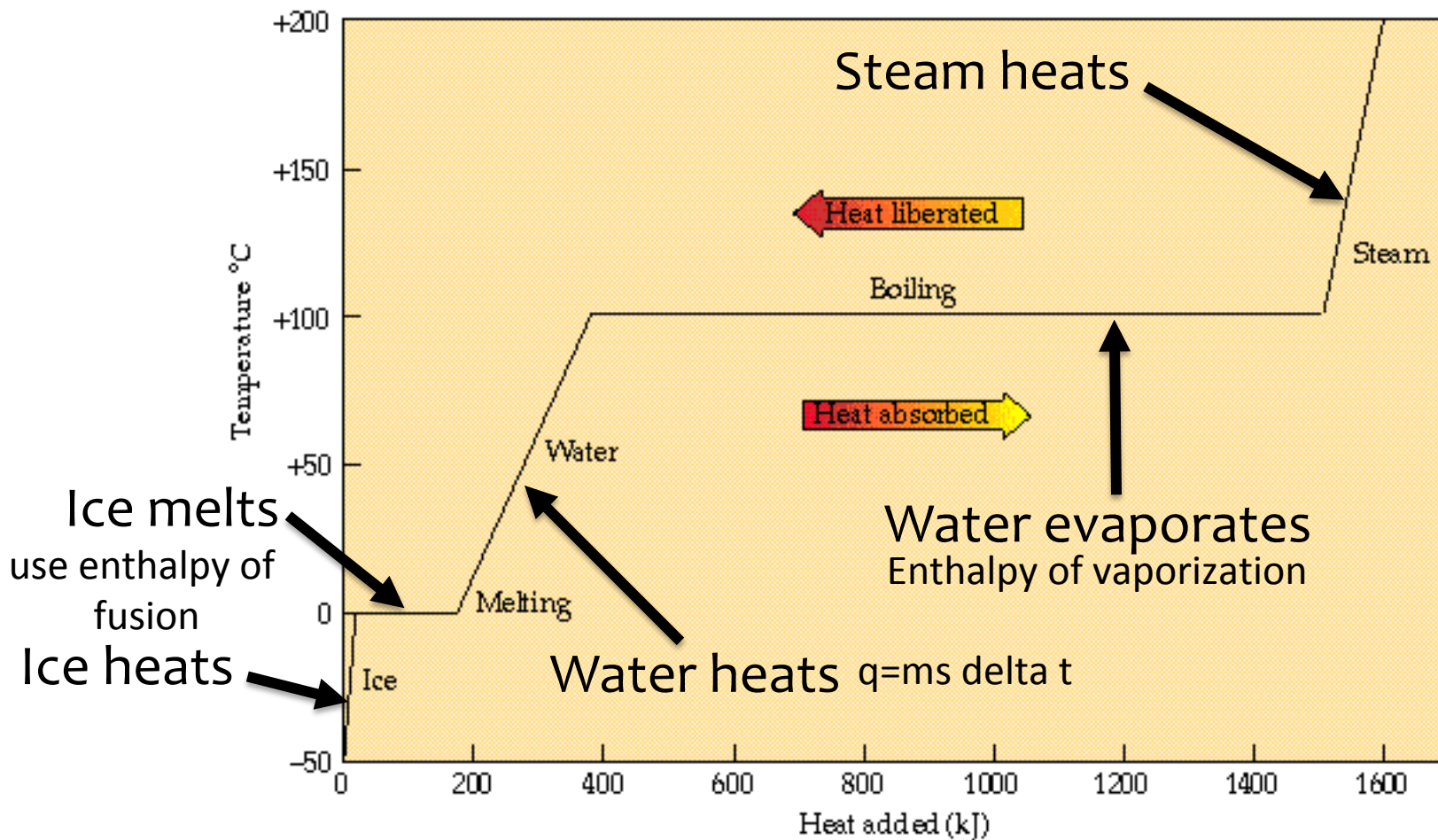
Changes of state involve energy:



(heat of fusion) / (enthalpy of fusion)



Heating / Cooling Curve of Water



Changes of State of Matter

Molar enthalpy of vaporization:



Molar enthalpy of fusion:



