Termodynamics – Forms of Energy

Energetic transformations during chemical and phycical processes, energy transfer, transformations of different kinds of energy, heat and work.

- Important are only initial and final states
- Does not depend on mechanism of transformations
- Predicts direction, spontaneity and extent of reactions
- Does not consider time, rate, or mechanisms

Heat
Chemical energy
Light
Mechanical work
Electrical energy
Nuclear energy

Heat and Energy

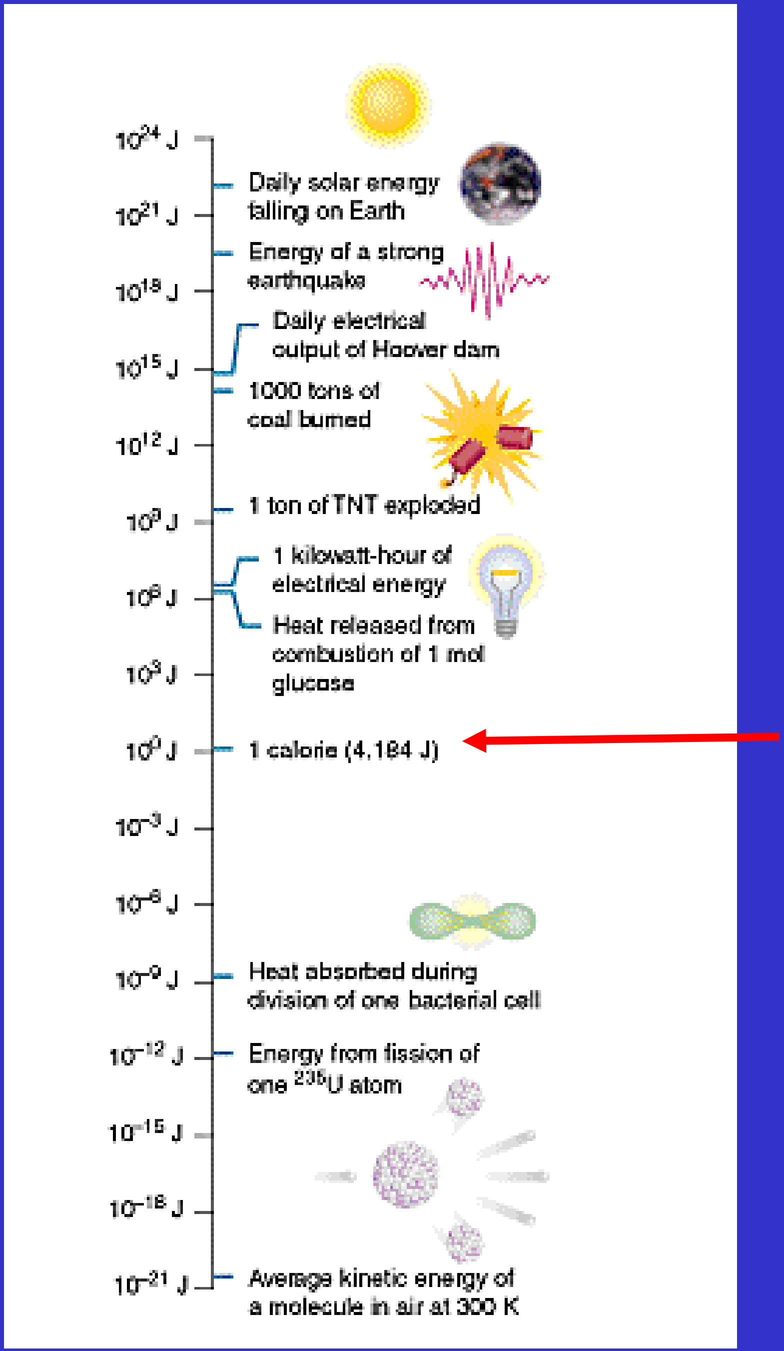
Benjamin Thomson count Rumdorf

1798 heat originates from mechanical work - drilling of cannon barrels

James Prescot Joule

1849 transformations of different kinds of energy to heat

Heat = Energy



Energy

1 Joule ≅ energy of a heartbeat

1 calorie = 4.1868 J

1 eV $(\text{molecule})^{-1} = 96.485\ \text{kJ mol}^{-1}$

Work

$W_{\text{mechan}} = F \times l = m \times a \times l$

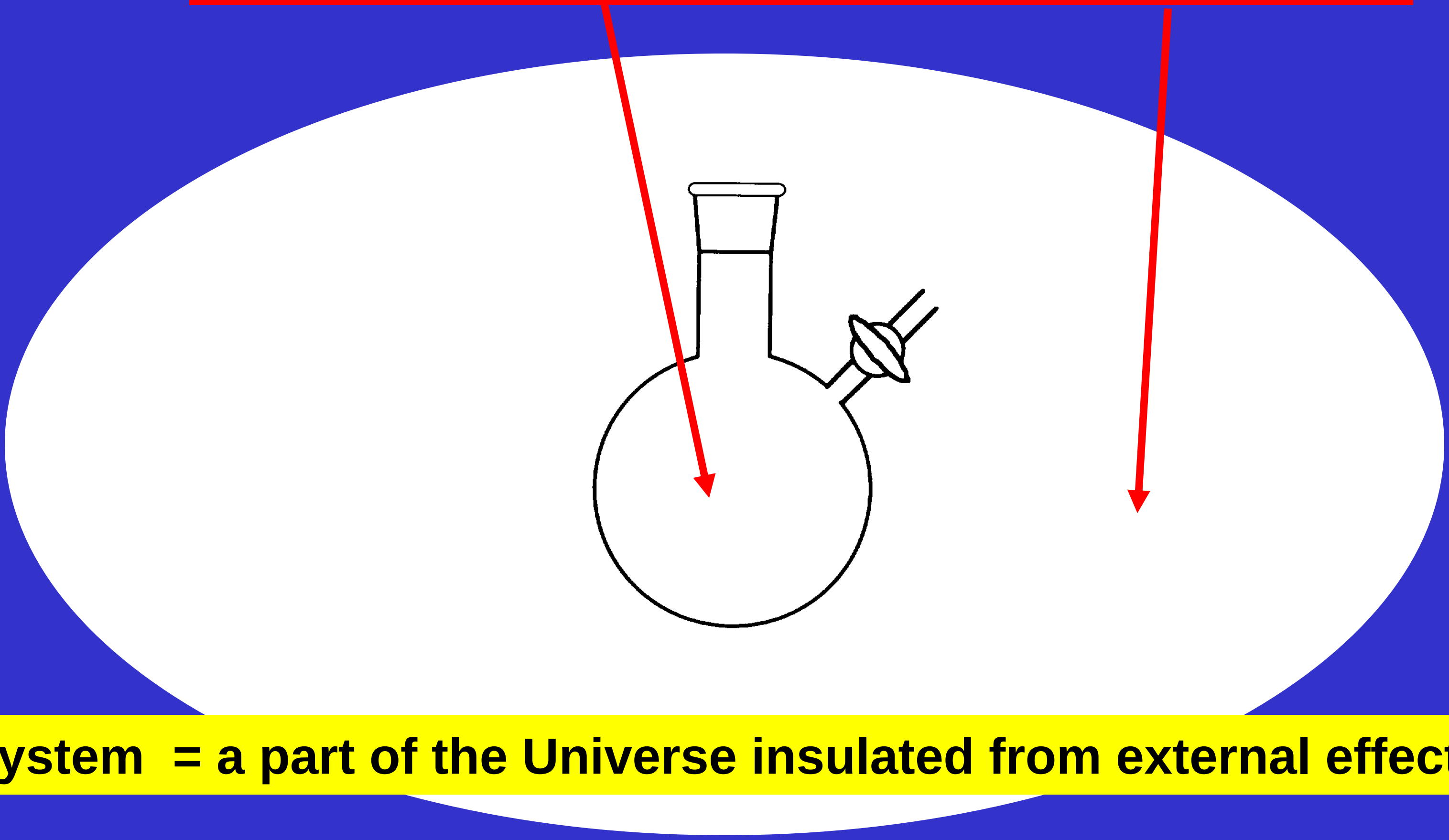
$1\ \text{J} = 1\ \text{N m} = 1\ \text{kg m}^2\ \text{s}^{-2}$

