



Module 3

Thermochemistry

Session Slides with Notes

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The First Law of Thermodynamics



$$\Delta U = Q - W$$

← pressure-volume work

$$= Q - P^* \Delta V$$

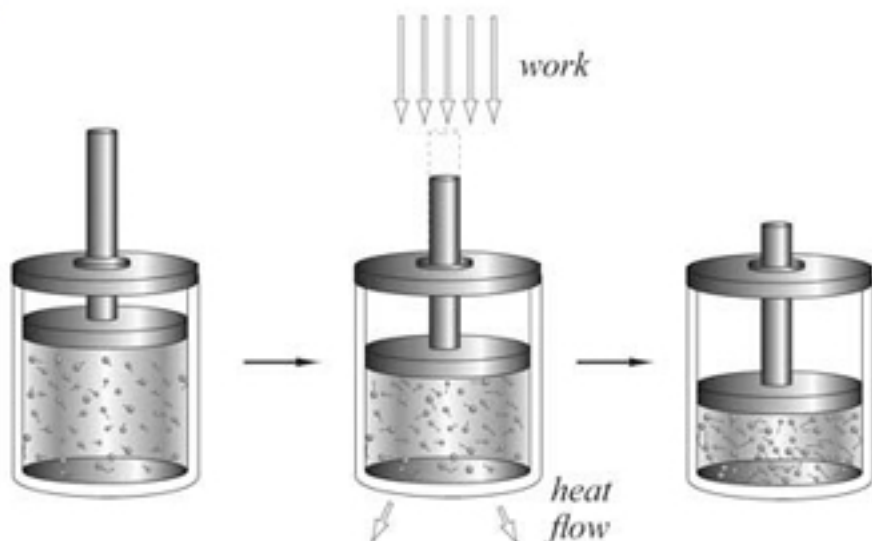
ΔU = internal energy change

Q = heat flow

W = macroscopic work

P^* = constant pressure

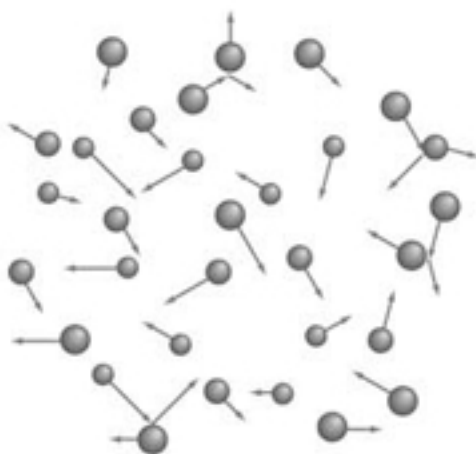
ΔV = volume change



Internal energy change results from the combination of heat flow and work between the system and its surroundings. In this example, the internal energy of our ideal gas system became greater (the particles are moving faster in the final state) because more energy entered the system through work than departed the system as heat flow.

The Internal Energy of an Ideal Gas Depends on Temperature

- internal energy is only the kinetic energy of the particles (translational)
- thermal energy



- no interaction at a distance forces
- point mass

$$\frac{U}{N} = \frac{3}{2}kT$$

$$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT$$

$$U = \frac{3}{2}NkT$$

U = internal energy
 N = number of molecules
 k = Boltzmann's constant
= R / Avogadro's number
 T = temperature

$$U = \frac{3}{2}nRT$$

n = moles of gas
 R = ideal gas constant

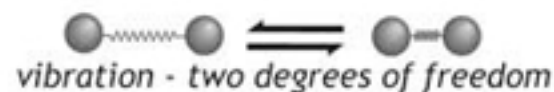
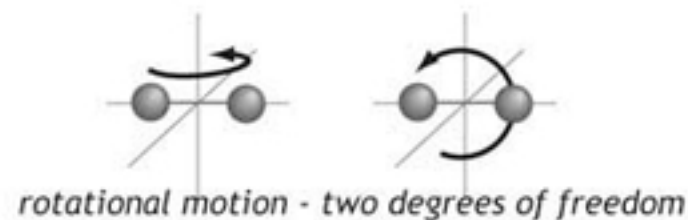
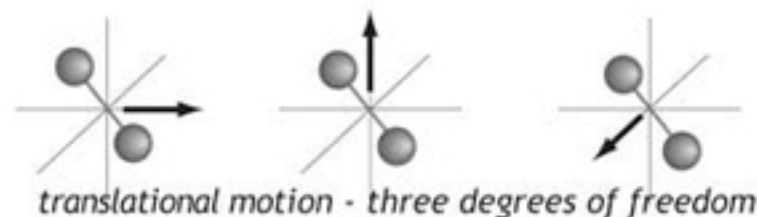
Molar Heat Capacities ($\text{J mol}^{-1} \text{K}^{-1}$)

