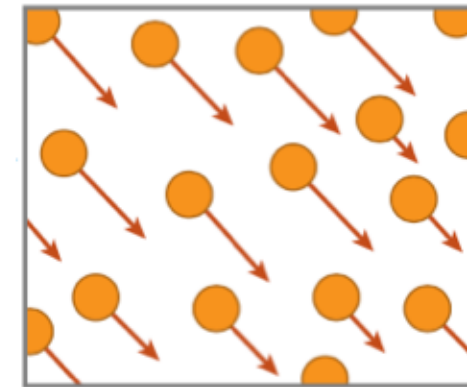
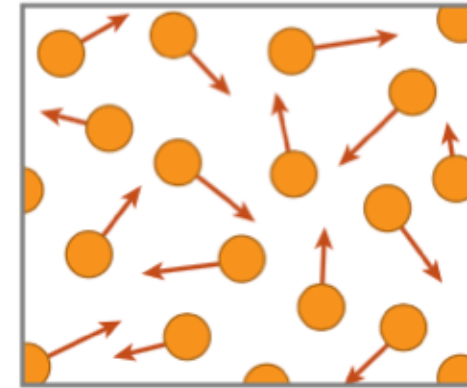


Unit 4 Review 1

FIRST LAW OF THERMODYNAMICS

Thermodynamics Basic Definitions

- **Heat (q):** energy derived from random molecular motion (always travels from high T to low T)
- **Work (w):** the energy derived from organized molecular motion (in chemistry, mostly as a result of compression or expansion at constant pressure)
- **Internal Energy (U):** the total energy (potential and kinetic) of a system, the surroundings, or the universe
- **Enthalpy (H):** the heat content of a system (seen most frequently as ΔH ; heat flow at constant pressure, q_p)



Thermodynamics Basic Definitions

$$\cdot \Delta U = U_f - U_i \quad \checkmark$$

$$\cdot \Delta U = q + w$$

$$\cdot q = m C_s \Delta T$$

$$\cdot q = n C_m \Delta T$$

$$\cdot q = m \Delta H_{\text{trans}}$$

$$\cdot q = n \Delta H_{\text{trans}}$$

$$\checkmark \cdot w = -P_{\text{ext}} \Delta V$$

$$\checkmark \cdot w = -\Delta n_{\text{gas}} RT$$

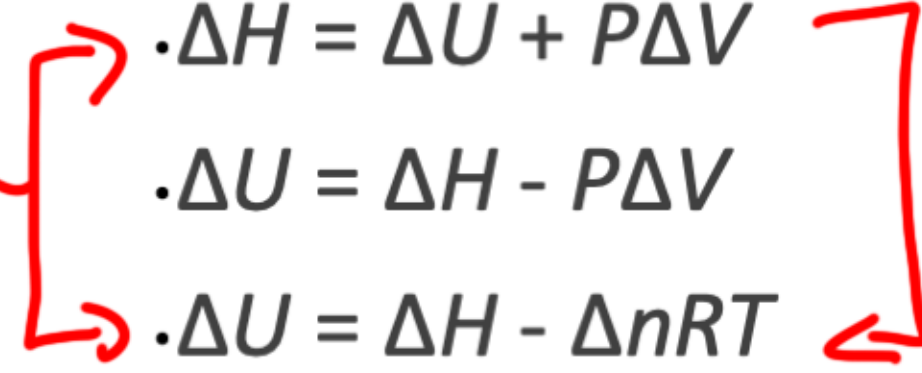
$$\cdot \Delta n_{\text{gas}} = (\# \text{mol gas prod}) - (\# \text{mol gas react})$$

