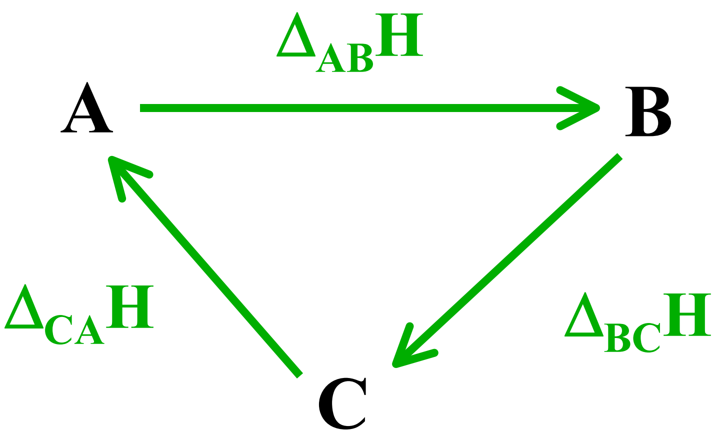
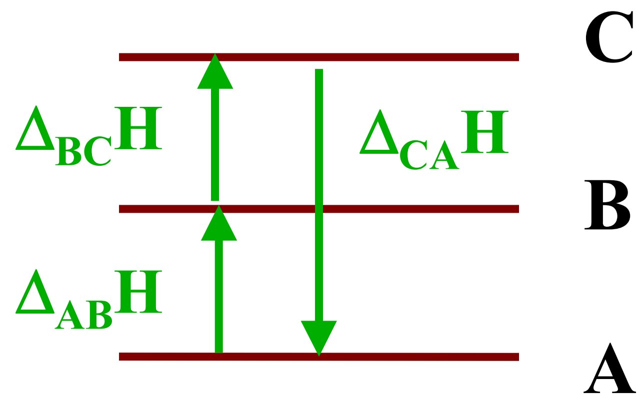
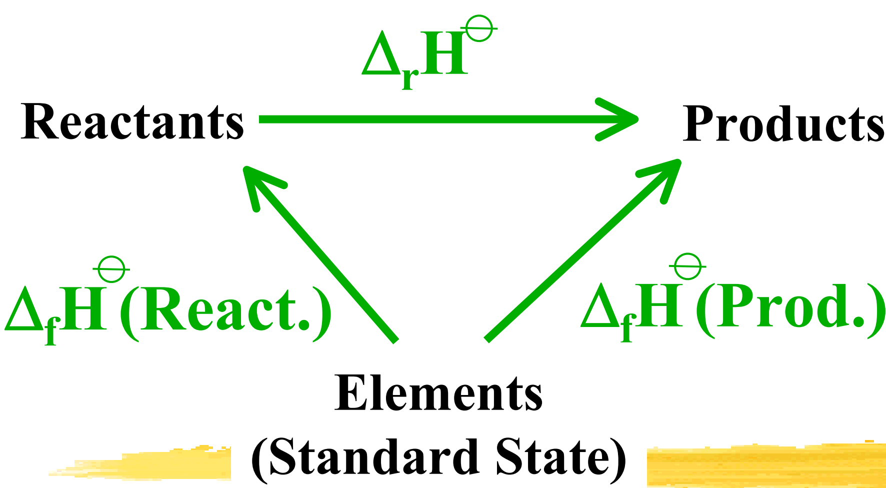
Hess's Law

$\boxed{\Delta H = 0 \text{ for a cyclic process}}$



$$\Delta_{AB}H + \Delta_{BC}H + \Delta_{CA}H = 0$$

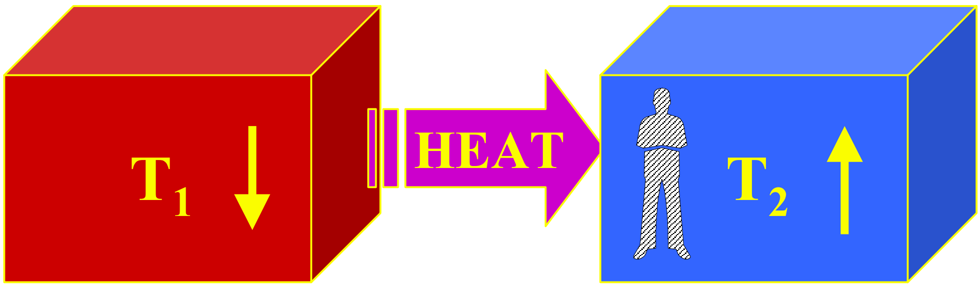




$$\boxed{\Delta_r H^\ominus = \sum \Delta_f H^\ominus(\text{Prod.}) - \sum \Delta_f H^\ominus(\text{React.})}$$

