

Heat Capacity: Extensive?

- Normally, C scales with size of system, but C per unit mass (or moles) does not:
 - \bar{C}_V, \bar{C}_P : Molar heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$)
 - C_V^*, C_P^* : Specific heat capacity ($\text{J mol}^{-1} \text{kg}$)
- When using molar or specific C , normal equations apply:

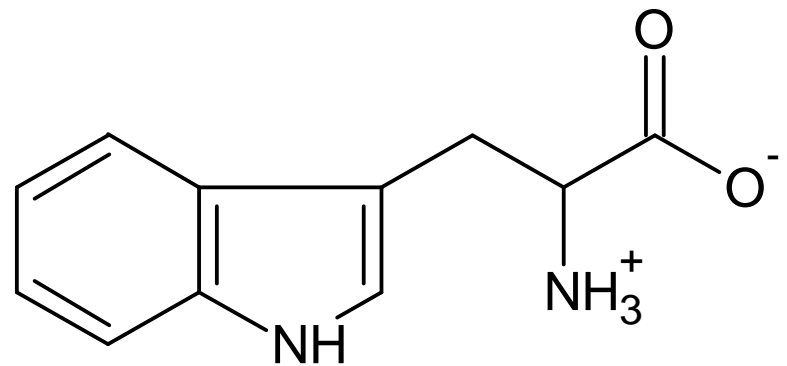
$$q = (mC_P^*)\Delta T \text{ or } q = (n\bar{C}_V)\Delta T$$

Internal Energy: Molecular Examples

System: Tryptophan Molecule

Contributions to E:

- Einstein mc^2 energy
- Bond vibrations
- Ionic interactions
- Covalent bonds
- Kinetic energy of nuclei moving within molecule

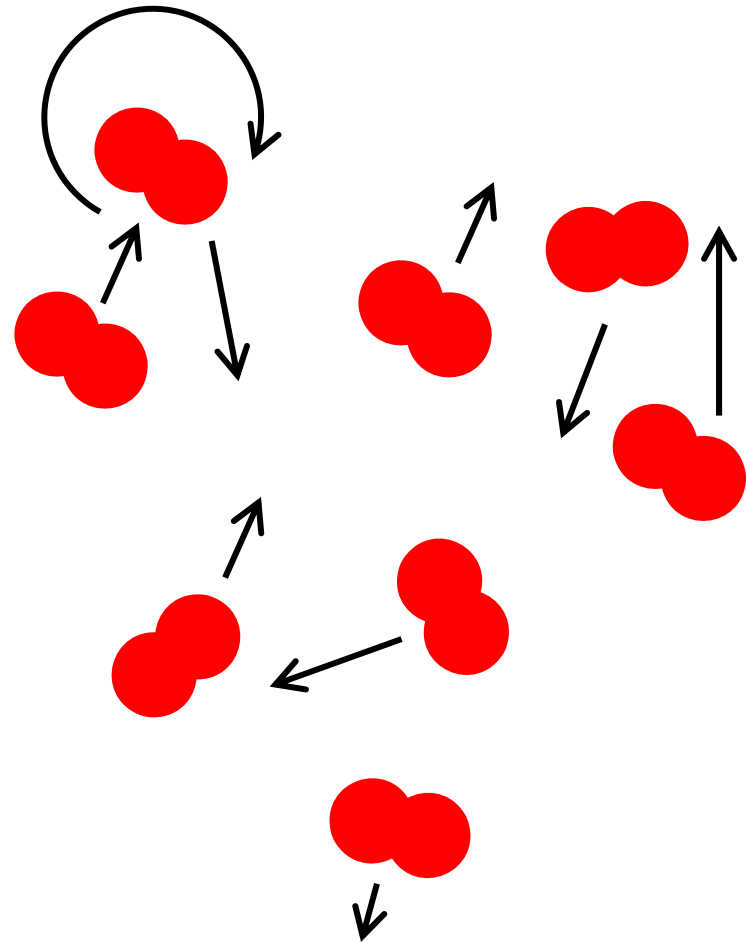


Internal Energy: Molecular Examples

System: Oxygen Gas

Contributions to E:

- Bond vibrations
- Covalent bonds
- Interactions energies
- Kinetic energy of gas molecules
- Rotational energy



Molecular Basis of Heat Capacity

- H-bonds in ice are inflexible, can't store much energy
- H-bonds in water can vibrate, rotate, move freely: can absorb lots of energy
- Very little H-bonding in water vapor: can't absorb energy



$$C_p = 38.09 \text{ J/K} \quad C_v = 38.08 \text{ J/K}$$



$$C_p = 75.33 \text{ J/K} \quad C_v = 74.53 \text{ J/K}$$



$$C_p = 37.47 \text{ J/K} \quad C_v = 28.03 \text{ J/K}$$

Molecular Basis of Heat Capacity

- Thought process:
“Where else can the energy go *besides* kinetic energies?”
 - Bond rotations
 - Bond vibrations
 - Molecular reorientation
 - *Degrees of molecular freedom*



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Question

I give you a container with 1 mol of N_2 gas with a pressure of 0.8 atm. Does it matter:

- If the 1 mol was formed directly or whether I purified it from the air?
- If I reduced the pressure by sucking some out with a syringe or by going up to high altitude before sealing the container?

State Variables

State variables describe the properties of the system, not how it got there.

- Pressure (P)
- Temperature (T)
- Internal Energy (E)
- Volume (V)
- Number (N)

HEAT AND WORK ARE NOT STATE VARIABLES!!

(why?)

State Equations: Combinations of State Variables

- Ideal Gas Law:

$$PV = NRT$$

- Van der Waals Gas:

$$\left(P + \frac{N^2 a}{V^2} \right) (V - Nb) = NRT$$

- Dalton's Law of Partial Pressures:

$$P_{tot} = \sum_i P_i = \sum_i \frac{N_i RT}{V}$$

Calculating Changes to E and H

Situation: A system undergoes a change in state
(P_1, V_1, T_1, \dots) \rightarrow (P_2, V_2, T_2, \dots)

- Step 1: Consider the *path* of change
 - Most changes are *irreversible*: the surroundings are changed in such a way that quantities can't be calculated easily
 - Devise a *reversible* path to get from state 1 to state 2: slow changes under fixed conditions; can be calculated
 - Since E and H are state functions, ΔE and ΔH (of the system) **must** be the same for both paths!

Calculating Changes to E and H

Situation: A system undergoes a change in state
 $(P_1, V_1, T_1, \dots) \rightarrow (P_2, V_2, T_2, \dots)$

- Step 2: Calculate q and w along the path
 - We will see examples of this
 - You will need to do some math
 - You may need to calculate (P, V, T) at intermediate points along your path

Calculating Changes to E and H

Situation: A system undergoes a change in state
 $(P_1, V_1, T_1, \dots) \rightarrow (P_2, V_2, T_2, \dots)$

- Step 3: Calculate ΔE and ΔH
 - Sum up individual contributions of q and w along the path
 - Because E and H are state functions, they *must* be correct regardless of your path

Example 1: Changes in a Liquid

You heat 1 mol of water from T_1 (at P_1, V_1) to T_2 (at P_2, V_2) in a microwave. What are ΔE and ΔH of the gas?

Summary: ΔE , ΔH for Liquids & Solids

- Constant Pressure:

- $q = \int C_P dT$ $w \cong -P(V_2 - V_1)$

- Constant Temperature:

$$q \cong 0 \qquad w \cong 0$$

- Constant Volume:

$$q = \int C_V dT \qquad w \cong 0$$

- Approximately, $\Delta E = \Delta H$

Example 2: Changes in an Ideal Gas

You heat 1 mol of gas from T_1 (at P_1, V_1) to T_2 (at P_2, V_2) in a nuclear reactor. What are ΔE and ΔH of the gas?

Summary: ΔE , ΔH for Ideal Gasses

- Constant Pressure:

$$q = N\bar{C}_P(T_2 - T_1) \quad w = -P(V_2 - V_1)$$

- Constant Volume:

$$q = N\bar{C}_V(T_2 - T_1) \quad w = 0$$

- Constant Temperature:

$$\Delta E = 0 \quad w = -NRT \ln \frac{V_2}{V_1} \quad q = -w$$