

Terminology

Energy

- capacity to do work

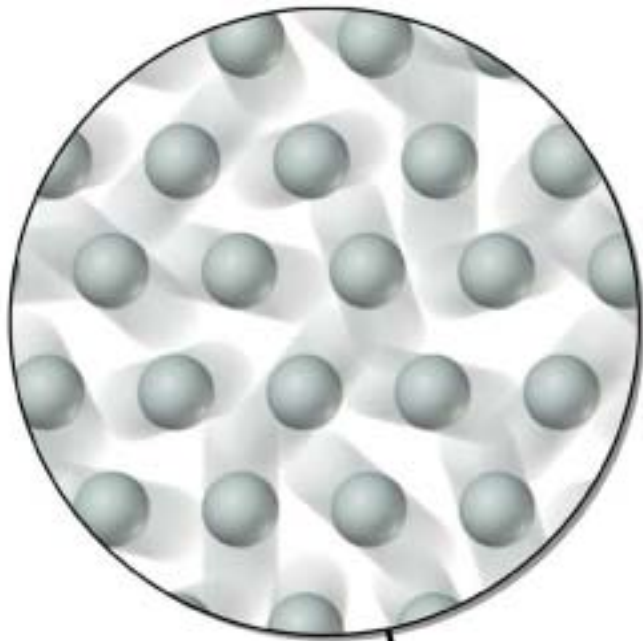
Kinetic Energy

- energy that something has because it is moving

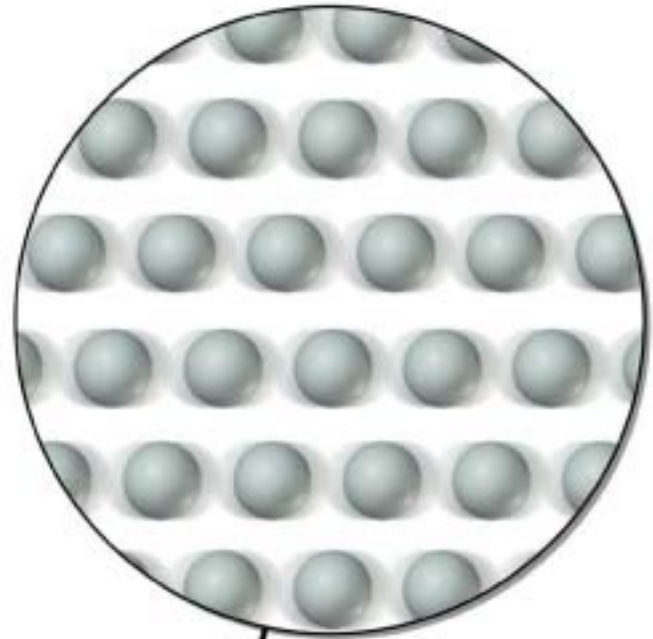
Potential Energy

- energy that something has because of its position

Hot and Cold Iron



Hot iron bar



Cold iron bar

Energy Units

$$1\text{J} = 1 \text{ kg m}^2/\text{sec}^2$$

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

$$1\text{kcal} = 1 \text{ Cal}$$

thus

$$1 \text{ Cal} = 1 \text{ kcal} = 1000 \text{ cal} = 4.184 \text{ kJ} = 4184 \text{ J}$$

Law of Conservation of Energy

- energy can neither be created nor destroyed
- the total amount of energy in the universe is a constant
- energy can be transformed from one form to another

First Law of Thermodynamics

- the total amount of energy in the universe is a constant
- the amount of heat transferred into a system plus the amount of work done on the system must result in a corresponding increase of internal energy in the system
- the total internal energy of a sample of matter depends on temperature, the type of particles, and how many of them there are in the sample