$W_{\text{el}} = P \times t$

$1\ \text{J} = 1\ \text{W s} = 1\ \text{kg m}^2\ \text{s}^{-2}$

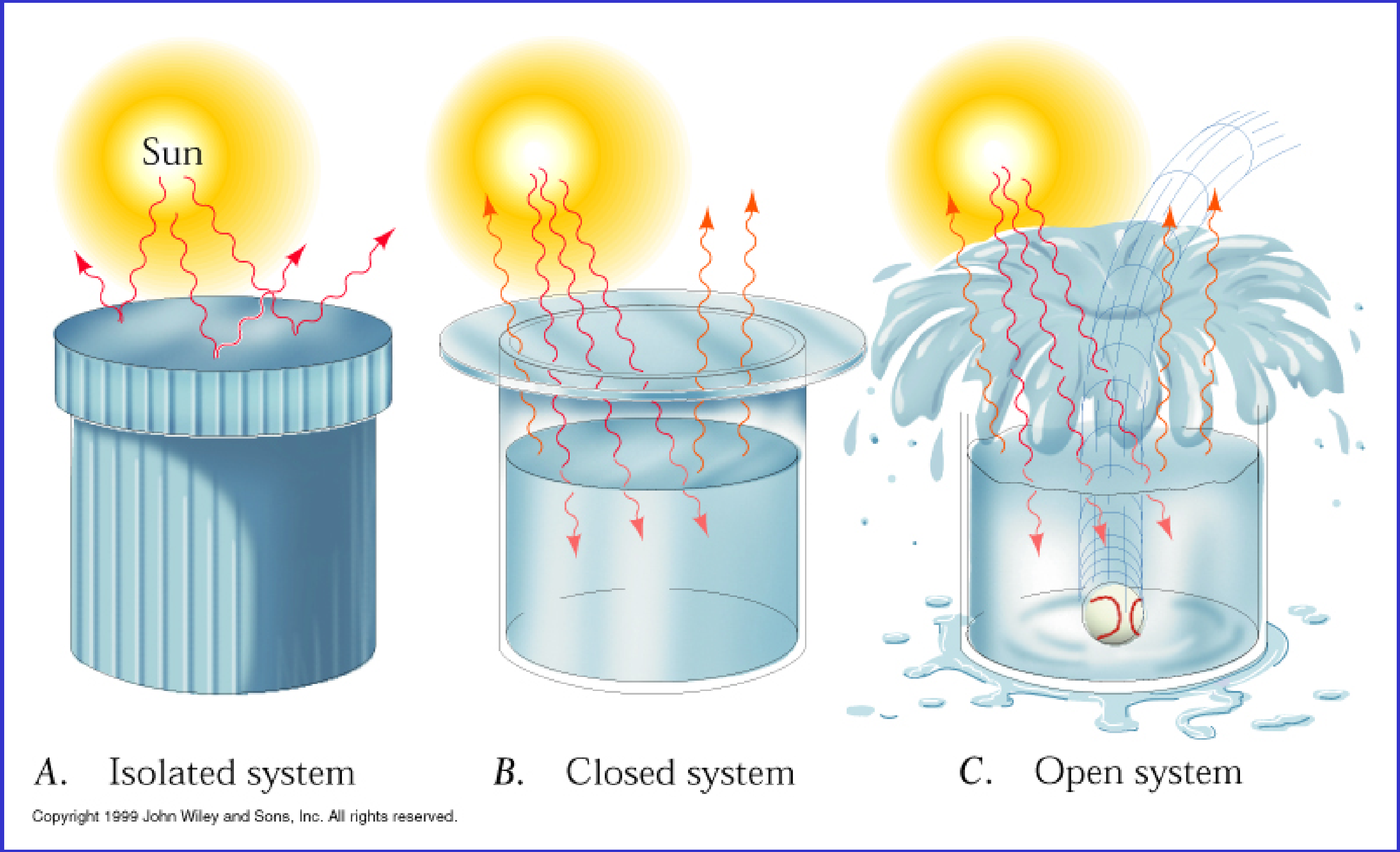
Universe, System, Surroundings

Universe = System + Surroundings



System = a part of the Universe insulated from external effects

Thermodynamic Systems



A. Isolated system *B.* Closed system *C.* Open system

Exchange of: Nothing Energy Energy and mass

Termodynamic Processes

Isothermal	Constant temperature	$dT = 0$
Isobaric	Constant pressure	$dp = 0$
Isochoric	Constant volume	$dV = 0$
Adiabatic	No exchange of heat	$dQ = 0$
Diathermal	Exchange of heat	$dQ \neq 0$

System Description

***Extensive variables**: depend on contributions from different parts of the system, are **additive** - mass, electrical charge, molar amount, ...