Look at Example 7-8 on page 264



Hess's Law: Determining ΔH

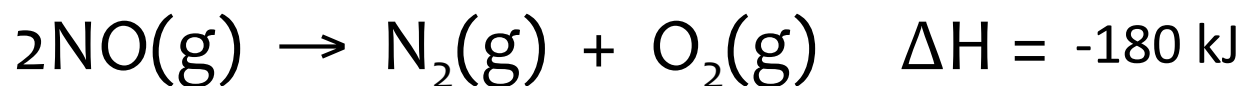
Reactants \rightarrow Products

- One of the real strengths in using enthalpies is that we can determine the enthalpies of many different processes using a much smaller subset of enthalpy values.
- The change in enthalpy is the same whether the reaction takes place in one step or a series of steps.
(**A State Function**)

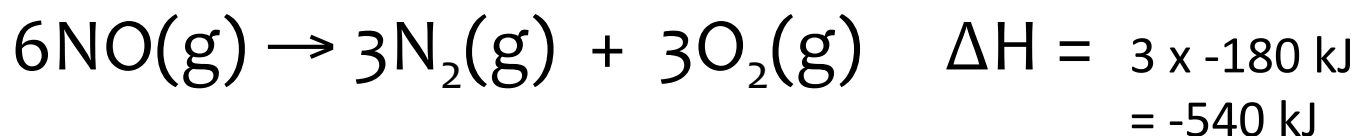


Calculations via Hess's Law

1. If a reaction is **reversed**, ΔH is also **reversed**.



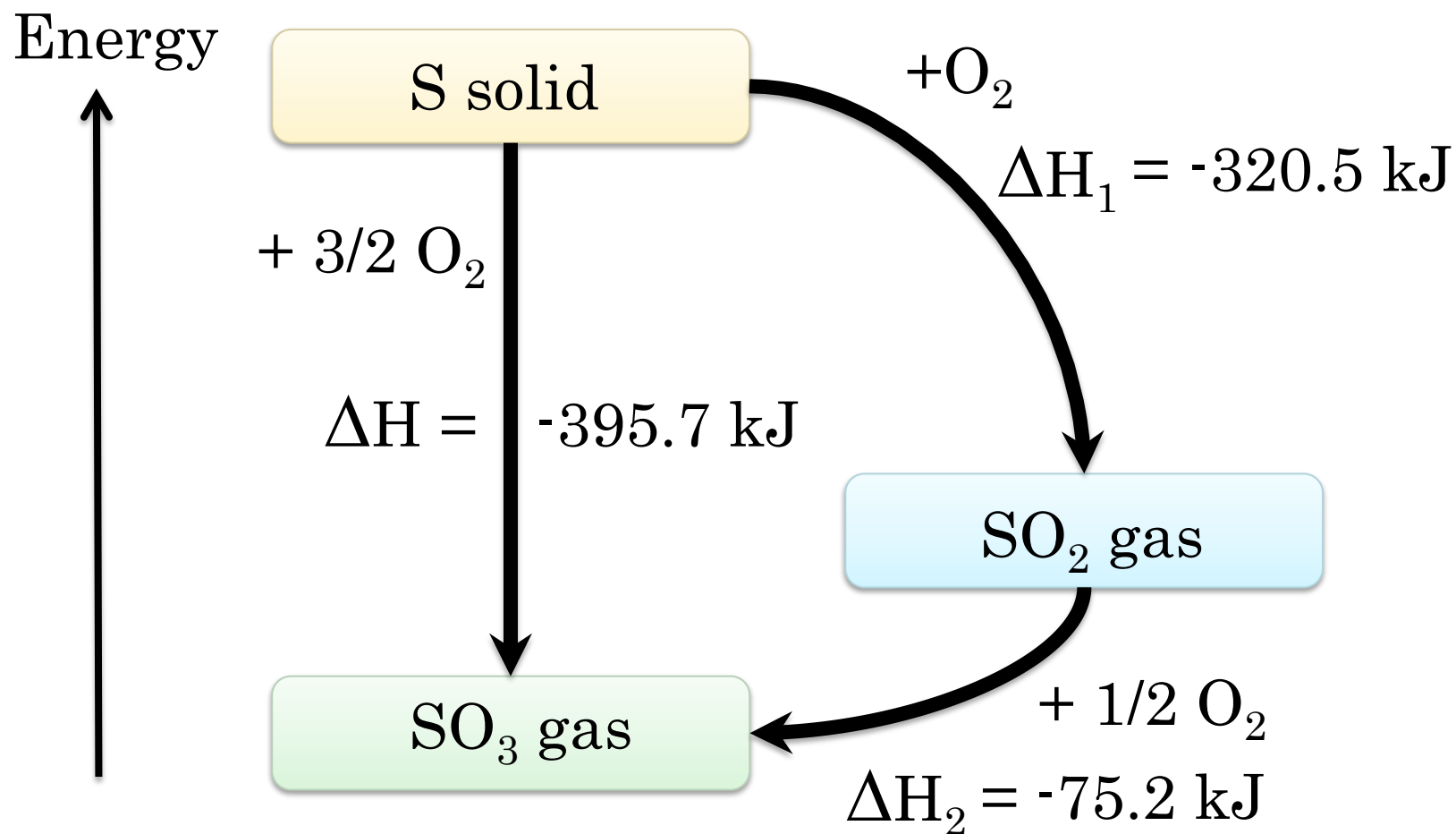
2. If the coefficients of a reaction are **multiplied** by an integer, ΔH is **multiplied** by that same integer.