He	20.5	N_2	29.5	H_2O	33.5
Ar	20.5	F_2	31.4	CO_2	37.2

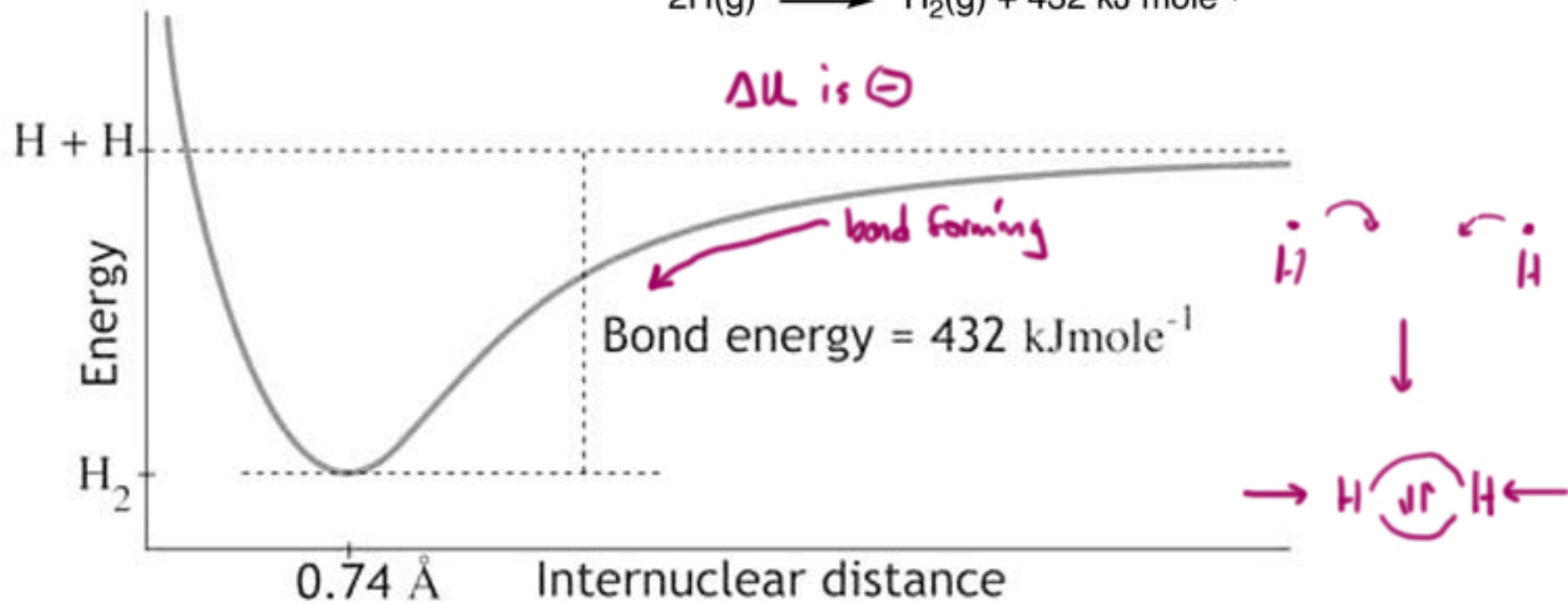
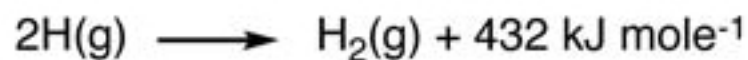
$\frac{\text{J}}{\text{mol K}}$