***Intensive variables** : **not additive** - temperature, pressure, viscosity, concentration, density, ...

Thermodynamic state of a system is described by **Intensive variables** (T, p, c)

State function : physical characteristic whose value depends on the state of the system

U, H, S, G are functions of T, p, c

Thermodynamic Processes

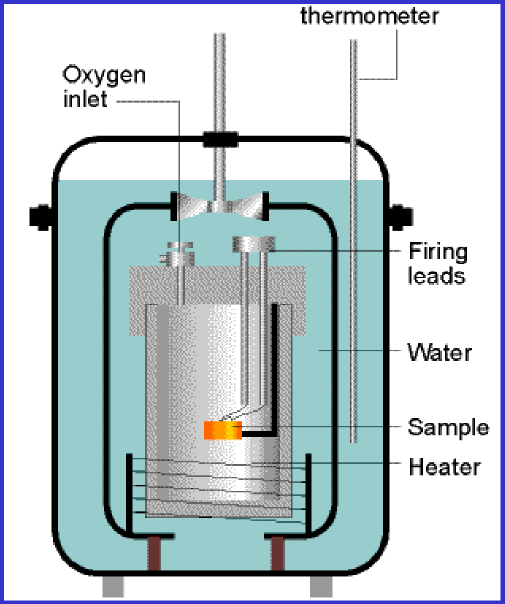
Thermodynamic processes procede from an initial to final state = equilibrium
At equilibrium, TD properties of a system are constant

Equilibria
- Thermal
- Phase
- Chemical

Thermodynamic processes
Reversibile - slow, always close to equilibrium, direction can be reversed
- Irreversibile – finite time, definite changes

Heat, Temperature, Calorimetry

Measuring of heat by changes in temperature



$Q = C \times \Delta T$

C = heat capacity $\Delta T = Q / C$

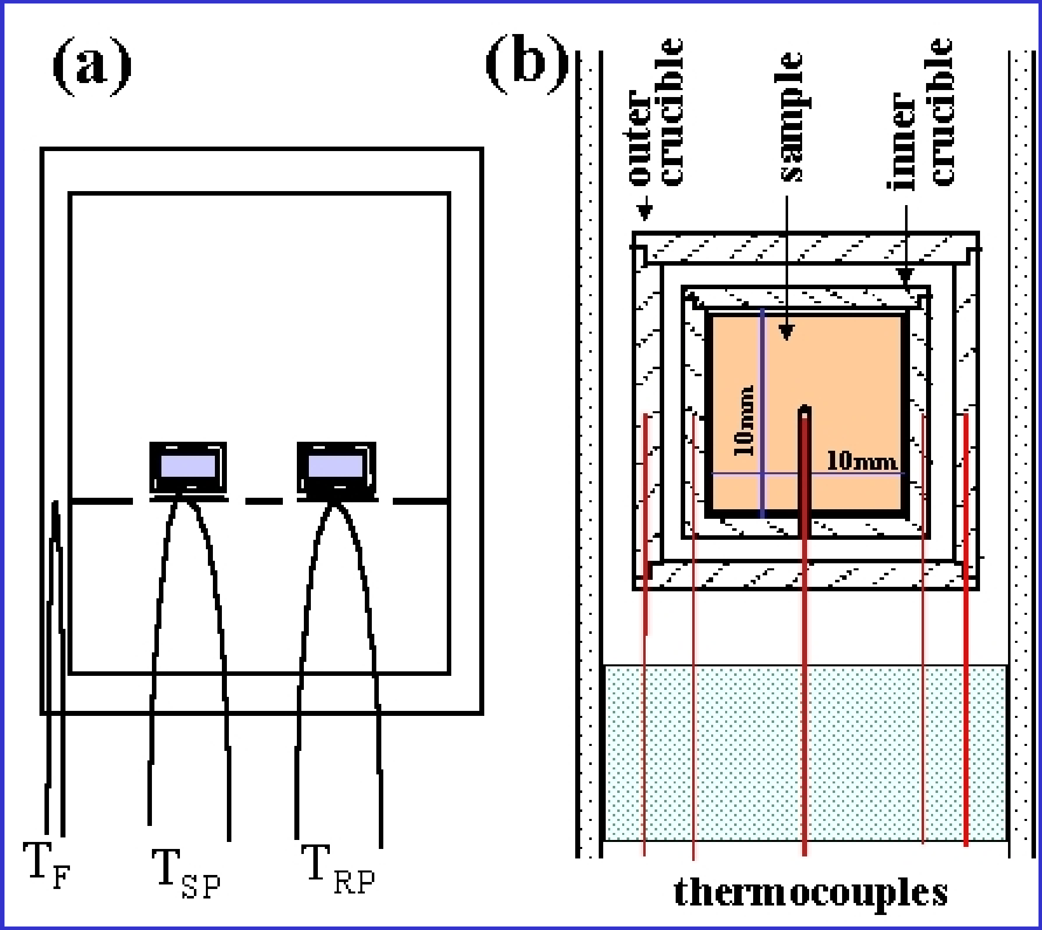
$Q = m \times c_s \times \Delta T$

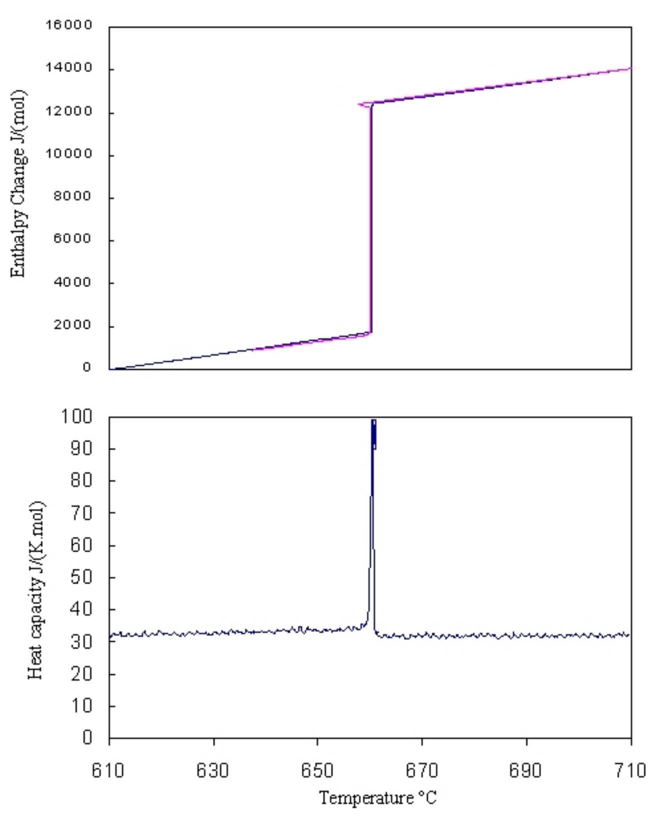
c_s = specific heat = amount of heat necessary to increase the temperature of 1 g of a compound by 1 K without a phase transformation [$\mathrm{J\ K^{-1}\ g^{-1}}$]

c_M = specific molar heat [$\mathrm{J\ K^{-1}\ mol^{-1}}$]

$c_M = M\ c_s$

DSC Differential Scanning Calorimetry





Dulong-Petit Rule

1819 P. L. Dulong (NCl_3), A. T. Petit – specific heat (c_s) is different for different compounds, BUT

specific molar heat c_M is constant for different compounds

$c_M = 3R = 24.94$ J K^{-1} mol^{-1}

For elements A > 35, at normal and high temps

Was used during 19th century for atomic mass estimates of elements: $c_M = M\,c_s$