Thermochemistry Terminology

chemical energy – energy associated with a chemical reaction

thermochemistry – the quantitative study of the heat changes accompanying chemical reactions

thermodynamics – the study of energy and its transformations

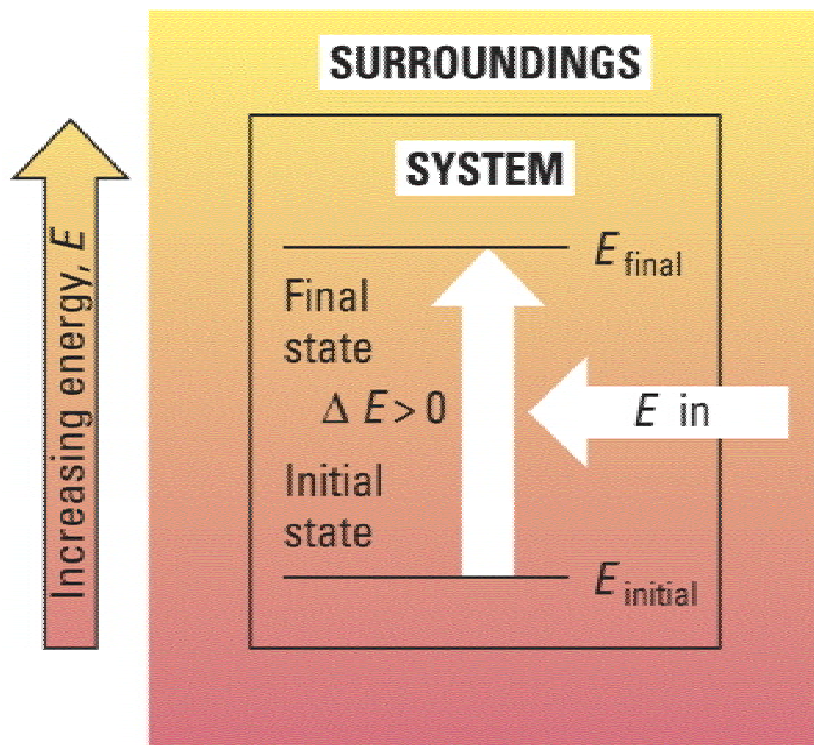
Thermochemistry Terminology

system \rightarrow that part of the universe under investigation

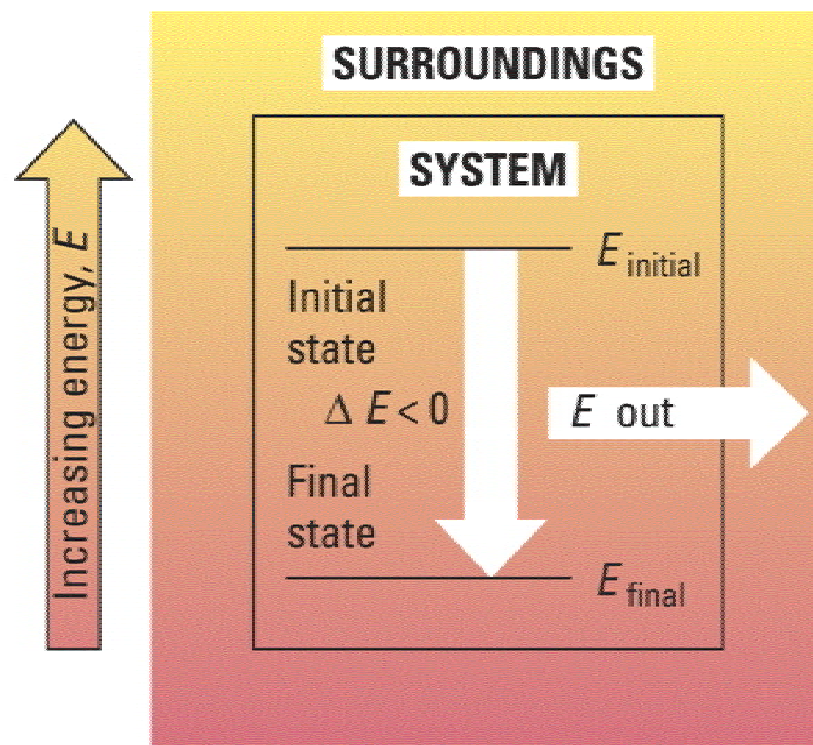
surroundings \rightarrow the rest of the universe

universe = system + surroundings

Internal Energy



ΔE positive: Internal energy increases.



ΔE negative: Internal energy decreases.