$$\cdot H = U + PV$$

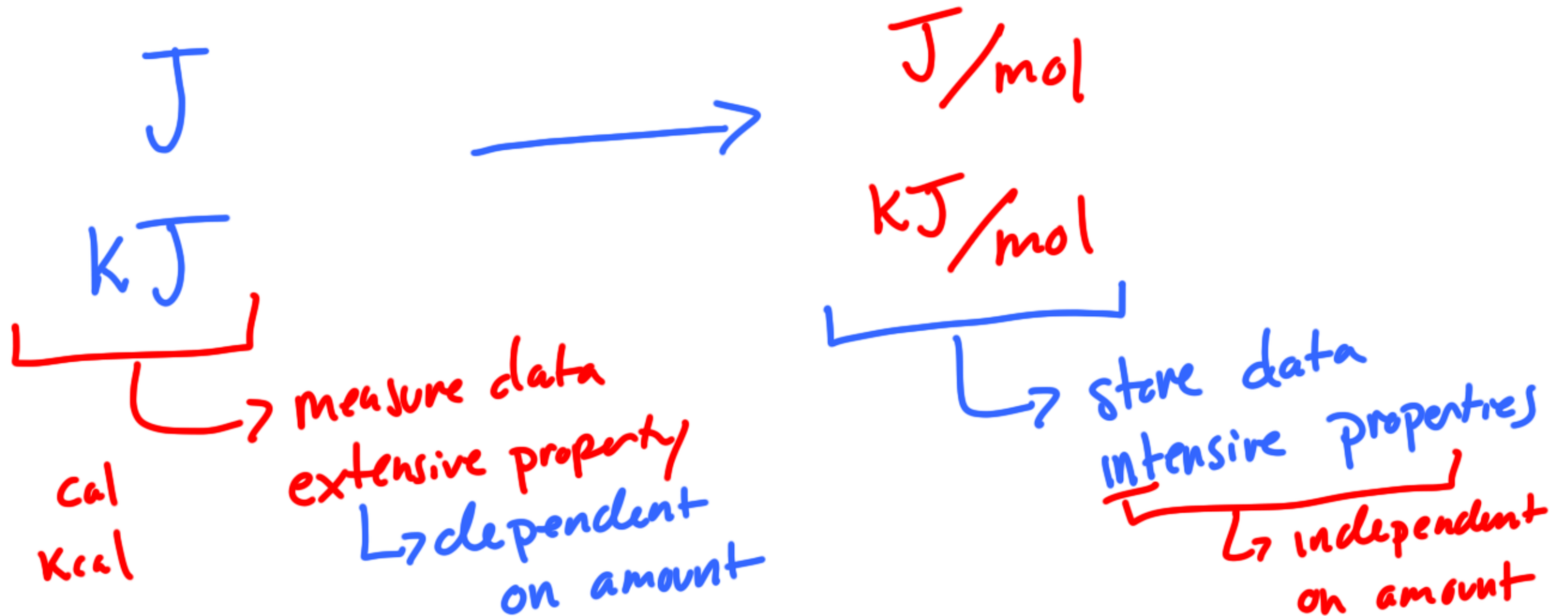
$$\cdot \Delta H = \Delta U + P \Delta V$$

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

$$\cdot \Delta U = \Delta H - \Delta n RT$$



Quick Energy Unit Breakdown



Heat Flow: System vs. Surroundings

- We define our environment in thermodynamics as the system and the surroundings. The system is the direct environment of the reaction and the surroundings is everything outside of this.

$q > 0$; endothermic (+), heat is absorbed

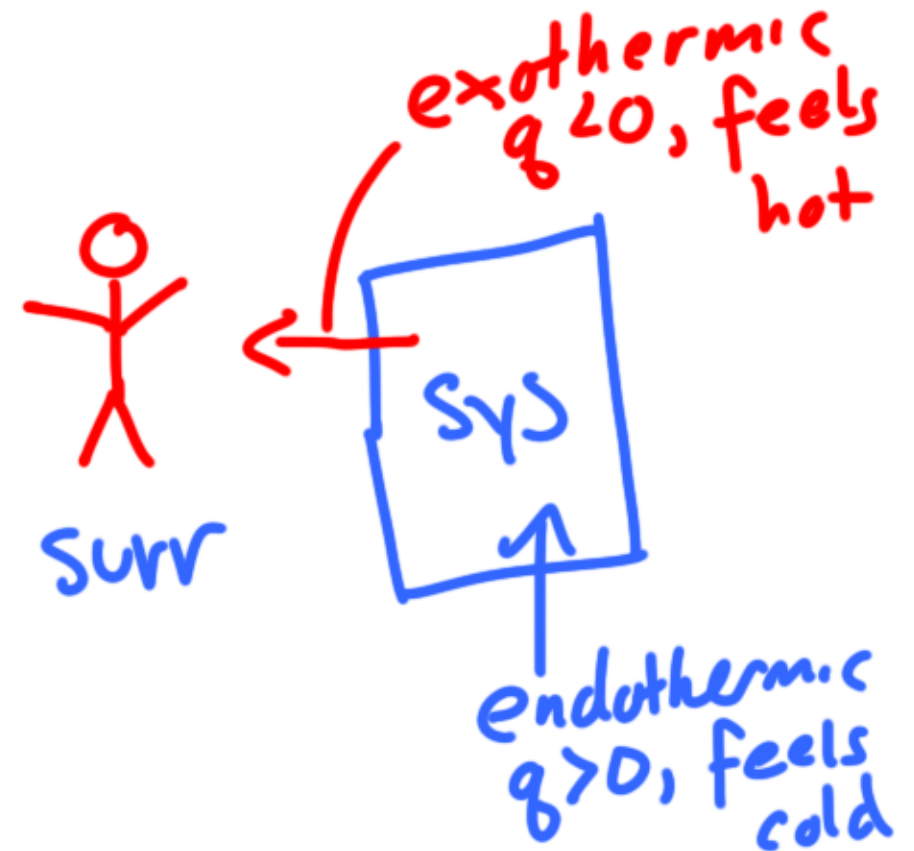
$q < 0$; exothermic (-), heat is released