(extensive function)

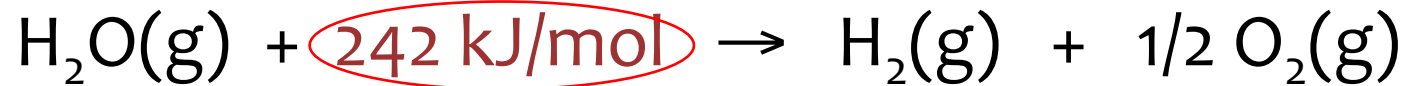


ΔH : A State Function = Independent of Path



Using Enthalpy

Consider the decomposition of water:



This is an **Endothermic** reaction : heat is absorbed by the system.

$$\Delta H = + 242 \text{ kJ/mol}$$

Reactants \rightarrow Products

The change in enthalpy is the same whether the reaction takes place in one step or a series of steps (State Function!)

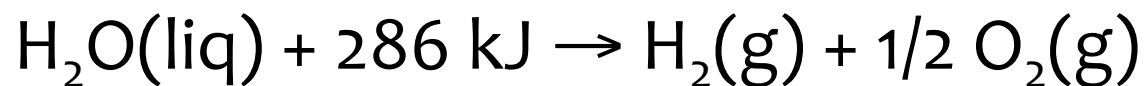
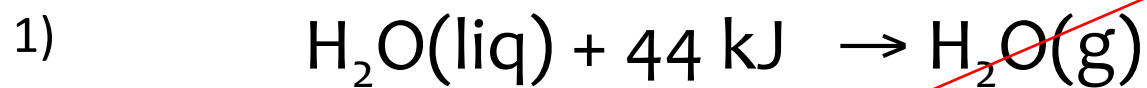


* from previous example*

Hess's Law

Making H_2 from H_2O involves two steps: (1 mole reaction)

Water turning into steam



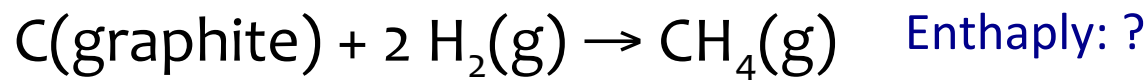
Example of **HESS'S LAW**:

The net ΔH is the **sum of the ΔH 's** of the individual steps

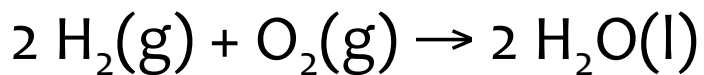


Example : Hess's Law

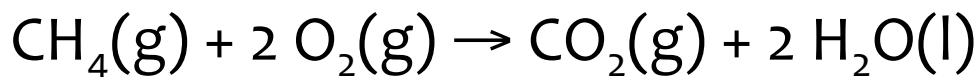
Using the thermochemical data below, calculate the enthalpy of the following reaction:



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



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



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

ANSWER: -74.7 kJ



Standard Enthalpy Values: An “anchor point”

- Measure the enthalpy change under standard conditions
 - ΔH values are labeled ΔH°
- Define a **standard state** (at the temperature of interest – often 298.15K): 25 degrees celcius , this is not the same as STP (0 degrees)
 - **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