First Law of Thermodynamics

internal energy $\rightarrow E$

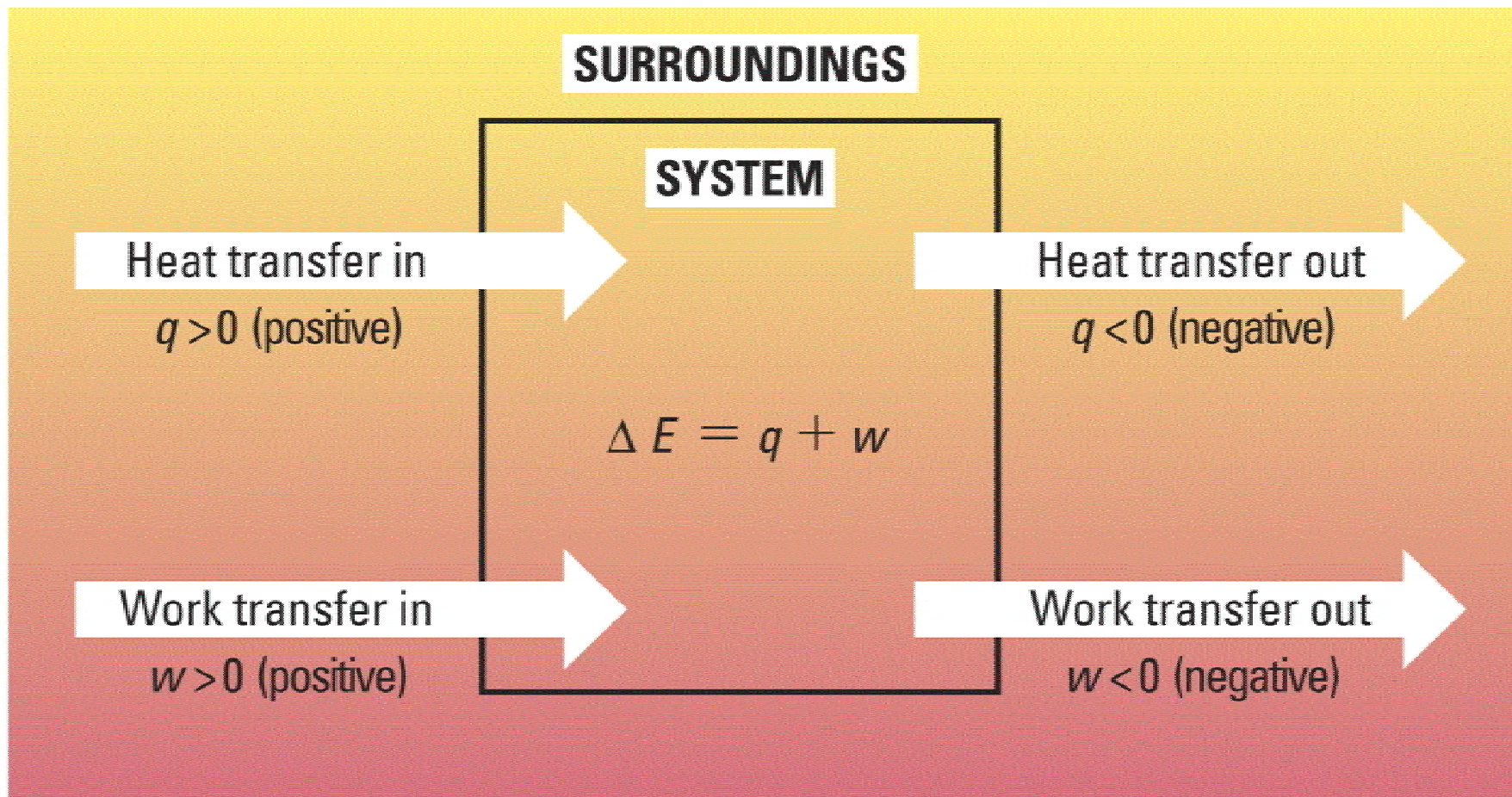
internal energy change $\rightarrow \Delta E$