$w > 0$; work energy in,

work is done on the system (+)

$w < 0$; work energy out,

work is done by the system (-)





The First Law of Thermodynamics

- ✓ The energy of the universe is always conserved


- The conclusions of this law are:

1. The internal energy change of the system is the sum of the heat and work
2. The internal energy loss of the system is the equal to energy gain of the surroundings
3. The internal energy change of the universe is zero and there is no energy or matter leaving


$$\Delta U_{sys} = q + w$$

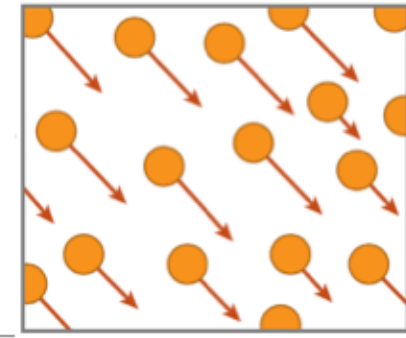

$$\Delta U_{sys} = -\Delta U_{surr}$$


$$\Delta U_{universe} = 0$$


$$q_{sys} = -q_{surr}$$

$$w_{sys} = -w_{surr}$$

First Law of Thermodynamics



$$\Delta U_{sys} = q + \underline{\underline{w}}$$

Work is the energy derived from **organized molecular motion**

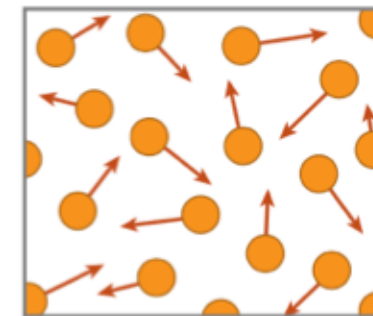
$w > 0$; work energy in, work is done on the system (+), compression

$w < 0$; work energy out, work is done by the system (-), expansion

Heat is the energy derived from **random molecular motion** (always travels from high T to low T)