$$KE_{total} = KE_{trans} + KE_{rot} + KE_{vib}$$

$$U = KE_{total} + PE_{total}$$

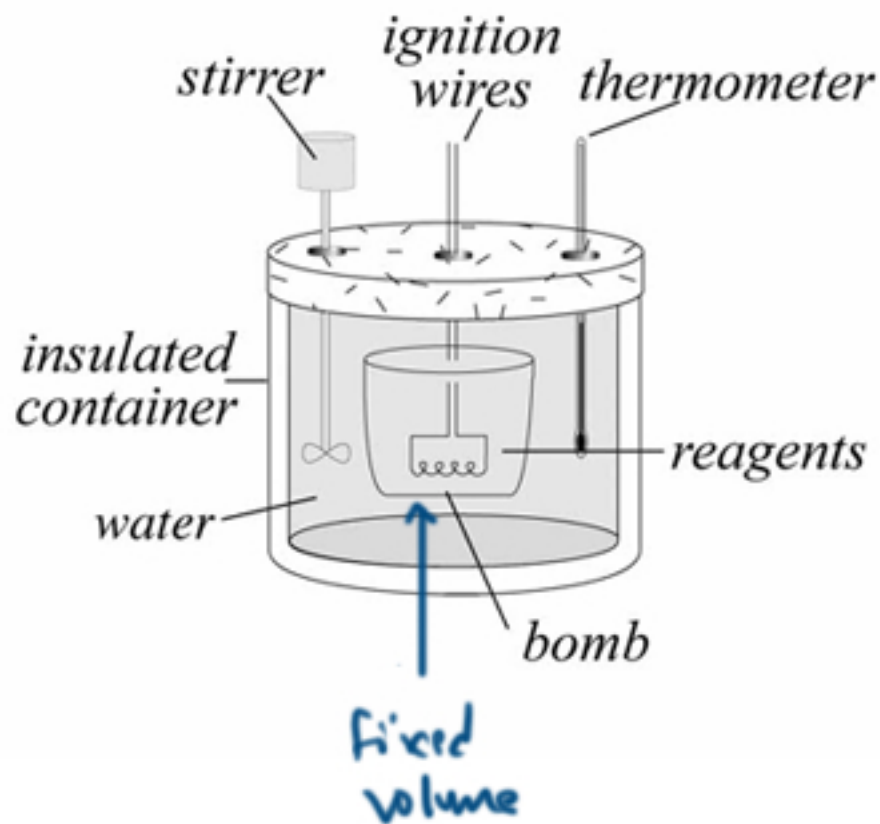


- Real substances may also have vibrational and rotational kinetic energy.
- even just the thermal energy is more complicated



With real substances, internal energy change can occur along lines of electrostatic potential energy.

$$\Delta U = Q - W$$



$$\Delta U = Q \quad (\text{constant volume, } W = 0)$$

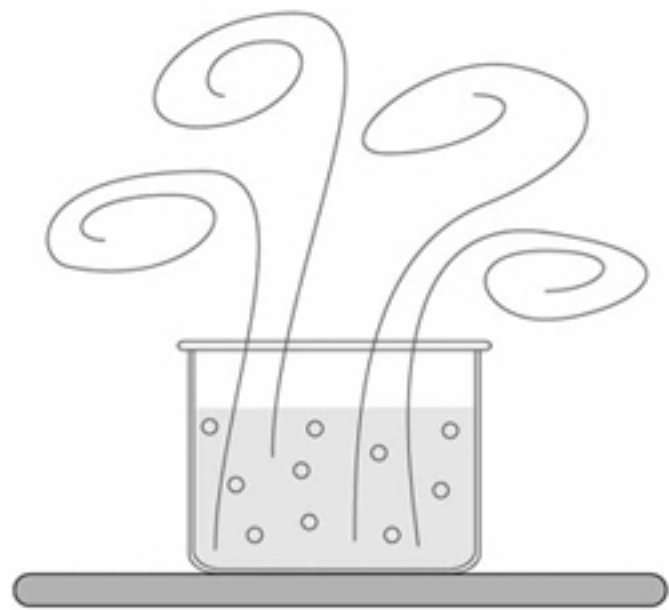
if $\Delta V = 0$, then $W = 0$

Internal energy change
will equal the heat flow

The enthalpy - a state function

$$H = U + PV \leftarrow \begin{array}{l} \text{think about} \\ \text{it as a} \\ \text{kind of} \\ \text{thermal} \\ \text{potential} \end{array}$$