heat $\rightarrow q$

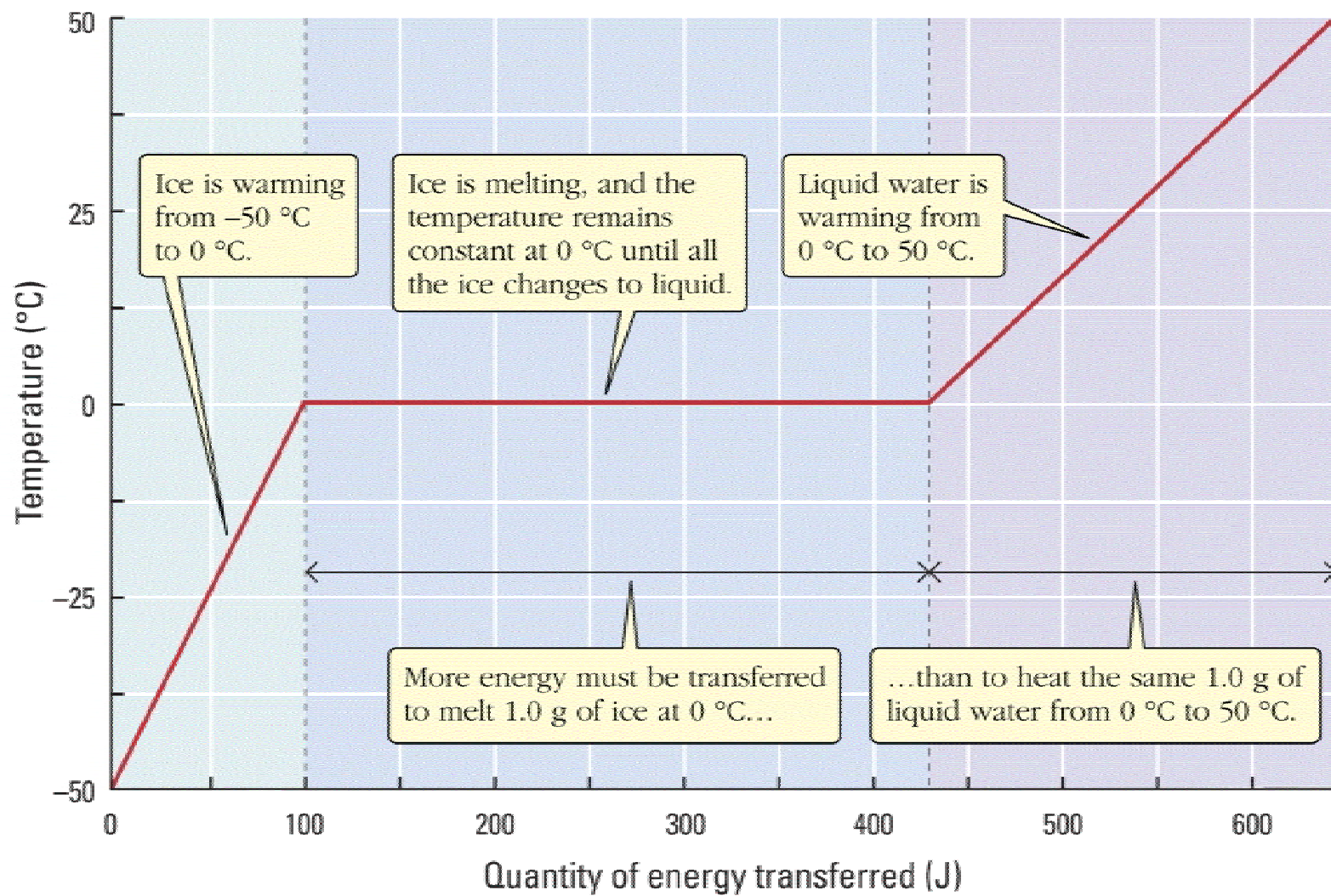
work $\rightarrow w$

$$\Delta E = q + w$$

Internal Energy, Heat, and Work



Freezing and Melting



Specific Heat

- the amount of heat necessary to raise the temperature of 1 gram of the substance 1°C
- Q , J, m , g, ΔT , $^{\circ}\text{C}$, c_s , s.h.
- independent of mass: intensive property
- substance dependent
- Specific Heat of Water = $4.184 \text{ J/g}^{\circ}\text{C}$

Heat

$$q = m \times \text{s.h.} \times \Delta T$$

where $q \rightarrow$ heat, J

$m \rightarrow$ mass, g

$\text{s.h.} \rightarrow$ specific heat, $\text{J/g} \times ^\circ\text{C}$

$\Delta T =$ change in temperature, $^\circ\text{C}$

Molar Heat Capacity

- the heat necessary to raise the temperature of one mole of substance by 1°C
- C_p and C_v
- substance dependent

Heat Capacity

- the heat necessary to raise the temperature 1°C
- C_p and C_v
- mass dependent: extensive property