$q > 0$; endothermic (+), heat is absorbed

$q < 0$; exothermic (-), heat is released

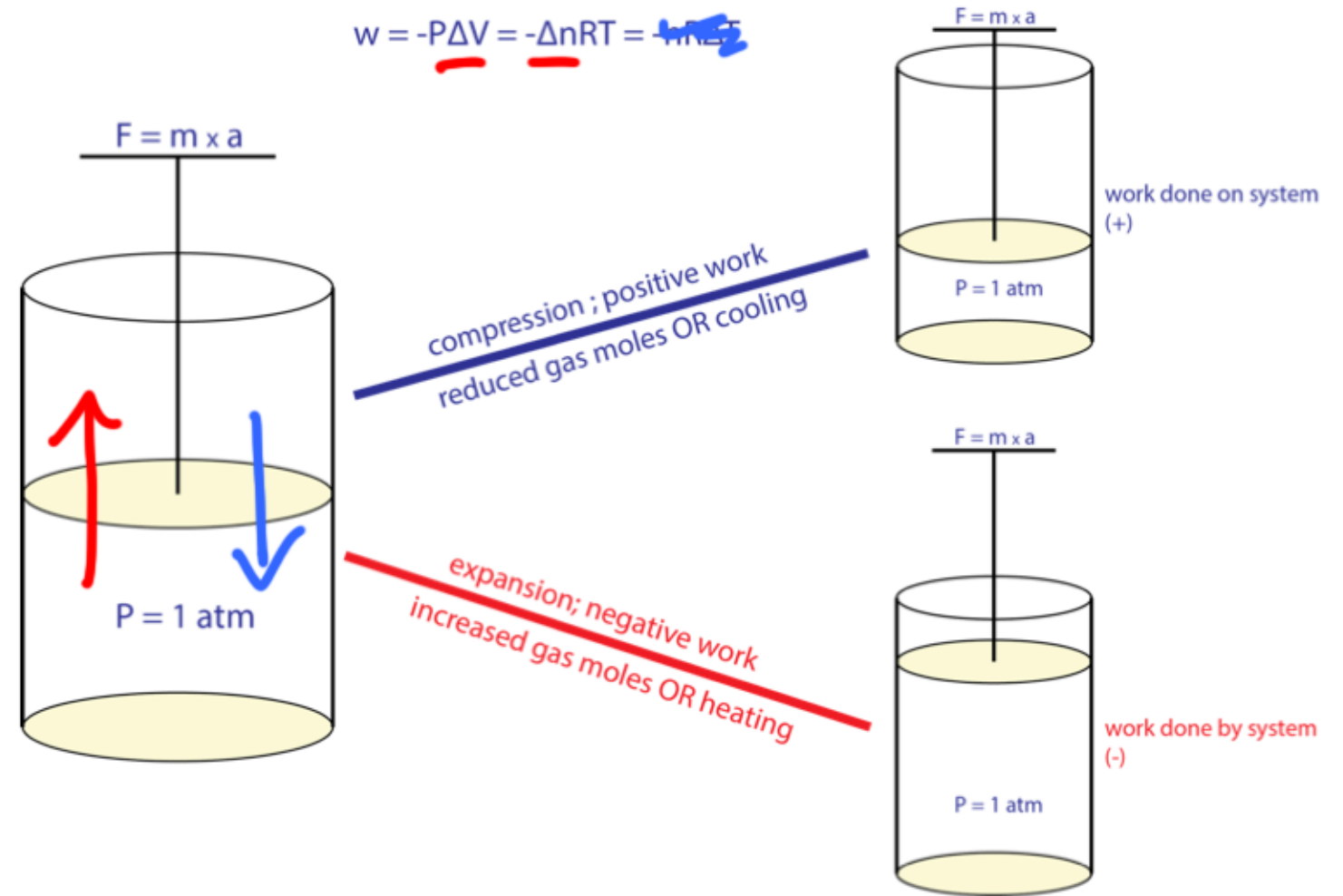


$$w = -P\Delta V \checkmark$$
$$w = -\Delta nRT \checkmark$$

Piston system \rightarrow constant pressure

Visualizing Chemical Work

- Work in chemistry is most often related to what we call "PV" work, where $w = -P\Delta V$
- We often think of experiments measuring "PV" work in the context of using a piston
- Pistons exert a variable force to maintain a constant pressure. This pressure is used to determine the work done by or on the system
- **When you are compressing your sample, you are doing work on the system (positive)**
- **When your sample expands, your system is doing work on the surroundings (the piston) to maintain the constant pressure (negative)**



Work Calculations

In chemistry we calculate work based on a change in volume at constant pressure.

- Provided a change in volume at constant pressure, the value of work is:

$$\rightarrow w = -P\Delta V$$

(atm)(L)

- However, if we are not provided a change in volume, we must rely on the change in gas moles of the balanced chemical reaction (Δn) to solve for work:

$$w = -\Delta nRT = -\cancel{\text{moles}} \cdot 8.314 \frac{\cancel{\text{J}}}{\cancel{\text{mol K}}} \cdot \cancel{\text{K}}$$

$$w = -P\Delta V \times 101.325 \frac{\text{J}}{\text{L}\cdot\text{atm}}$$

J

change in volume

provided a reaction

Remember from the first unit that liquids, solids, and aqueous phase compounds contribute negligible volumes to the system.

$$w = -P\Delta V^* = -\Delta nRT$$

Δn is **ONLY** the change in gas moles!