A state function whose change equals heat flow (as long as P is constant)



$$\Delta U = Q - W \text{ (benchtap) 1st law}$$

$$H = U + PV \leftarrow \text{the enthalpy}$$

$$\Delta H = \Delta U + \Delta(PV) \\ \text{if P is constant}$$

$$\Delta H = \Delta U + P\Delta V \leftarrow P\Delta V = \text{work}$$

summation law

$$\Delta H = (Q - W) + P\Delta V$$

$$\Delta H = Q \text{ (constant pressure)}$$

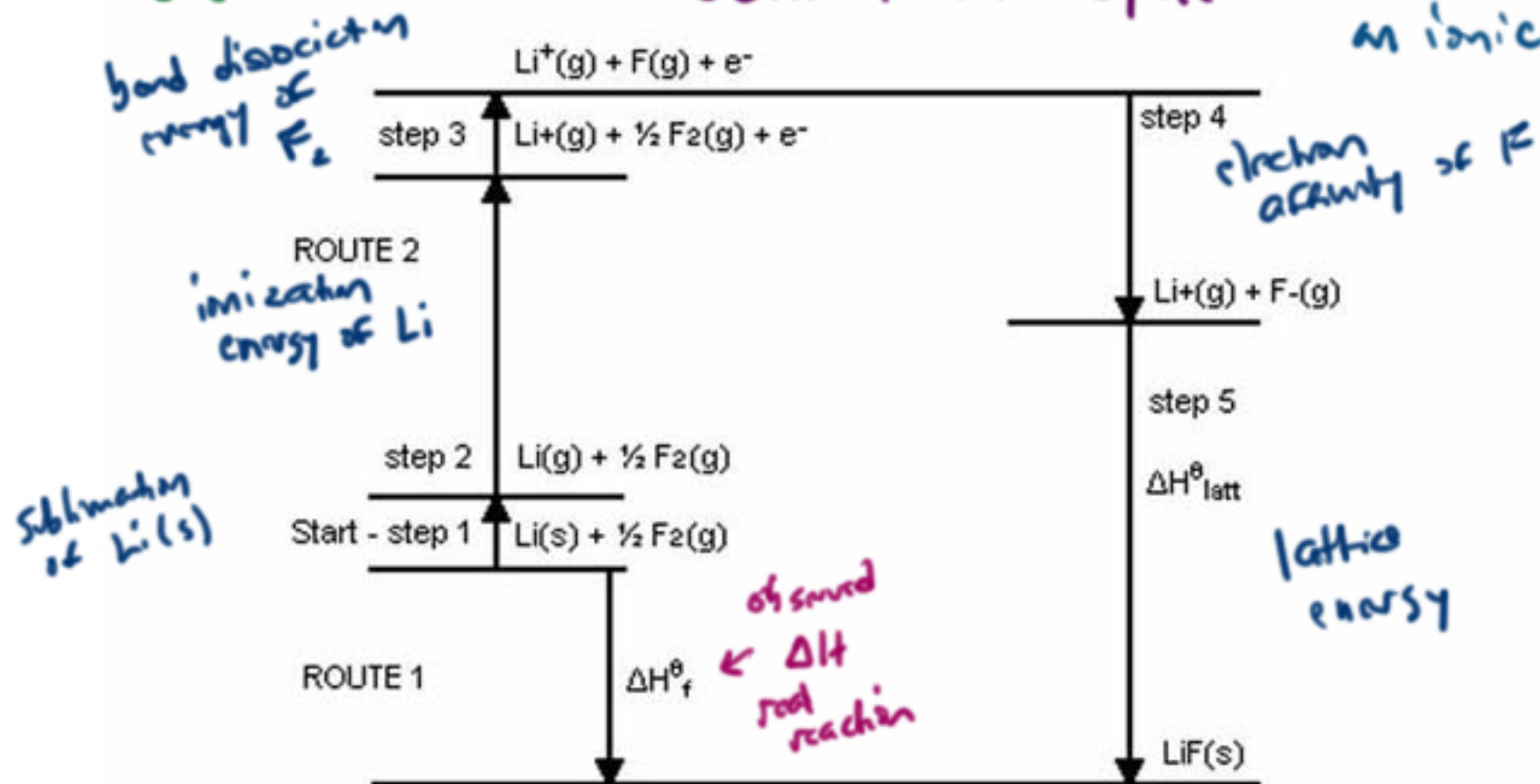
Now we can treat heat flow as path independent.

Hess' Law of Heat Summation



Born-Haber Cycle

Formation of an ionic compound.