Bi $c_s = 0.123$ J K^{-1} mol^{-1}

$$\boxed{c_s = \frac{c_M}{M}}$$

Zeroth Law of Thermodynamics

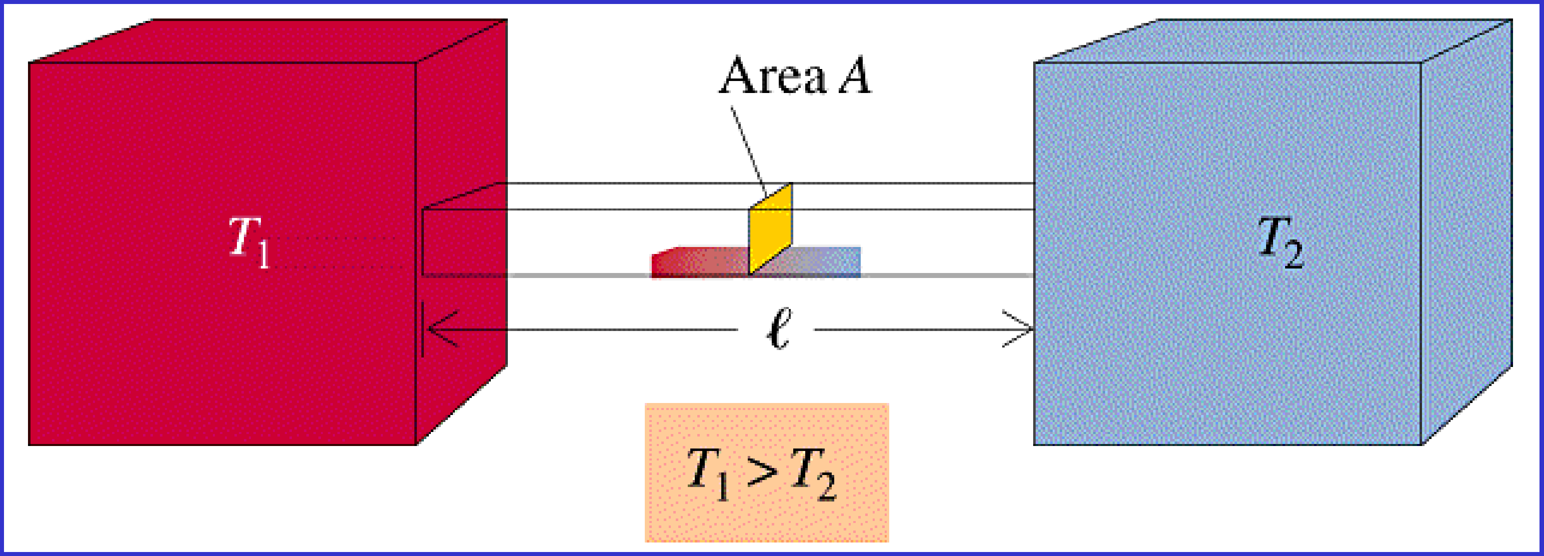
If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

$T_A = T_C$ and $T_B = T_C$ then $T_A = T_B$

An empirical definition of temperature

If there is no heat energy transfer between two bodies in thermal contact, then they are both at the same temperature.

Heat Transfer



$$\frac{Q}{t} = \frac{KA\left(T_1^{hot} - T_2^{cold}\right)}{l}$$

Q = heat
t = time
K = thermal conductivity
A = area
T = temperature
l = length

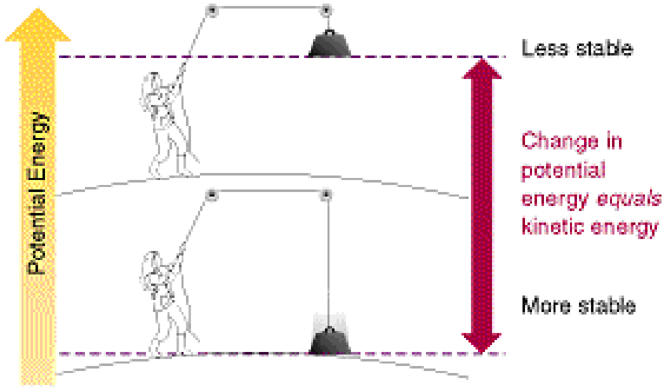
Kinetic and Potential Energy

Kinetic energy E_k – active, does work

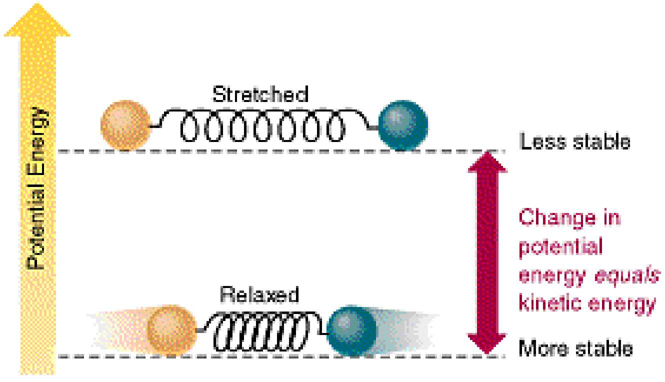
$$\boxed{E_k = \frac{1}{2}mv^2}$$

Potential energy – inactive, ready to do work, outcome of relative position or structure

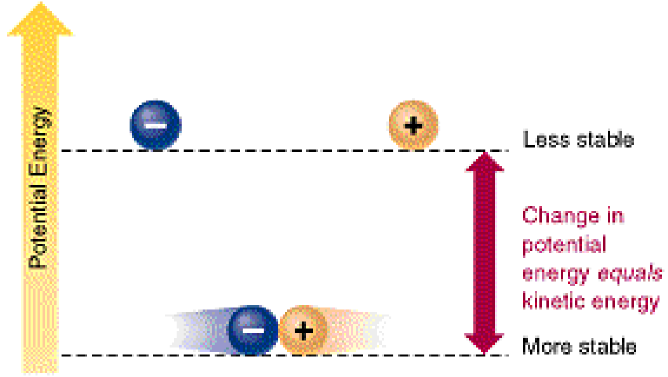
Kinetic and Potential Energy



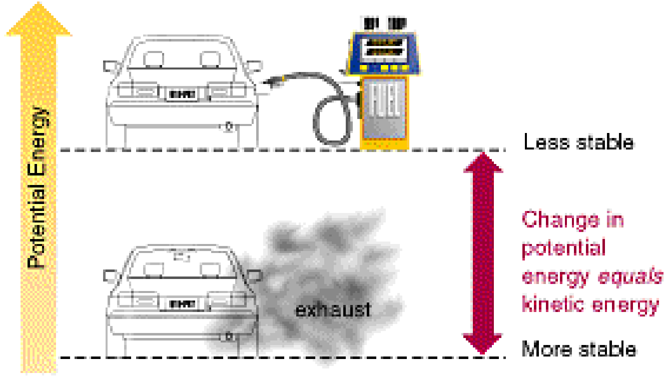
A A gravitational system. The E_p gained when a weight is lifted is converted to E_k as the weight falls.