Heat Capacity

$$C = m \times \text{s.h.}$$

where $C \rightarrow$ heat capacity, $\text{J}/^\circ\text{C}$

$m \rightarrow$ mass, g

$\text{s.h.} \rightarrow$ specific heat, $\text{J}/\text{g}^\circ\text{C}$

Heat Transfer

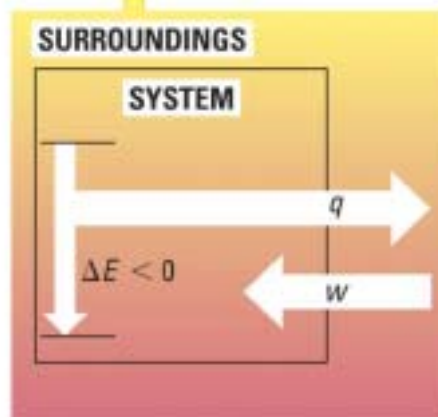
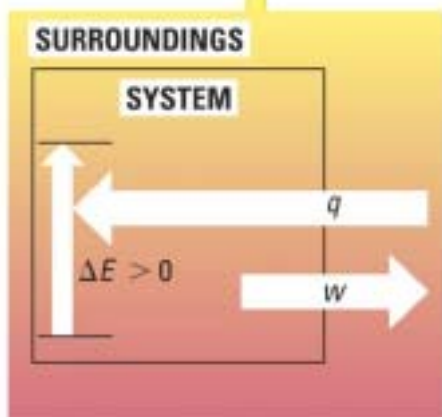
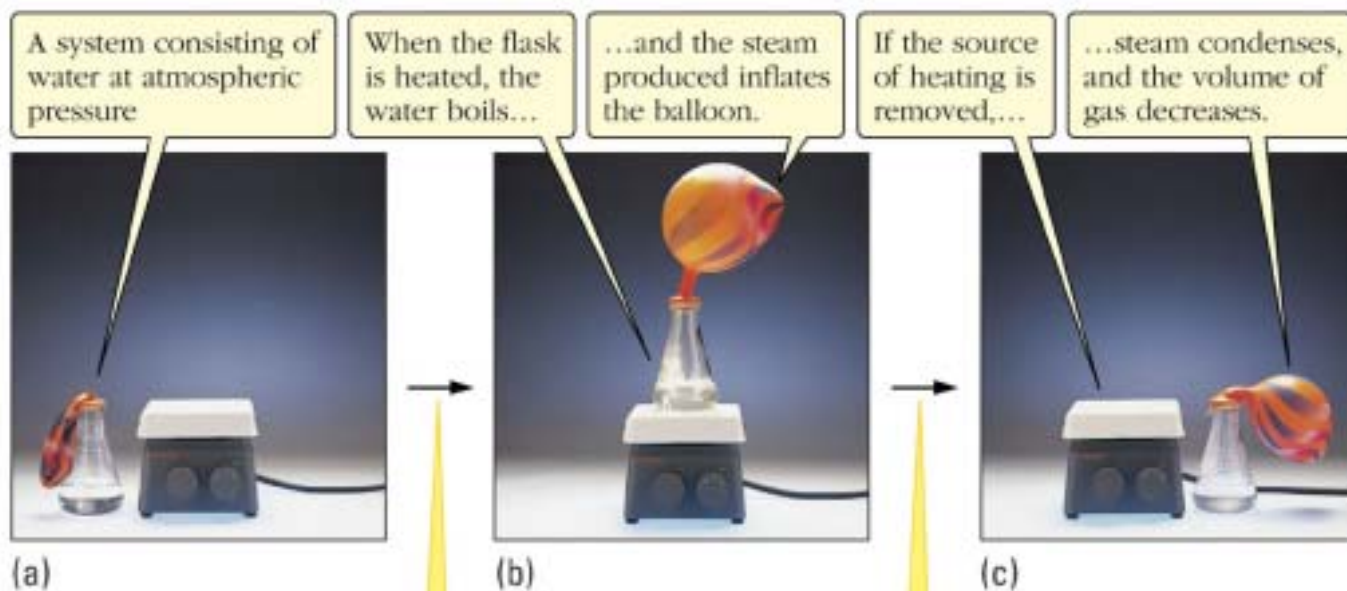
$$Q_{\text{lost}} = - Q_{\text{gained}}$$

$$(m \times \text{s.h.} \times \Delta T)_{\text{lost}} = - (m \times \text{s.h.} \times \Delta T)_{\text{gained}}$$