Demonstration of Hess' Law

$$H = U + PV$$

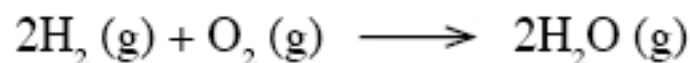
A positive value of ΔH for a reaction ^{at STP} means that:

- A. The internal energy of the substance has increased. (only if ΔV is 0)
- B. Heat is given off to the environment during the reaction.
- C.** Heat is absorbed from the environment during the reaction.
- D. The reaction is exothermic.

$$H = U + PV$$

$$H = U + PV$$

Which of the following statements is true about the following exothermic reaction, when carried out at constant temperature and pressure?



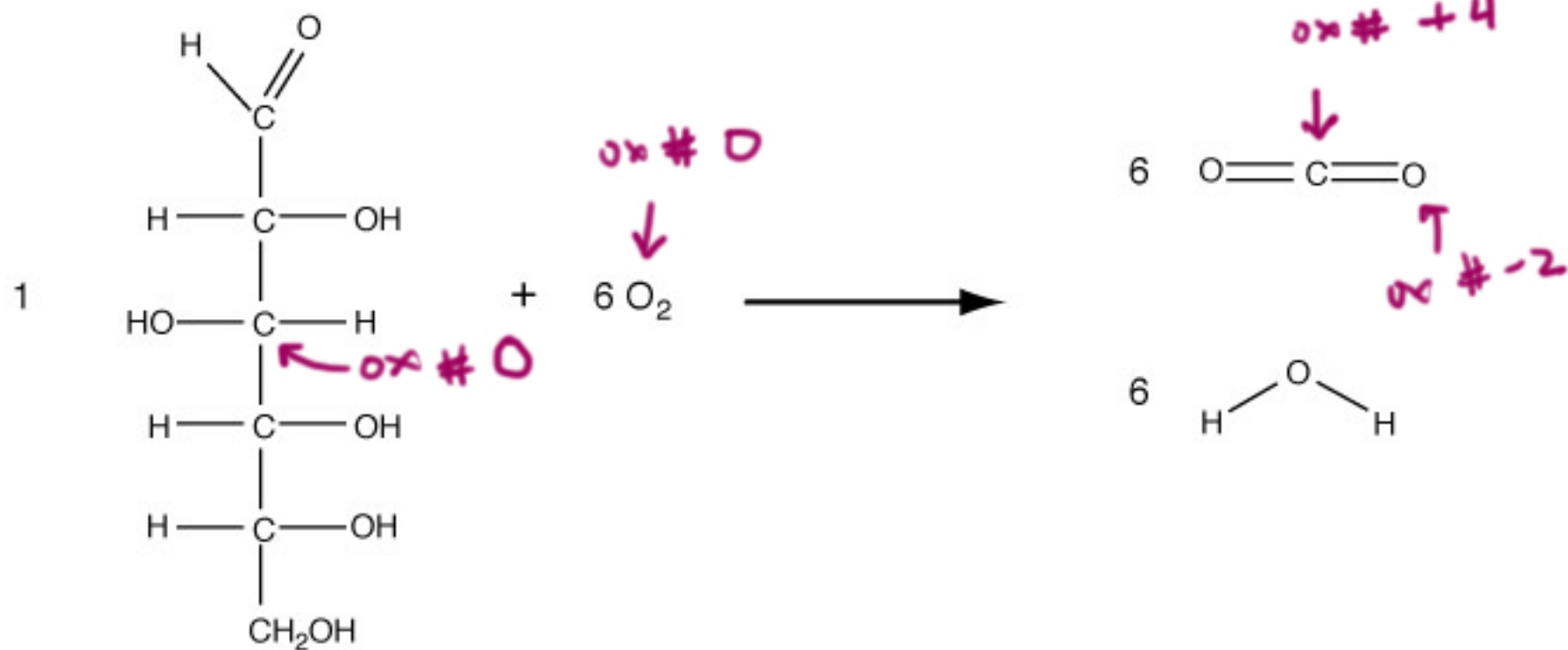
- 3 moles* *2 moles*
- A. The magnitude of the change in internal energy over the reaction is greater than the magnitude of the enthalpy change.
- B.** The magnitude of the change in internal energy over the reaction is less than the magnitude of the enthalpy change.
- C. The magnitude of the change in internal energy over reaction is equal to the magnitude of the enthalpy change.
- D. Impossible to determine any of the above from given information.