Heat

Heat always flows from the “hot” object to the “cool” object



- Initially $T_1 > T_2$
- Heat flow will continue until $T_1 = T_2$

Temperature change ($\Delta T = T_{final} - T_{initial}$) is proportional to the heat (q) received

$$q \propto \Delta T \qquad \Rightarrow q = C\,\Delta T$$

Proportionality constant is the **heat capacity C**

If heat flows out of the system:

$\Delta T = T_f - T_i < 0$

$q < 0$

If heat flows into the system:

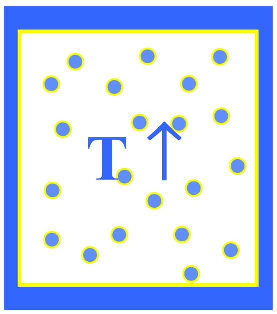
$\Delta T = T_f - T_i > 0$

$q > 0$

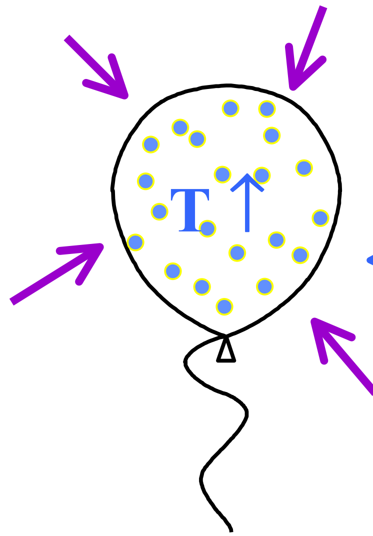
Heat capacities

$$\boxed{q \propto \Delta T \qquad\qquad q = C\,\Delta T}$$

The value of C depends on the process:



Closed system
Constant volume



Closed system
Constant pressure

1 atm

Experimentally:

$$\underbrace{\boxed{q_v = C_v\,\Delta T}}_{= \Delta U}$$

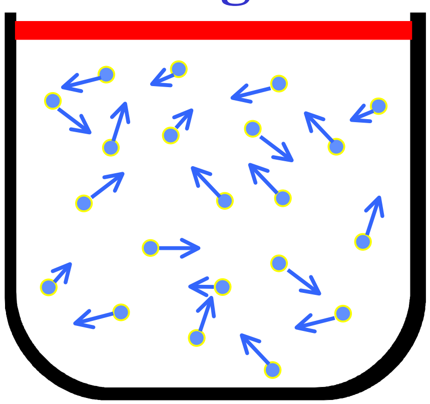
$$\underbrace{\boxed{q_p = C_p\,\Delta T}}_{= \Delta H}$$

Internal Energy U

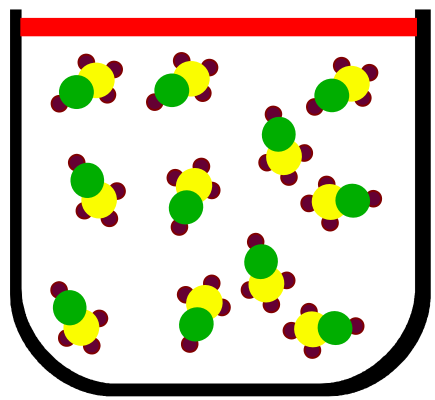
Internal Energy U:

The sum of all of the kinetic and potential energy contributions to the energy of all the atoms, ions, molecules, etc. in the system