ΔT = final temperature – initial temperature

$$\Delta T = T_{\text{f}} - T_{\text{i}}$$

Vaporization and Condensation



Heat Flow in Reactions

exothermic – reaction that gives off energy

$$q < 0$$

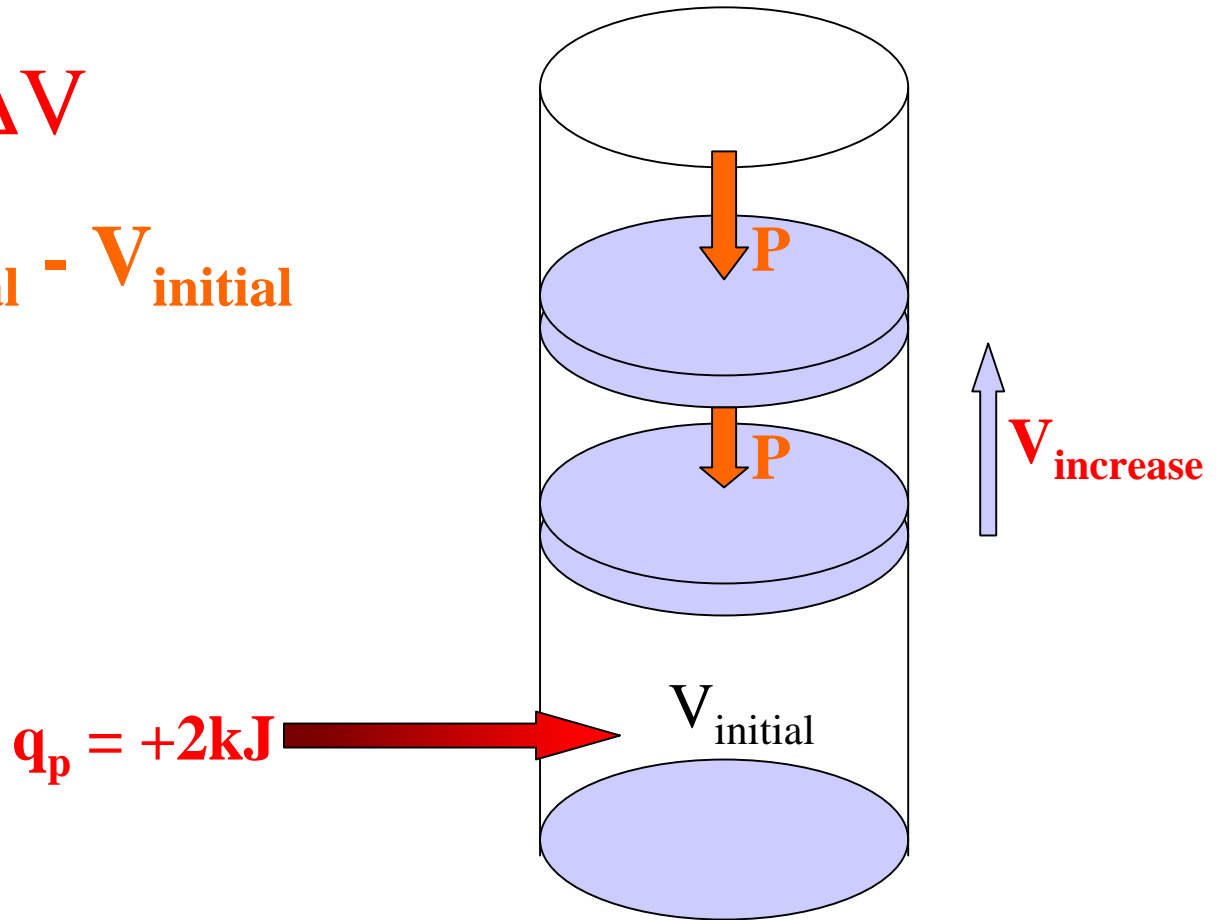
endothermic – reaction that absorbs energy