Is ΔH equal
to ΔU ?

$$\Delta U = Q - W$$

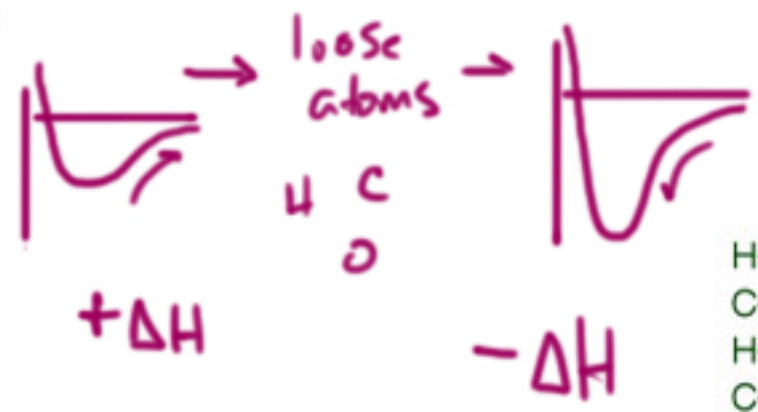
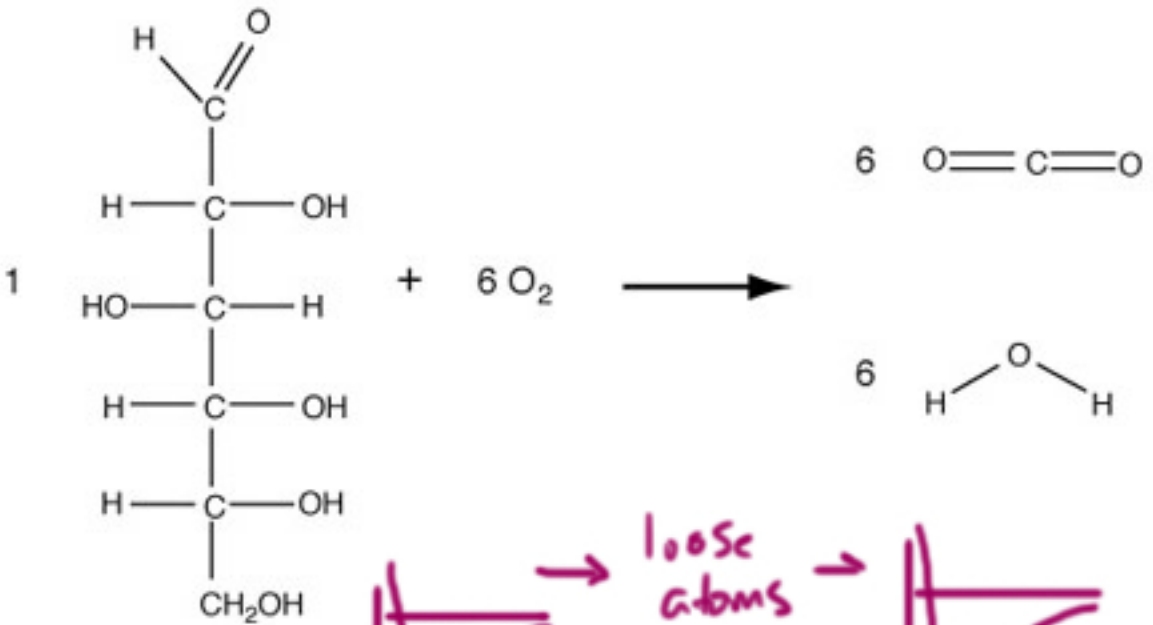
Is the volume
changing?

Combustion of Glucose



Glucose

$$\Delta H \sim -3000 \text{ kJ}$$



Bond Energy KJ/mole	
H-C	411
C-C	346
H-O	459
C-O	359
C=O	799
O=O	494

Sum it all up

$\Delta H \sim -3000 \text{ kJ}$

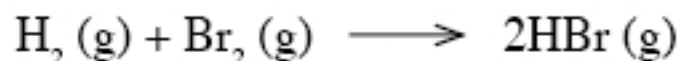
Given these bond energies:

H-H (435 kJ/mol)