B A system of two balls attached by a spring. The E_p gained when the spring is stretched is converted to E_k of the moving balls when it is released.



C A system of oppositely charged particles. The E_p gained when the charges are separated is converted to E_k as the attraction pulls them together.



D A system of fuel and exhaust. A fuel is higher in chemical E_p than the exhaust. As the fuel burns, some of its E_p is converted to E_k of the moving car.

Kinetic and Potential Energy

Kinetic

Translation

Rotations

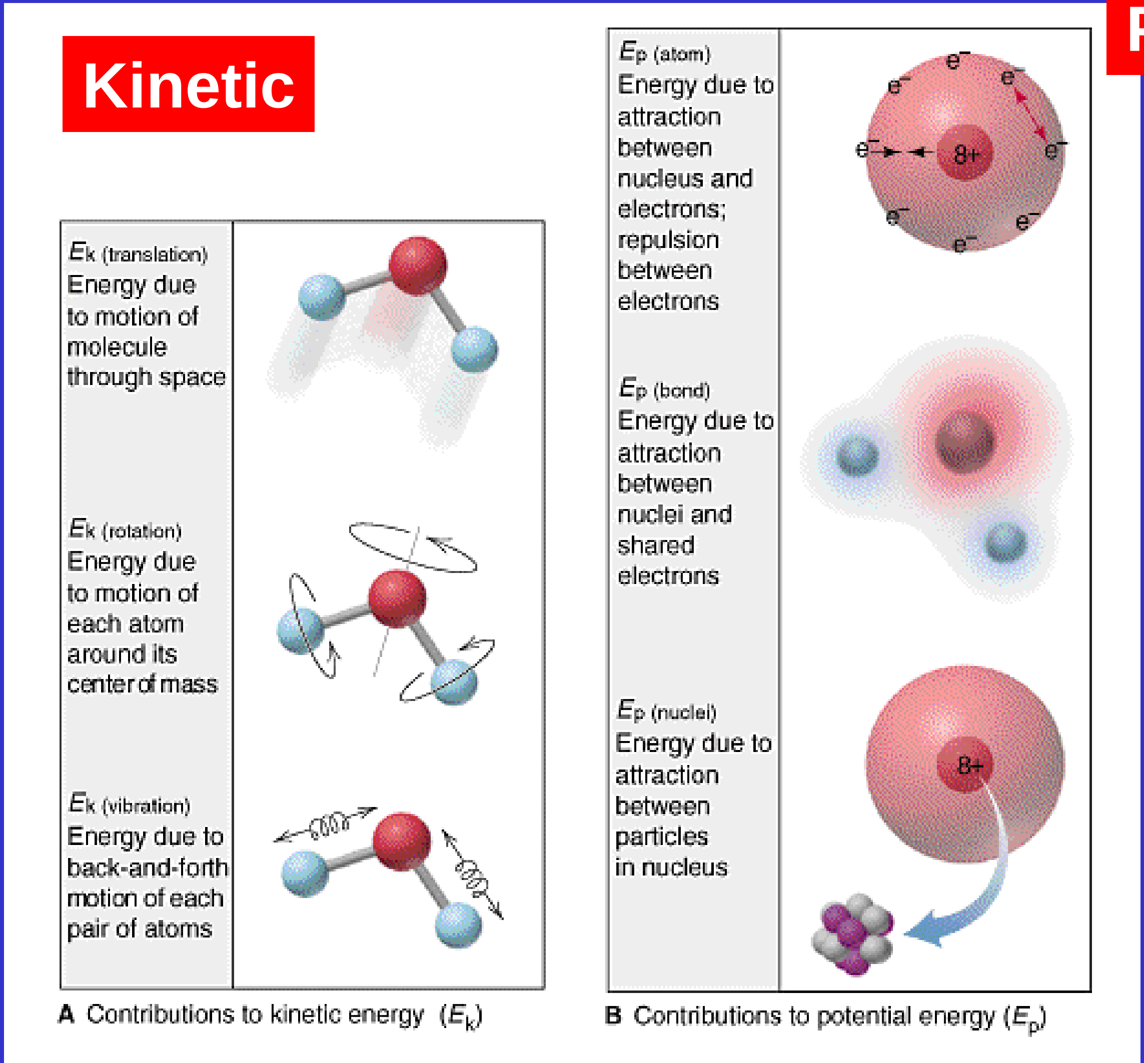
Vibrations

Potential

Electronic (e-n / e-e inside atom)

Bonding (valence e in molecules)

Nuclear



E_k (translation) Energy due to motion of molecule through space

E_k (rotation) Energy due to motion of each atom around its center of mass

E_k (vibration) Energy due to back-and-forth motion of each pair of atoms

A Contributions to kinetic energy (E_k)

E_p (atom) Energy due to attraction between nucleus and electrons; repulsion between electrons

E_p (bond) Energy due to attraction between nuclei and shared electrons

E_p (nuclei) Energy due to attraction between particles in nucleus

B Contributions to potential energy (E_p)