ΔH°_f = standard molar enthalpy of formation

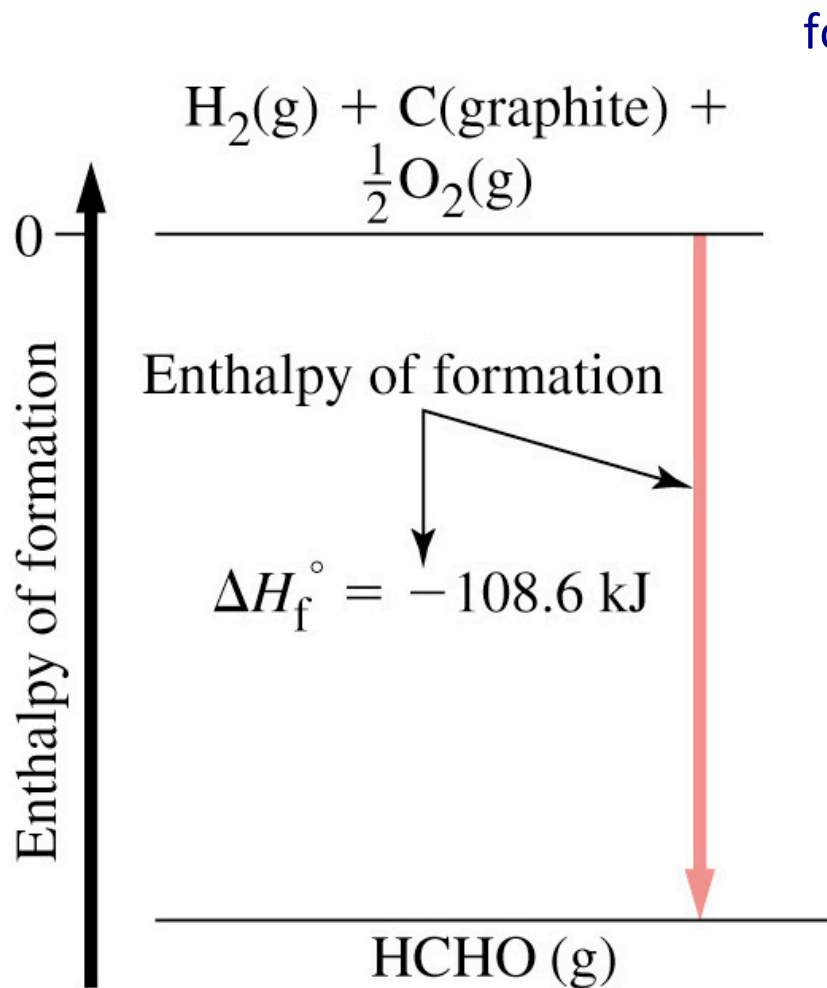
- This is the enthalpy change when **1 mol** of **compound** is formed from the reference form of the **elements** under standard conditions.
- The standard enthalpy of formation of a pure element in its reference state is: zero



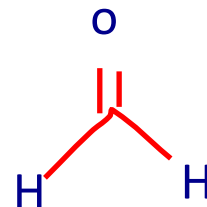
ON MIDTERM, ALSO ON PRACTICE MIDTERM

*X-Men powers question

Standard Enthalpies of Formation

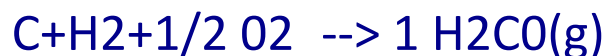


formaldehyde



Need:

- graphite (C)
- hydrogen gas (H_2)
- oxygen (O_2)