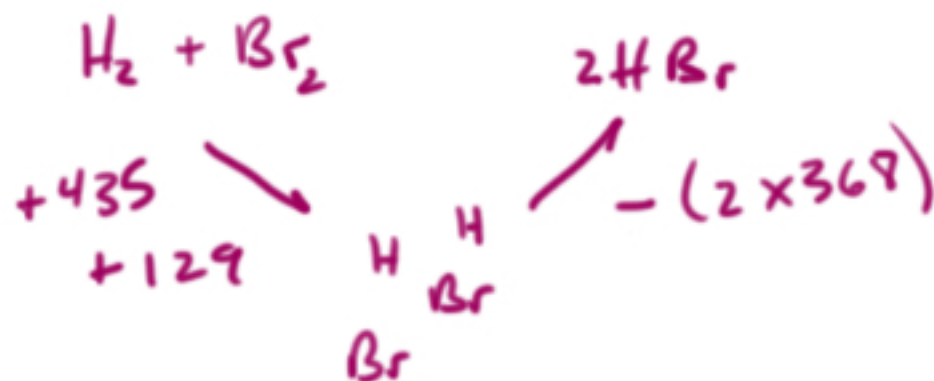
Br-Br (192 kJ/mol)

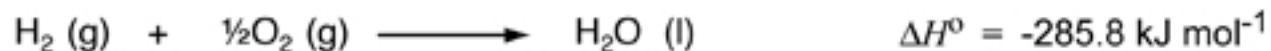
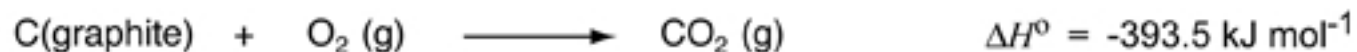
H-Br (368 kJ/mol)

Which is following would be the best estimate of the enthalpy change of the following reaction?