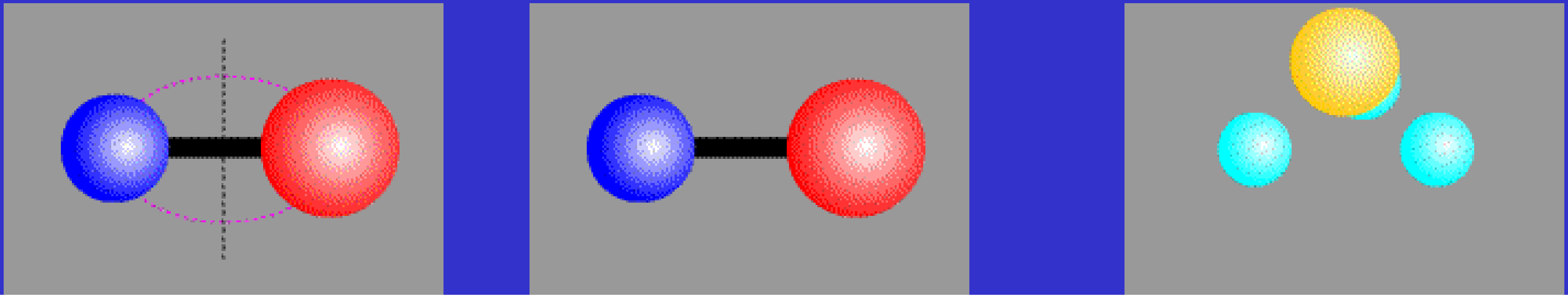
Molecular Energies

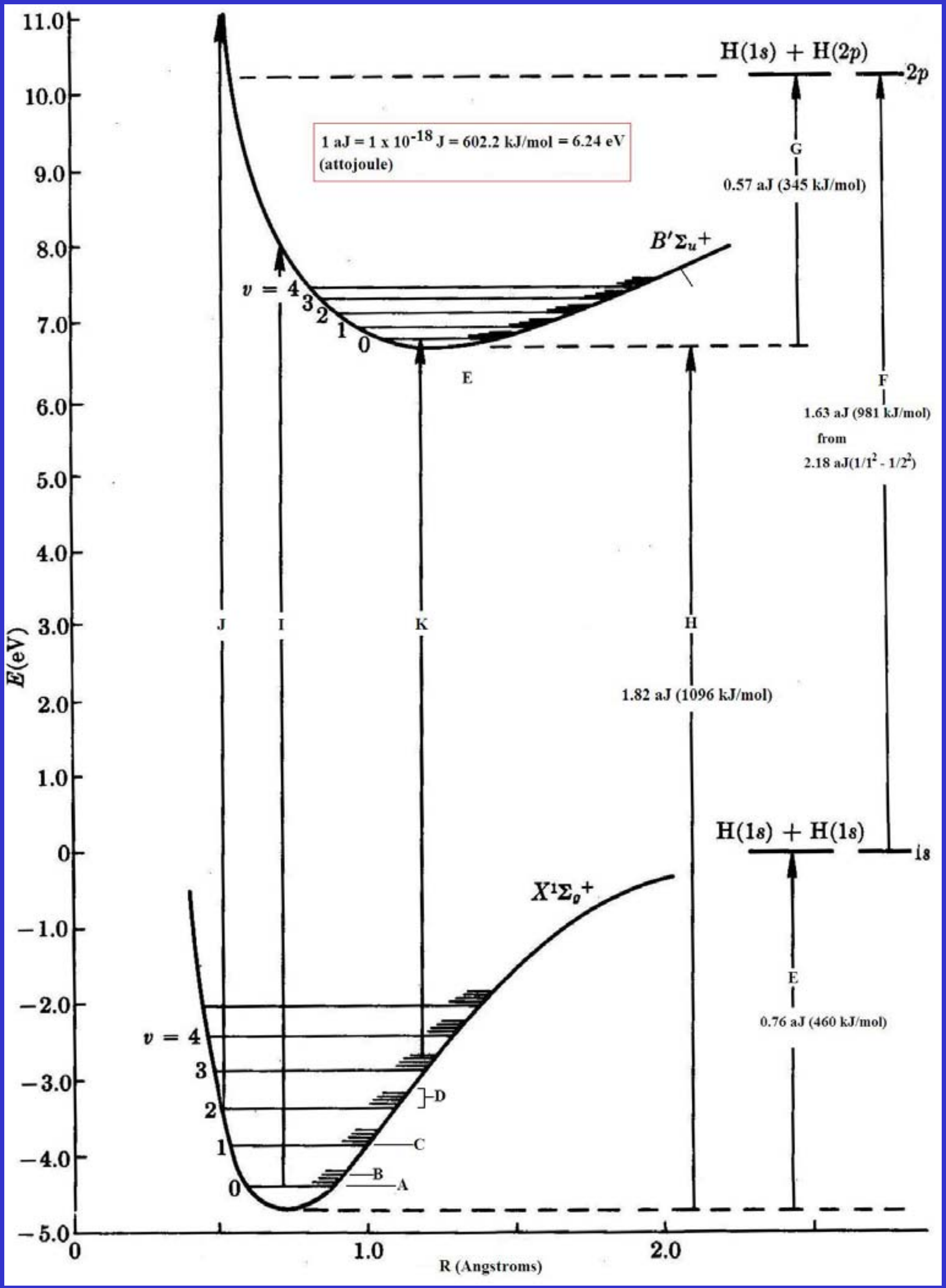
Total energy of molecules

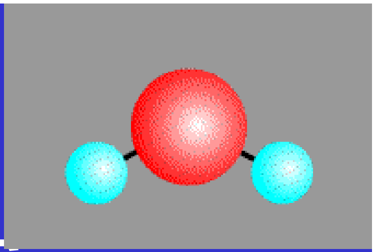
Individual componets of E_{tot} are independent – very different magnitudes

$$E_{tot} = \text{transl.} + \text{rotat} + \text{vibrat} + \text{electron}$$

E(elektron)	100 kJ mol^{-1}	UV - visible
E(vibrat)	1.5 – 50 kJ mol^{-1}	Infrared
E(rotat)	0.1 – 1.5 kJ mol^{-1}	Microwave and far IR




11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
−3.0
−4.0
−5.0
E(eV)
0
1.0
2.0
R (Angstroms)
H(1s) + H(2p)
2p
1 aJ = 1 x 10^{-18} J = 602.2 kJ/mol = 6.24 eV
(attojoule)
G
0.57 aJ (345 kJ/mol)
$B'\Sigma_u+$
v = 4
3
2
1
0
E
F
1.63 aJ (981 kJ/mol)
from
2.18 aJ($1/1^2$ - $1/2^2$)
J
I
K
H
1.82 aJ (1096 kJ/mol)
H(1s) + H(1s)
1s
$X^1\Sigma_g^+$
E
0.76 aJ (460 kJ/mol)
v = 4
3
2
1
0
D
C
B
A



Energy States – Vibrational Levels

Quantization of vibrational energy

$E(\text{vibrat}) = h\upsilon_0 \, (v + ½)$

v = vibrational quantum number

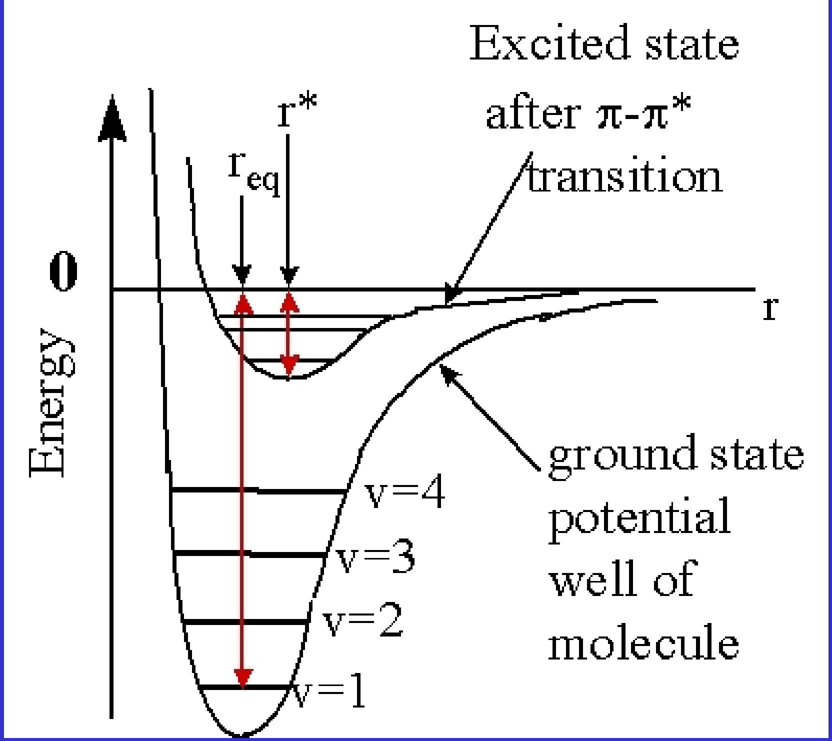
Selection rule $\Delta v = \pm 1$

Zero Point Energy:

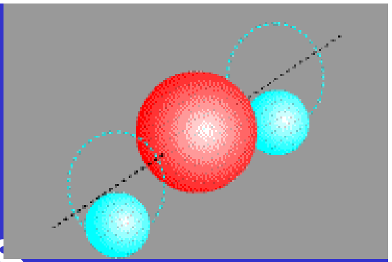
For v = 0 $E(\text{vibrat}) = ½ \, h\upsilon_0$

H_2 $E(\text{disoc}) = 432 \text{ kJ mol}^{-1}$

$E(v = 0) = 25 \text{ kJ mol}^{-1}$

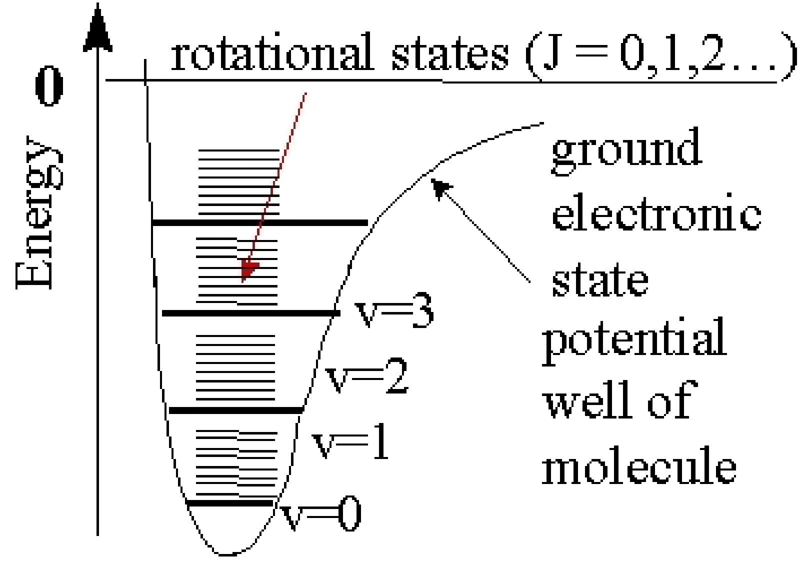


At normal temperature, molecules are in their vibrational **ground** state v = 0, not enough energy to populate higher levels



Energy States – Rotational Levels

Quantization of rotational energy



E(rotat) = $(\hbar^2/2I)\,J(J+1)$
J = rotational quantum number
I = rotational momentum ($\mu\, r^2$)

Selection rule $\Delta J = \pm 1$

At normal temperature, molecules are **in many excited** rotational states, rotational energy is comparable to thermal motion energy of molecules

Internal Energy, U

U is a state function – depends on T, p, ...

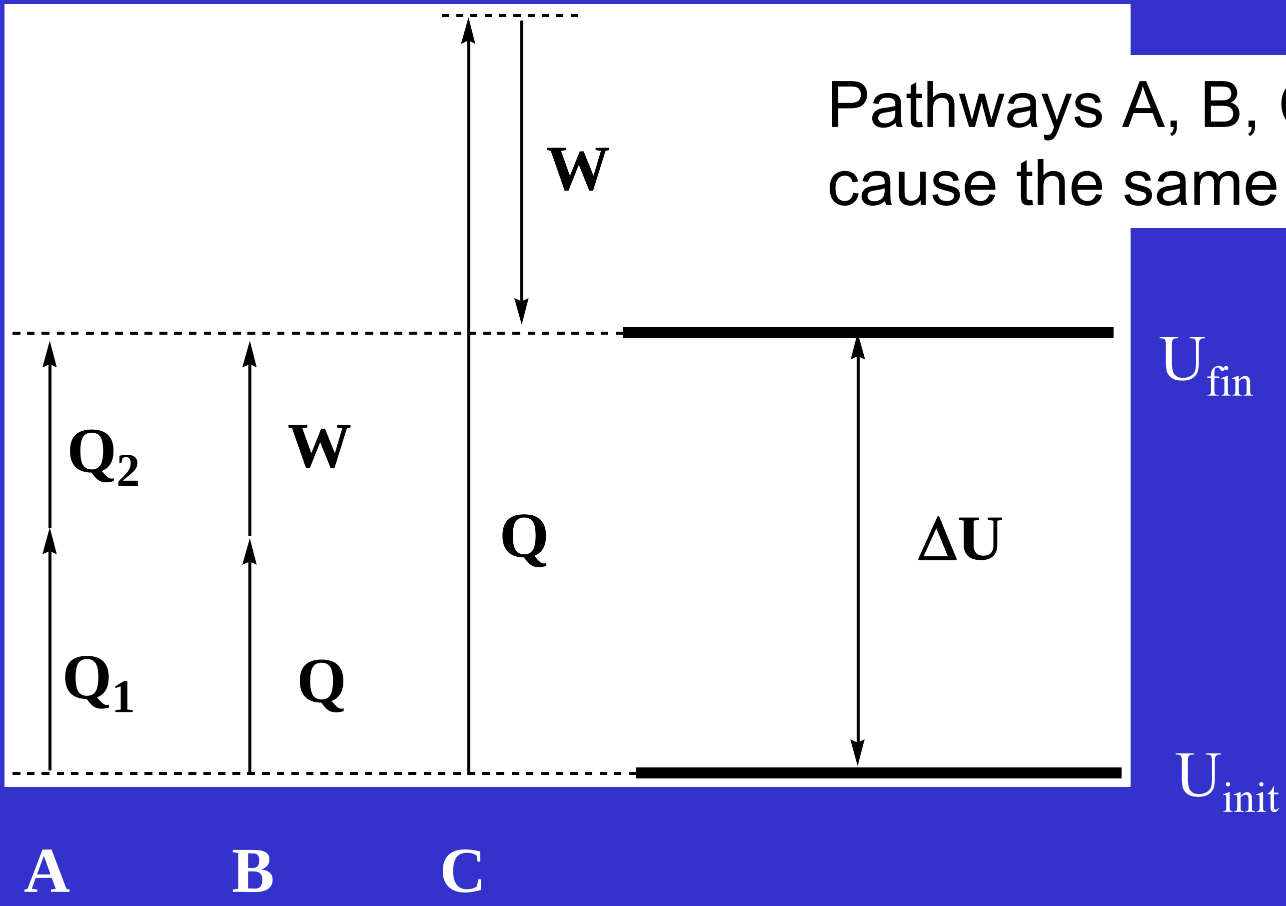
U = Sum of translational, rotational, vibrational, lattice vibrations, bond energies,.....