$$Q_p = \Delta H_{\text{knought f H}_2\text{CO}}$$

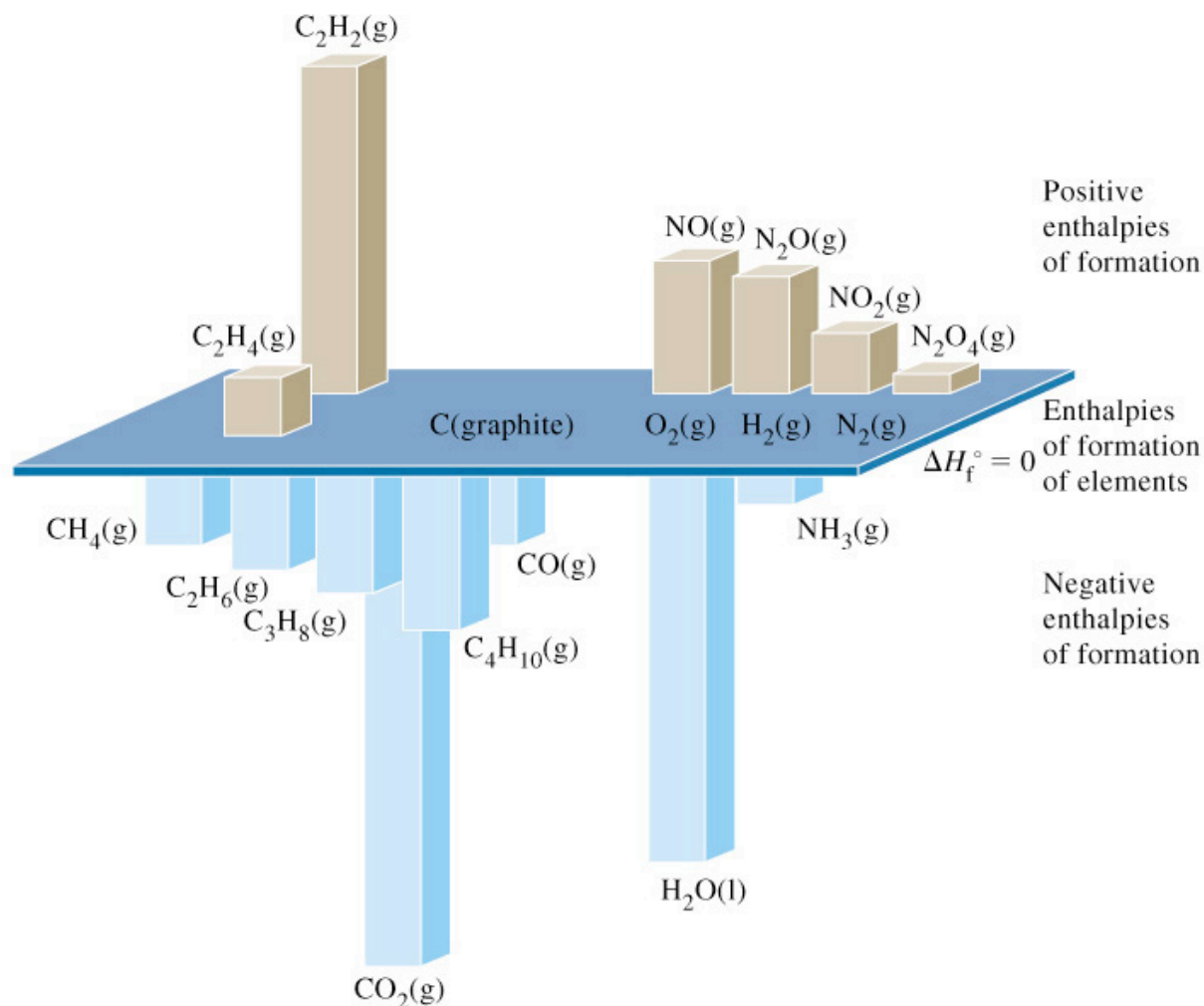


Standard Enthalpies of Formation

Positive

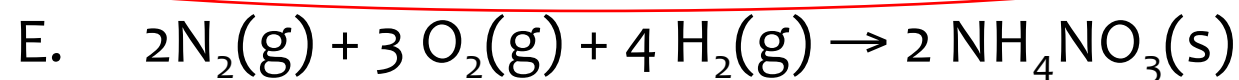
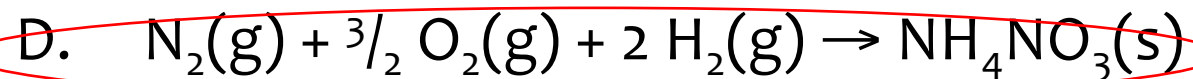
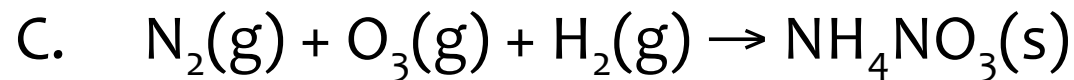
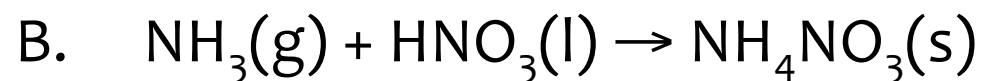
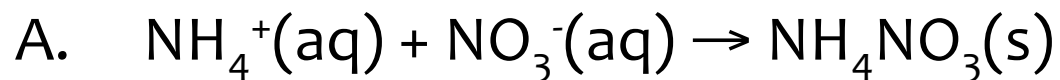
--> elements lie on the plane because their enthalpies are zero

Negative



Your Turn...

Which of the following equations represents the ΔH_f° of ammonium nitrate, NH_4NO_3 ?

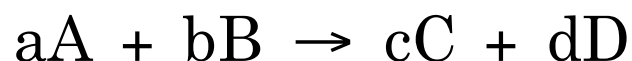


Not allowed to use fractions!