Heat Flow, q

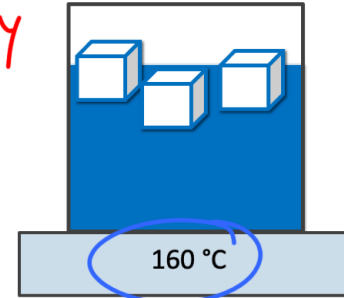
fusion = melting

Heat flow can be directed toward the potential or kinetic energy of the system.

1. Heat of a Temperature Change:

$$q = mC_s\Delta T$$

→ Kinetic Energy



2. Heat of a Phase Change:

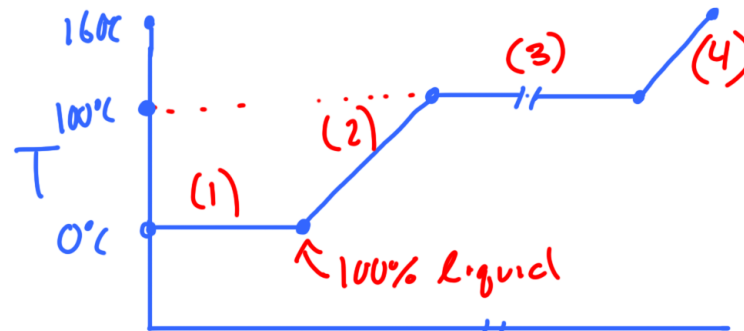
$$q = m\Delta H_{trans}$$

→ Potential Energy

(phase transition)

→ heat flow @ constant pressure

ice @ 0°C → gas @ 160°C



(1) melting ice
 $q = m\Delta H_{fus}$

(2) heating water
 $q = mC_s\Delta T$

(3) boiling water
 $q = m\Delta H_{vap}$

(4) heating steam/steam
 $q = mC_s\Delta T$

Definition of Enthalpy

c) heating steam/54J
 $q = m \underline{C_s} \Delta T$

Definition of Enthalpy

- **Enthalpy (H):** a state function that describes the heat content of a system, given by the equation:

$$H = U + PV$$

- However, in chemistry we are more concerned with the change in enthalpy, ΔH , which is simply the heat flow at constant pressure, q_p

$$\Delta H = q_p$$

Change in enthalpy derivation at constant pressure:

$$\begin{aligned} H &= U + PV \\ \Delta H &= \Delta U + \Delta(PV) \\ \Delta H &= (q - P\Delta V) + P\Delta V + \Delta PV \\ \Delta P &= 0 \\ \Delta H &= q \end{aligned}$$

First Law Restated

$$\Delta U = q_p + w$$

↓ ↓

$$\Delta U = \Delta H - \Delta nRT$$

Conceptual Foundations

combustion
↳ exothermic

Describe the following processes as endothermic or exothermic. Is work done on or by the system?

1. 100 mL water at 25°C is boiled and the steam is heated to 120 °C.

endo, by sys; $q > 0$, $w < 0$

2. Copper metal is cooled from 60°C to 35°C.

exo, $w = \emptyset$; $q < 0$

3. The combustion of hydrogen at room temperature.

exo, $w > 0$ (on sys)



4. The REVERSE reaction (the hydrolysis of water)

endo, $w < 0$ (by sys)

Basic Work Question

Consider a system where 2.50 L of ideal gas expands to 6.25 L against a constant external pressure of 330 torr. Calculate the work (w) for this system. Answer in joules. Is work done on or by the system?

$$W = -P\Delta V \times 101.325$$

(atm)(L)

$$-165\text{J} = -\left(\frac{330\text{ torr}}{760\text{ torr/atm}}\right)(6.25\text{ L} - 2.50\text{ L}) \times 101.325\frac{\text{J}}{\text{atm}\cdot\text{L}}$$

