# Heat Capacity: Extensive?

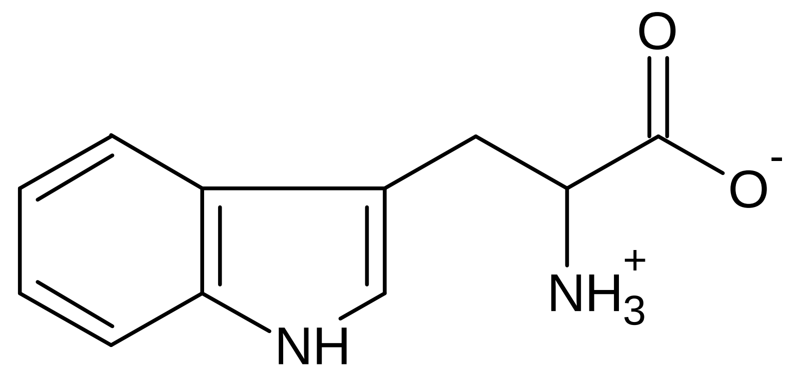
- Normally, C scales with size of system, but C per unit mass (or moles) does not:
  - $\bar{C}_V$, $\bar{C}_P$ : Molar heat capacity (J mol$^{-1}$ K$^{-1}$)
  - $C_V^*$, $C_P^*$ : Specific heat capacity (J mol$^{-1}$ kg)

- 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:

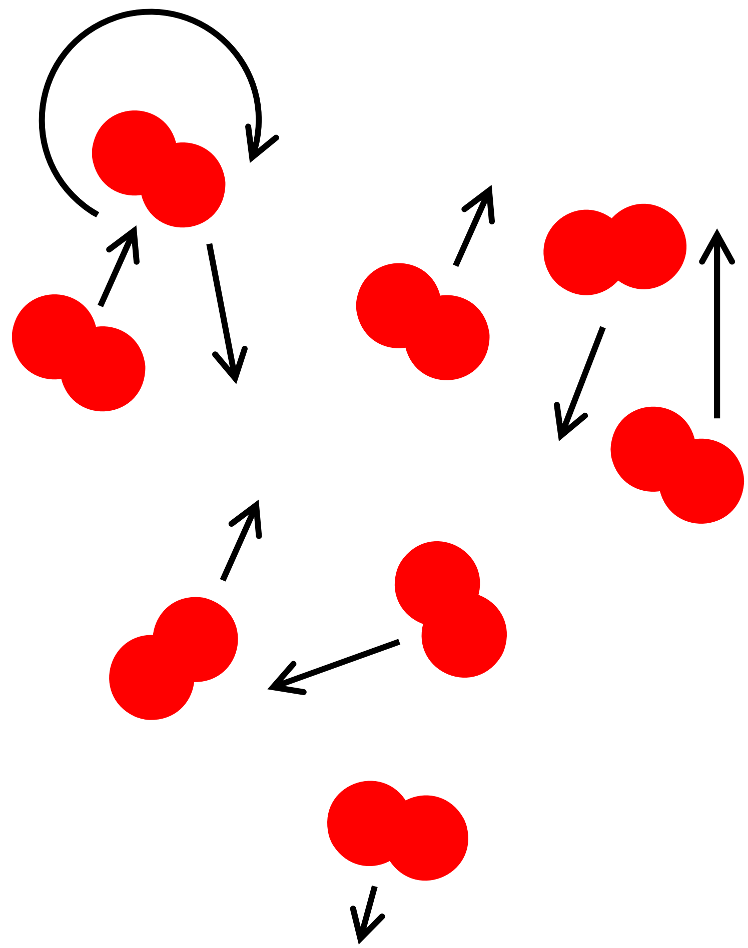
- Einstein $mc^2$ energy
- Bond vibrations
- Ionic interactions
- Covalent bonds
- Kinetic energy of nuclei moving within molecule

# 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 J/K    $C_V$= 38.08 J/K

$C_P$ = 75.33 J/K    $C_V$= 74.53 J/K

$C_P$ = 37.47 J/K    $C_V$ = 28.03 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*

$C_P$ = 38.09 J/K    $C_V$= 38.08 J/K

$C_P$ = 75.33 J/K    $C_V$= 74.53 J/K

$C_P$ = 37.47 J/K    $C_V$ = 28.03 J/K

# 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
$(P_1, V_1, T_1, \ldots) \rightarrow (P_2, V_2, T_2, \ldots)$

- 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, $\Delta E$ and $\Delta H$ (of the system) ***must*** be the same for both paths!

# Calculating Changes to E and H

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

- 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 $(P_1, V_1, T_1, \ldots) \rightarrow (P_2, V_2, T_2, \ldots)$

- 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 as long as you start and end at the right state

# **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 $\Delta E$ and $\Delta H$ of the gas?

# **Summary:** ΔE, ΔH for Liquids & Solids

- Constant Pressure:
  - $q = \int C_P dT \quad w \cong -P(V_2 - V_1)$
- 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 $\Delta E$ and $\Delta H$ of the gas?

# **Summary:** ΔE, ΔH for Ideal Gasses

- Constant Pressure:

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

- Constant Volume:

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

- Constant Temperature:

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