Changes in Enthalpy

- using standard enthalpies of formation, ΔH_f° , 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:

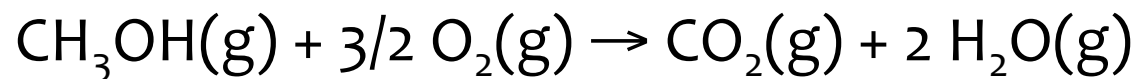
$$\Delta H_{\text{rxn}}^\circ = \sum n \Delta H_f^\circ(\text{products}) - \sum m \Delta H_f^\circ(\text{reactants})$$

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



Example 2: Using ΔH_f° Values

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

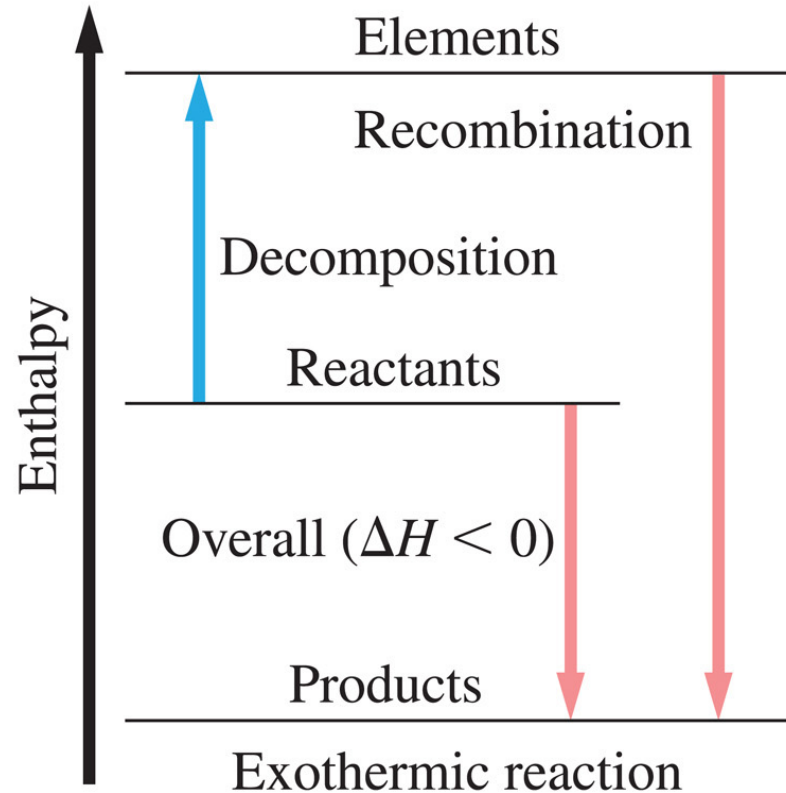
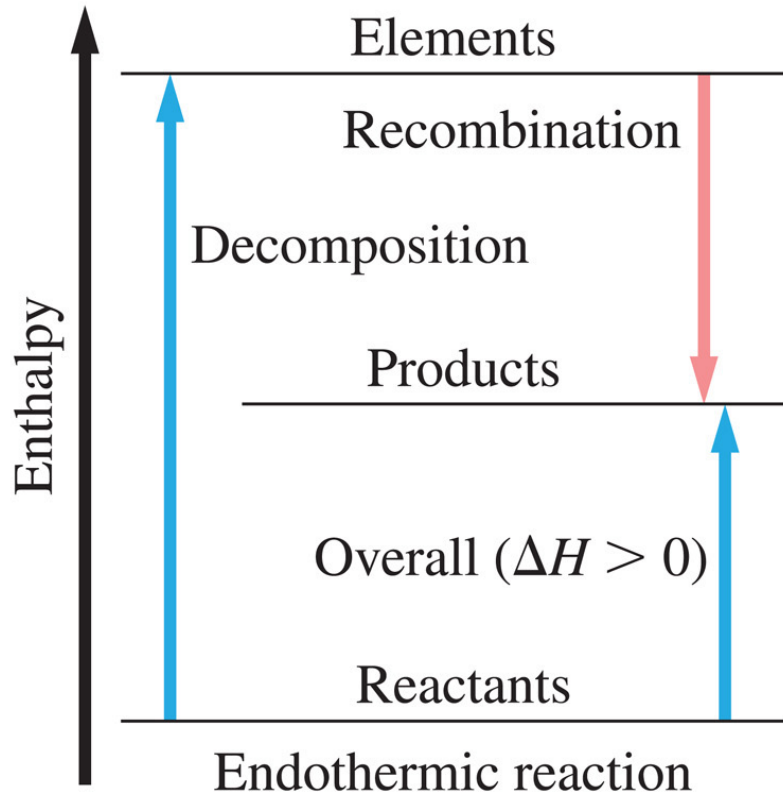


$$\Delta H_{\text{rxn}}^\circ = \sum \Delta H_f^\circ(\text{prod}) - \sum \Delta H_f^\circ(\text{react})$$