$$q > 0$$

Expansion Type Work

$$w = -P\Delta V$$

$$\Delta V = V_{\text{final}} - V_{\text{initial}}$$



First Law of Thermodynamics

$$\Delta E = q + w$$

At constant V , $w_{\text{expansion}} = 0$

$$\Delta E = q_v + 0 = q_v$$

At constant P , $w_{\text{expansion}} = -P\Delta V$

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

$$\Delta H = \Delta E + \Delta(PV) = (q_p - P\Delta V) + P\Delta V + V\Delta P$$

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

Enthalpy

Enthalpy → heat at constant pressure

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

Exothermic Reaction

$$\Delta H = (H_{\text{products}} - H_{\text{reactants}}) < 0$$



Endothermic Reaction

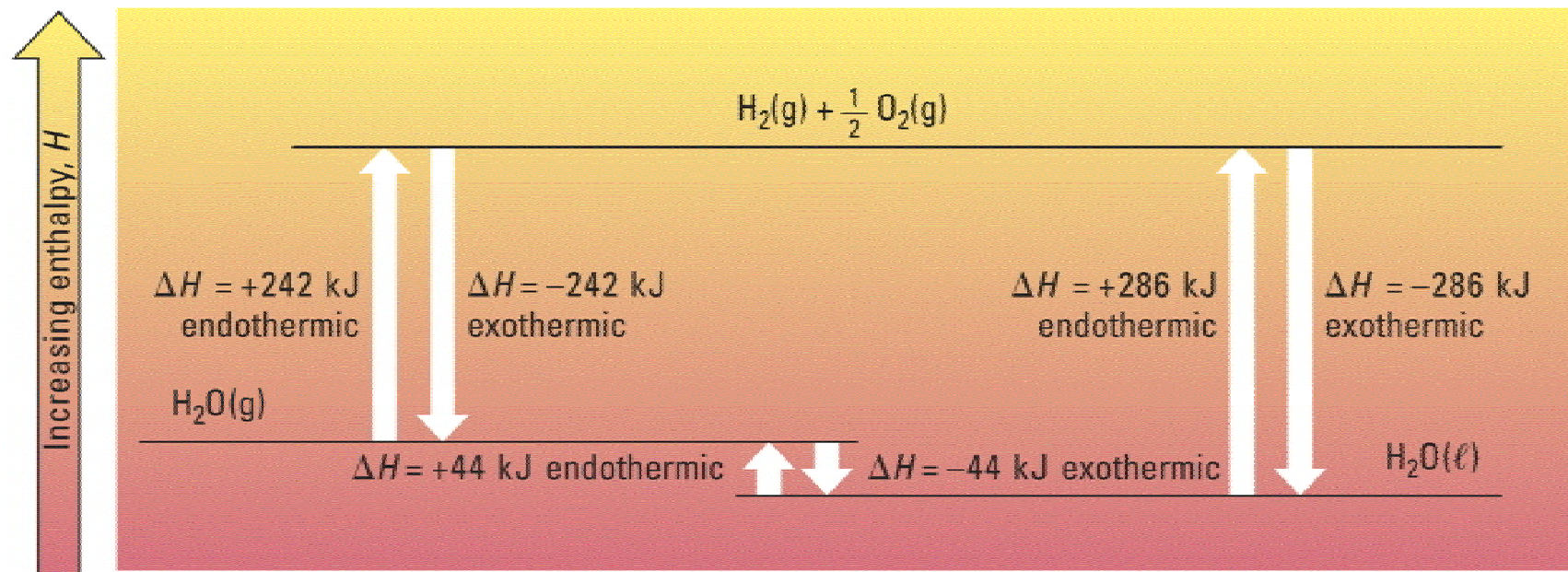
$$\Delta H = (H_{\text{products}} - H_{\text{reactants}}) > 0$$



Standard State Enthalpy

- enthalpy at thermodynamic standard conditions of 298 K, 1 atm, and 1molar for solutions

Enthalpy Diagram



Laws of Thermochemistry

(1st law of Thermodynamics)

1. The magnitude of ΔH is directly proportional to the amount of reactant or product.
2. ΔH for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction.