He gas

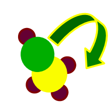


Methanol Gas

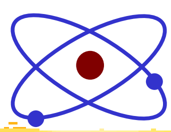


Translational Energy

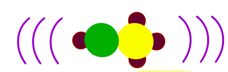
Rotational Energy



Electronic Energy



Vibrational Energy

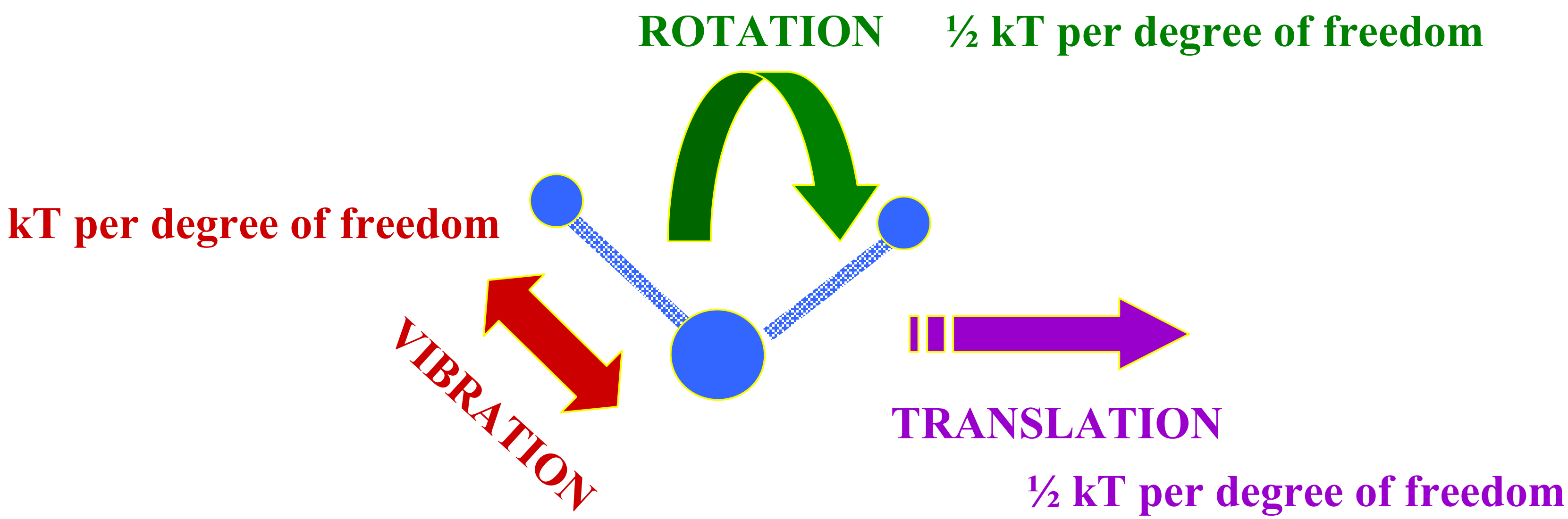


Nuclear Energy

Bond Energy

Storage of heat energy in a perfect gas

Classically heat energy can be stored in a gas as internal energy with:

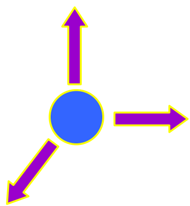


When quantization of energy levels is taken into account, contributions to the heat capacity can be considered classically only if $E_n \ll kT$. Energy levels with $E_n \geq kT$ contribute little, if at all, to the heat capacity (they are not excited!).

Since vibrational energies are generally comparable to or greater than kT, only rotations and translations store much energy under normal conditions.

The internal energy of a perfect gas

ATOMS:



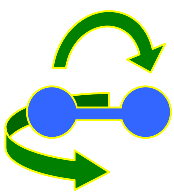
3 Translations per atom

$$U = N\,(3 \times \tfrac{1}{2}\,kT)$$

$$\boxed{U = n\,\frac{3}{2}\,RT}$$

# of atoms (or molecules) = nN_A $\quad R = N_A k$

LINEAR MOLECULES:



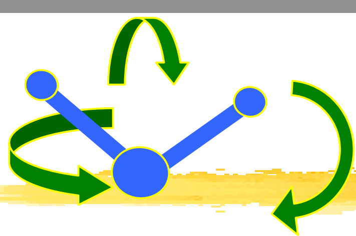
3 Translations per molecule

2 Rotations per molecule

$$U = N\,\frac{3}{2}\,kT + N\,(2 \times \tfrac{1}{2}\,kT)$$

$$\boxed{U = n\,\frac{5}{2}\,RT}$$

NON-LINEAR MOLECULES:



3 Translations per molecule

3 Rotations per molecule

$$U = N\,\frac{3}{2}\,kT + N\,(3 \times \tfrac{1}{2}\,kT)$$

$$\boxed{U = n\,3RT}$$

Molar heat capacity of a perfect gas

Constant Volume

$q_v = C_v \Delta T$

$\Delta U = C_v \Delta T$

$C_v = \Delta U/\Delta T = nC_{v,m}$

molar heat capacity @ constant V

$pV = nRT$

$p\Delta V = nR\Delta T$

Constant Pressure

$q_p = C_p \Delta T$

$\Delta H = C_p \Delta T$

$\Delta U + p\Delta V = C_p \Delta T$

$\Delta U + nR\Delta T = C_p \Delta T$

$C_p = \Delta U/\Delta T + nR = nC_{p,m}$

1. ATOMS: $U = n\frac{3}{2}RT$

20.8 J K^{-1}mol^{-1}

$\Delta U/\Delta T = n\frac{3}{2}R$	$C_{v,m} = \frac{3}{2}R$	$C_{p,m} = C_{v,m} + R = \frac{5}{2}R$

2. LINEAR MOLECULES: $U = n\frac{5}{2}RT$

29.1 J K^{-1}mol^{-1}

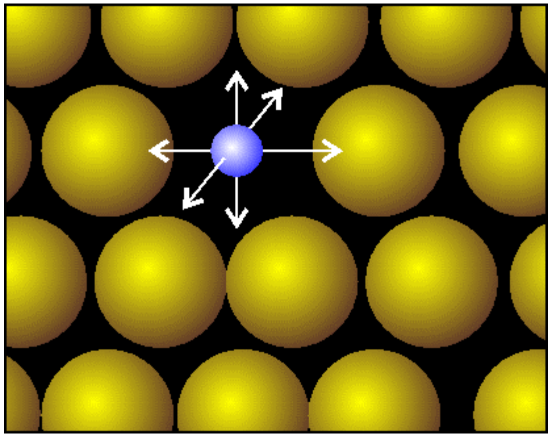
$\Delta U/\Delta T = n\frac{5}{2}R$	$C_{v,m} = \frac{5}{2}R$	$C_{p,m} = C_{v,m} + R = \frac{7}{2}R$

3. NON-LINEAR MOLECULES: $U = n\,3RT$

33.3 J K^{-1}mol^{-1}

$\Delta U/\Delta T = n\,3R$	$C_{v,m} = 3R$	$C_{p,m} = C_{v,m} + R = 4R$

Molar heat capacity of a solid



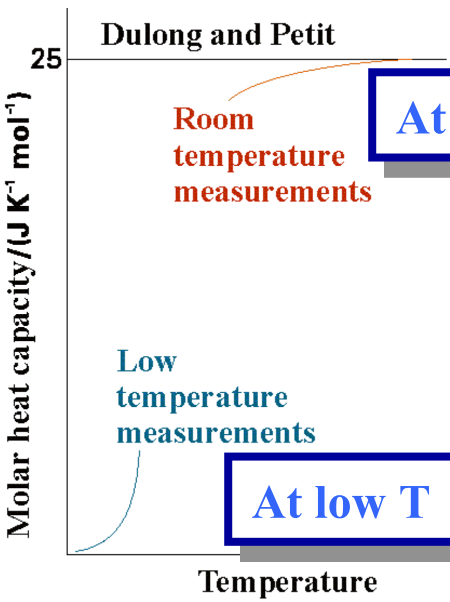
Heat = thermal motion of atoms

For vibrational motion U = kT per degree of freedom. For a solid:

$$\text{d.o.f.} = 3N - 6 \approx 3N$$

$$U = 3\,NkT \qquad U = 3\,nRT$$

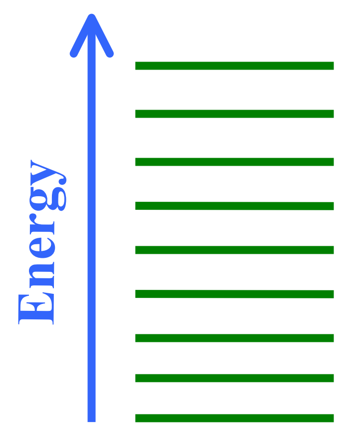
$$C_{v,m} = 3R$$



At high T $C_{v,m} \rightarrow 3R$

At low T $C_{v,m} \rightarrow 0$

Quantized Energy Levels



$$\frac{N_{upper}}{N_{lower}} = e^{-\Delta E/kT}$$

Classical Behavior:
$\Delta E << kT$

Non-Classical Behavior:
$\Delta E \geq kT$