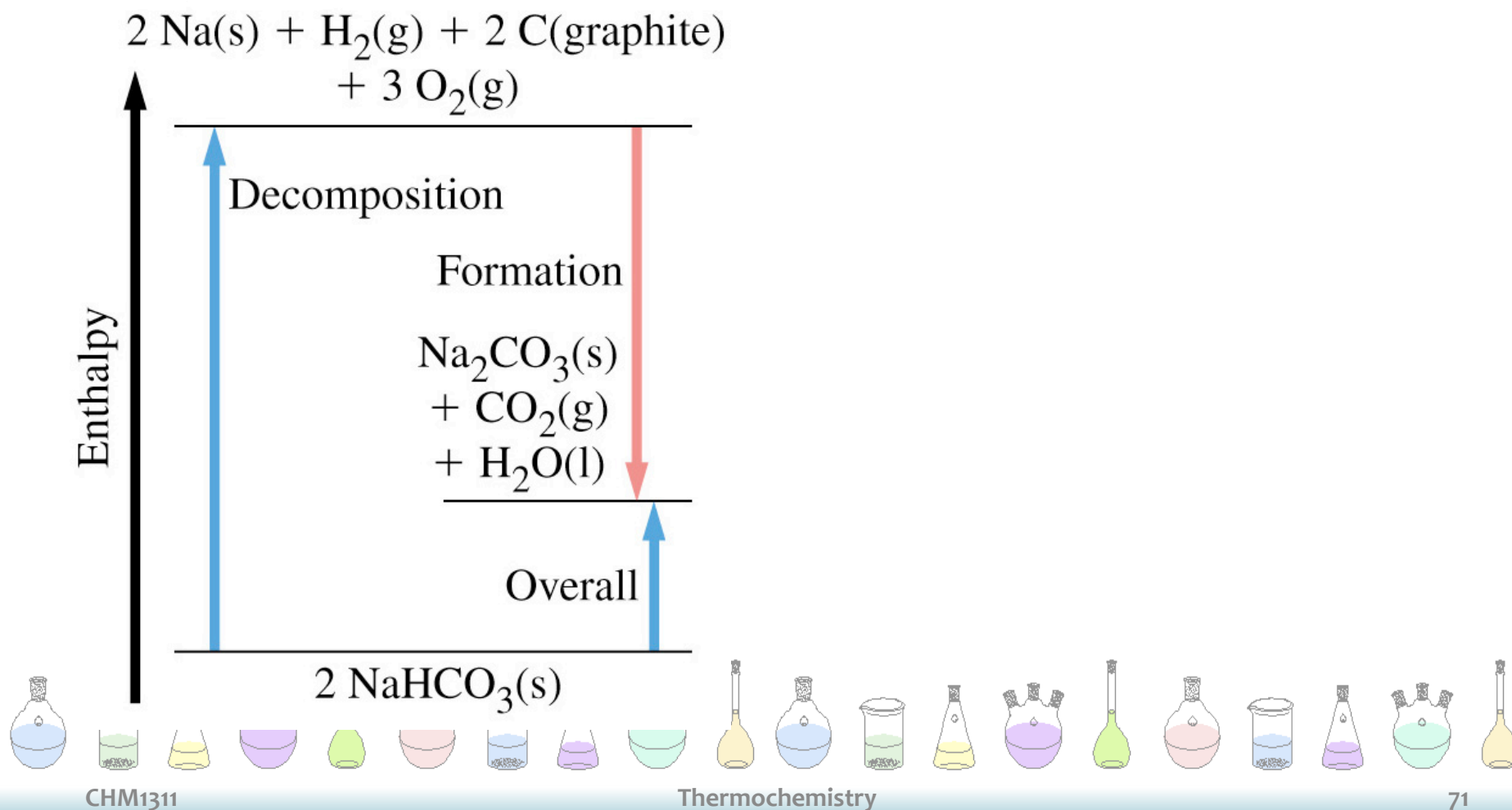
$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \{\Delta H_f^\circ(\text{CO}_2) + 2 \Delta H_f^\circ(\text{H}_2\text{O})\} - \{3/2 \Delta H_f^\circ(\text{O}_2) + \Delta H_f^\circ(\text{CH}_3\text{OH})\} \\ &= \{(-393.5 \text{ kJ}) + 2(-241.8 \text{ kJ})\} - \{0 + (-201.5 \text{ kJ})\} \\ &= \mathbf{-675.6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