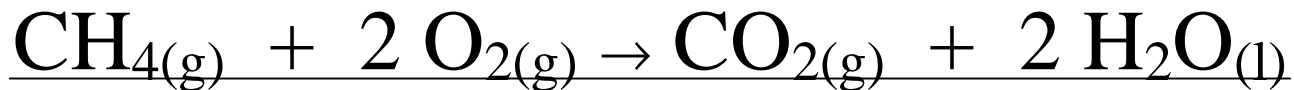
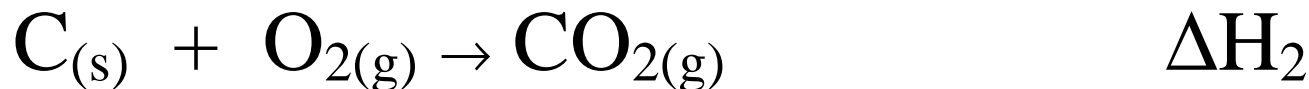
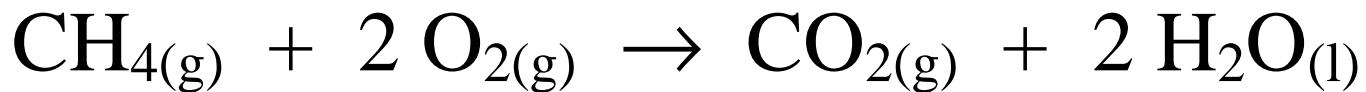
Laws of Thermochemistry

3. The value of H for the reaction is the same whether it occurs directly or in a series of steps.

$$\Delta H_{\text{overall}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$$

also called Hess' Law

EXAMPLE



$$\Delta\text{H}_{\text{overall}} = \Delta\text{H}_1 + \Delta\text{H}_2 + \Delta\text{H}_3$$

Standard Enthalpy of Formation

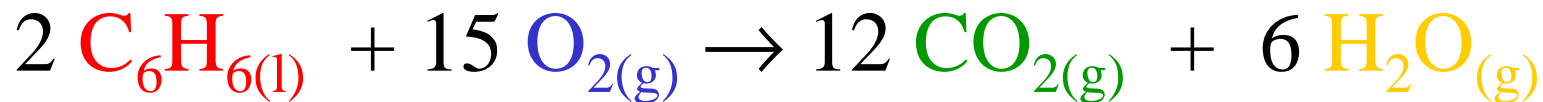
the enthalpy associated with the formation of a substance from its constituent elements under standard state conditions

Calculation of ΔH°

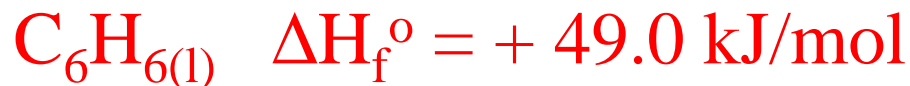
$$\Delta H^\circ = \sum c \times \Delta H_f^\circ \text{ products} - \sum c \times \Delta H_f^\circ \text{ reactants}$$

Example

What is the value of ΔH_{rx} for the reaction:



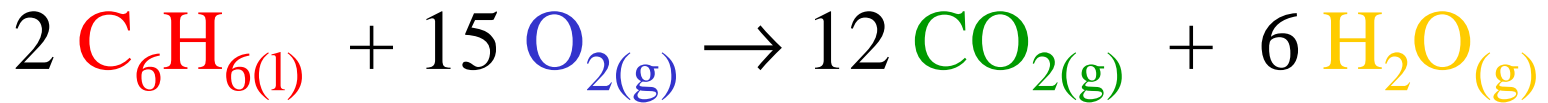
From J



$$\Delta H_{\text{rx}} = [\sum c \times \Delta H_f^\circ]_{\text{product}} - [\sum c \times \Delta H_f^\circ]_{\text{reactants}}$$

Example

What is the value of ΔH_{rx} for the reaction:



From J

$\text{C}_6\text{H}_{6(l)} \quad \Delta H_f^\circ = + 49.0 \text{ kJ/mol}; \quad \text{O}_{2(g)} \quad \Delta H_f^\circ = 0$

$\text{CO}_{2(g)} \quad \Delta H_f^\circ = - 393.5; \quad \text{H}_2\text{O}_{(g)} \quad \Delta H_f^\circ = - 241.8$

$$\Delta H_{\text{rx}} = [\sum c \times \Delta H_f^\circ]_{\text{product}} - [\sum c \times \Delta H_f^\circ]_{\text{reactants}}$$

$$\begin{aligned} \Delta H_{\text{rx}} &= [12(- 393.5) + 6(- 241.8)]_{\text{product}} \\ &\quad - [2(+ 49.0) + 15(0)]_{\text{reactants}} \text{ kJ/mol} \\ &= - 6.2708 \times 10^3 \text{ kJ} \end{aligned}$$

Energy Resources in the U.S.