- A. -26 kJ
- B. -109 kJ**
- C. 259 kJ
- D. 109 kJ





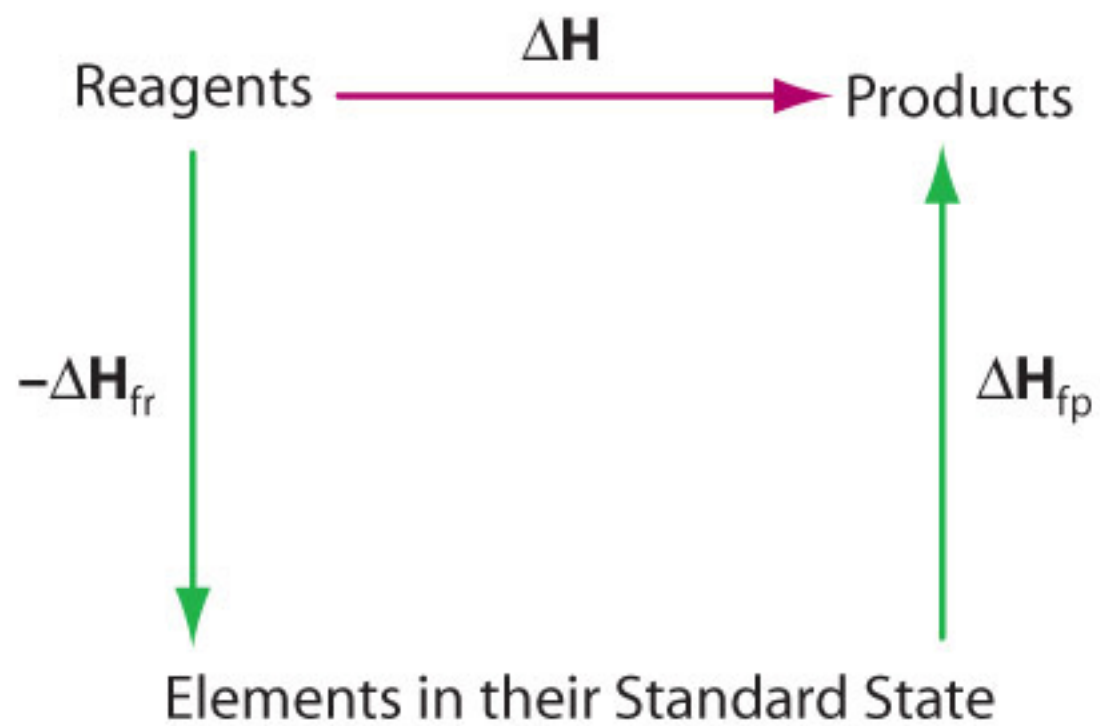
Standard states
of the elements

$\text{C}_{\text{graphite}}$ H_2
 $\text{Na}(\text{metal})$ S_8

$$\Delta H = \Delta H_f^{\text{products}} - \Delta H_f^{\text{reactants}}$$

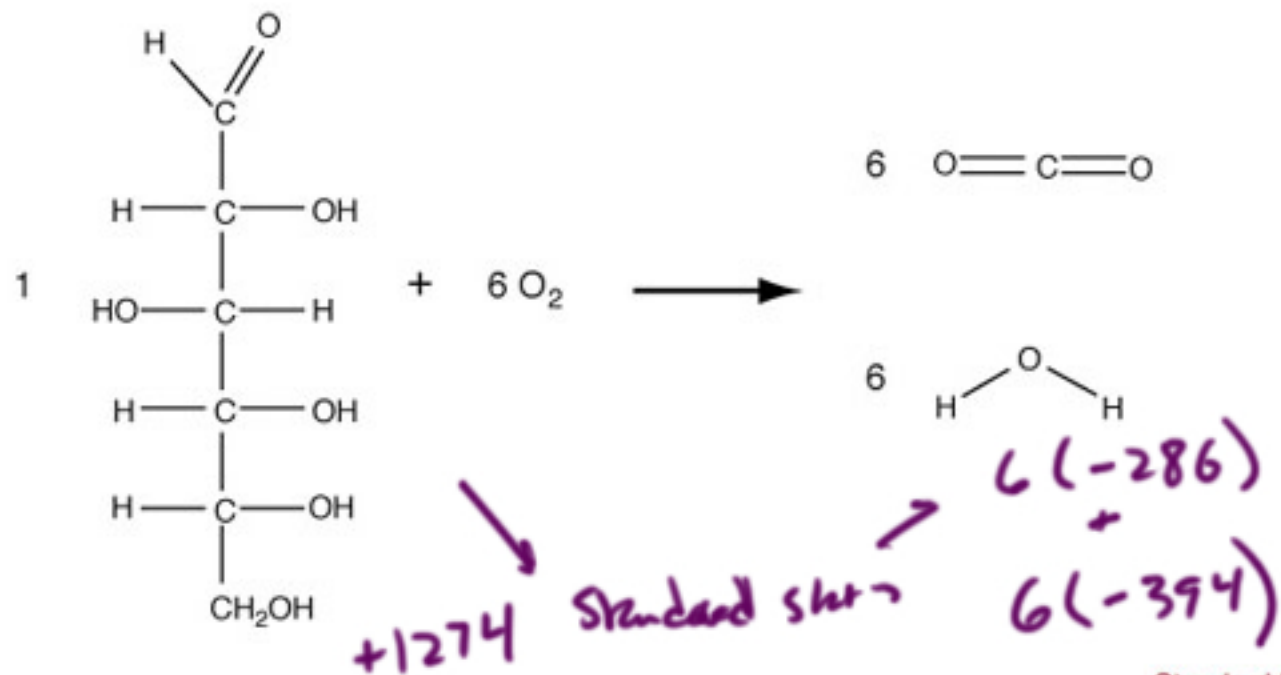
Standard enthalpies of formation

Chemical Compound	Phase (matter)	Chemical formula	ΔH_f° in kJ/mol
Ammonia (Ammonium Hydroxide)	aq	NH ₃ (NH ₄ OH)	-80.8
Ammonia	g	NH ₃	-46.1
Copper (II) sulfate	aq	CuSO ₄	-769.98
Sodium carbonate	s	Na ₂ CO ₃	-1131
Sodium chloride (table salt)	s	NaCl	-411.12
Sodium hydroxide	aq	NaOH	-469.6
Sodium hydroxide	s	NaOH	-426.7
Sodium nitrate	s	NaNO ₃	-424.8
Sulfur dioxide	g	SO ₂	-297
Sulfuric acid	l	H ₂ SO ₄	-814
Silica	s	SiO ₂	-911



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

$$\Delta H = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$



Standard Enthalpies
KJ/mole

Glucose	-1274
O ₂	0
CO ₂	-286
H ₂ O	-394



coupled with



- glycolysis
- pyruvate dehydrogenase complex
- TCA
- electron transport system