Using Enthalpy Diagrams

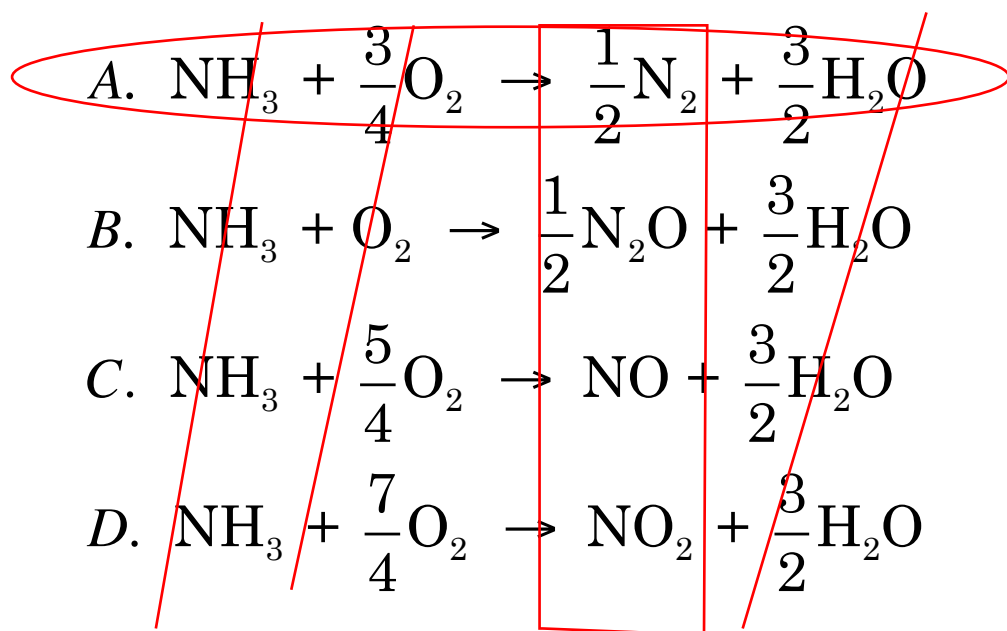


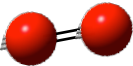
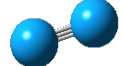
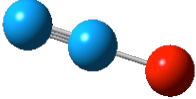
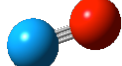
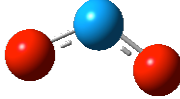
Standard Enthalpies of Reaction



Your Turn...

Given the heats of formation of the potential products of the Ostwald process, which reaction is the **most exothermic**?



		$\Delta H_f^\circ / \text{kJ mol}^{-1}$
O_2		0
N_2		0
N_2O		82.1
NO		90.2
NO_2		33.2



Ionic Reactions

- Many reactions would be easily treated using a net ionic reaction.
- The problem is that we cannot determine an enthalpy of formation for a single type of ion (cation or anion)!
- We can define a new anchor point for ionic reactions: arbitrarily select an ion with ΔH_f° equal to **zero** in (aq) solution – **$H^+(aq)$**



Enthalpies of Formation of Ions in Aqueous Solutions

TABLE 7.3 Some Standard Molar Enthalpies of Formation of Ions in Aqueous Solution at 298.15 K, ΔH_f°

Ion	kJ/mol	Ion	kJ/mol
H^+	0	OH^-	-230.0
Li^+	-278.5	Cl^-	-167.2
Na^+	-240.1	Br^-	-121.6
K^+	-252.4	I^-	-55.19
NH_4^+	-132.5	NO_3^-	-205.0
Ag^+	105.6	CO_3^{2-}	-677.1
Mg^{2+}	-466.9	S^{2-}	33.05
Ca^{2+}	-542.8	SO_4^{2-}	-909.3
Ba^{2+}	-537.6	$S_2O_3^{2-}$	-648.5
Cu^{2+}	64.77	PO_4^{3-}	-1277
Al^{3+}	-531		



Chapter 7: 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



Chapter 7: Suggested Problems

5, 17, 31, 37, 39, 49,

51, 55, 57, 63, 65*

(*note: 2-propanol = $\text{CH}_3\text{CHOHCH}_3$)

69, 75, 79, 87, 97, 112

MIDTERM ONE MATERIAL ENDS HERE