Expansion Work Question

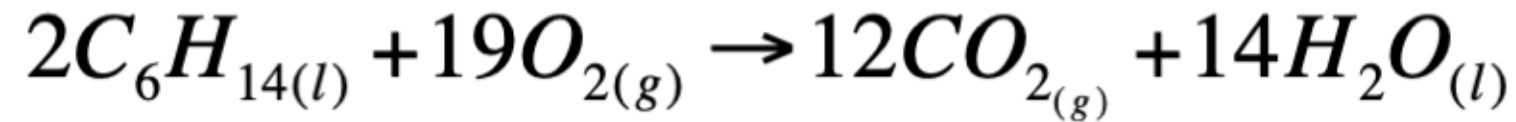
Calculate the value of work when a gas expands from 13.5 to 22.9 liters against a pressure of 3.8 atm at constant temperature. Is work done on or by the system? Answer in joules.

$$w = -P\Delta V^* \times 101.325 \frac{\text{J}}{\text{L}\cdot\text{atm}}$$

$$-3619\text{J} = -(3.8 \text{ atm}) (22.9 - 13.5 \text{ L}) \times 101.325 \frac{\text{J}}{\text{L}\cdot\text{atm}}$$

↳ work done by system

Chemical Work Question



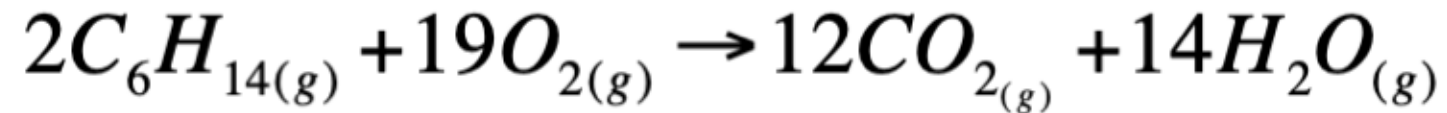
Calculate the work in the combustion of hexane at standard conditions. Is work done on or by the system?

$$w = -\Delta nRT$$

$$+17352 \text{ J} = - (12 - 19 \text{ mol}) (8.314 \frac{\text{J}}{\text{mol K}}) (298.15 \text{ K})$$

↳ on system

Chemical Work Question



Calculate the work in the combustion of hexane at 110°C. Is work done on or by the system?

$$w = -\Delta nRT$$

$$-15,928 \text{ J} = - (26 - 21 \text{ mol}) (8.314 \frac{\text{J}}{\text{mol K}}) (383.15 \text{ K})$$

↳ by system

Conceptual Question I

Which of the following statements is/are true regarding the first law of thermodynamics?

I. For a gas phase reaction run in a closed, rigid container, $\Delta U_{\text{sys}} = q_v$

II. $\Delta U_{\text{sys}} = -\Delta U_{\text{surr}}$ ✓

~~III.~~ A positive change in internal energy for the system must be matched with a negative change in internal energy for the universe

IV. $\Delta U_{\text{universe}} = \Delta U_{\text{sys}} + \Delta U_{\text{surr}}$
↳ = 0

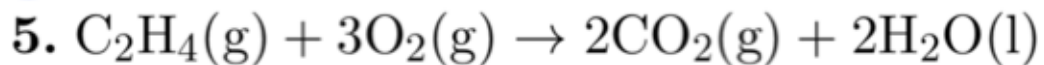
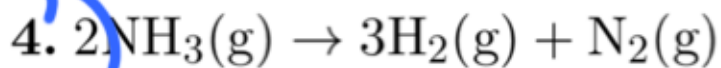
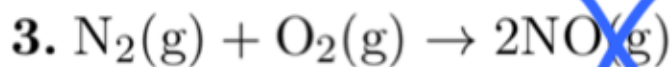
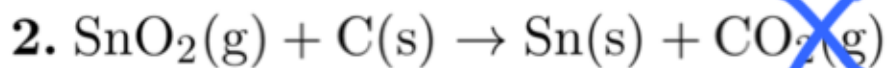
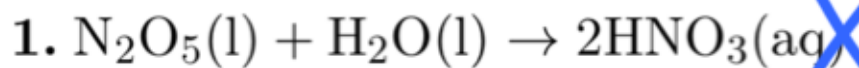
$$\Delta U = q_v + P\Delta V = q$$

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

$$\Delta U_{\text{sys}} = -\Delta U_{\text{surr}}$$

Conceptual Question II

For which of the following reactions is $\Delta U_{\text{sys}} < \Delta H_{\text{sys}}$ at constant external pressure?



$$\Delta U_{\text{sys}} = \Delta H - \Delta nRT$$

$$\Delta n > 0$$

$$w = 0$$