The value of U cannot be measured or calculated

Changes of U can be measured during exchange of:
heat Q, work W, electrical energy E_{el}

$\Delta U = U_{fin} - U_{init}$
Does not depend on mechanism or pathway of transformation of U, but only on initial and final states

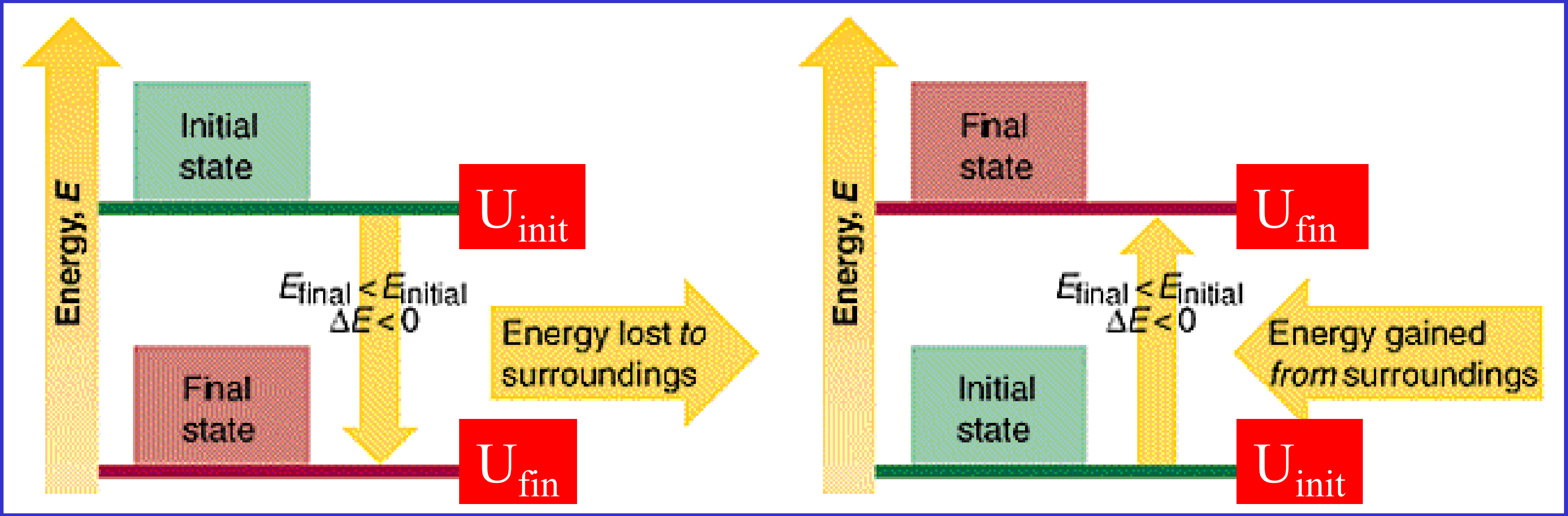
Changes of U



Pathways A, B, C
cause the same change in ΔU

$$\Delta U = U_{fin} - U_{init}$$

Exchange of Energy (Heat Q, Work W,...)



$$\Delta U = U_{fin} - U_{init} < 0$$

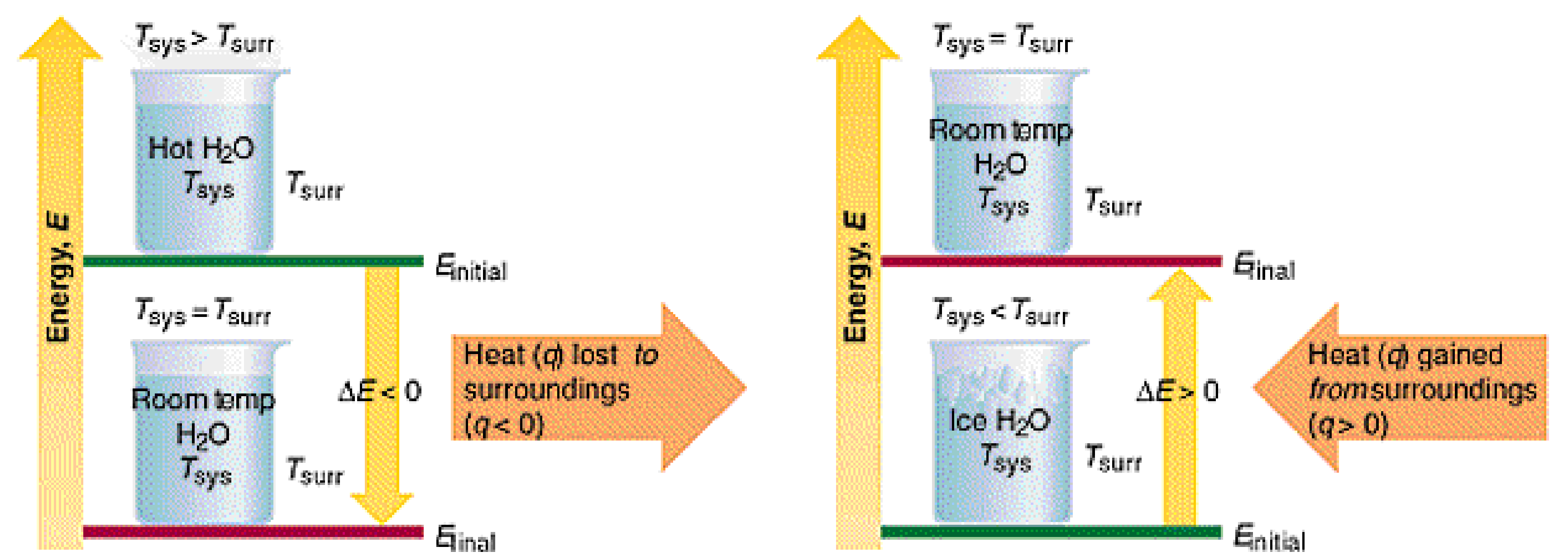
$$\Delta U = U_{fin} - U_{init} > 0$$

Energy released to surroundings

Energy acquired from surroundings

Exchange of Heat, Q

Heat, Q is not a state function

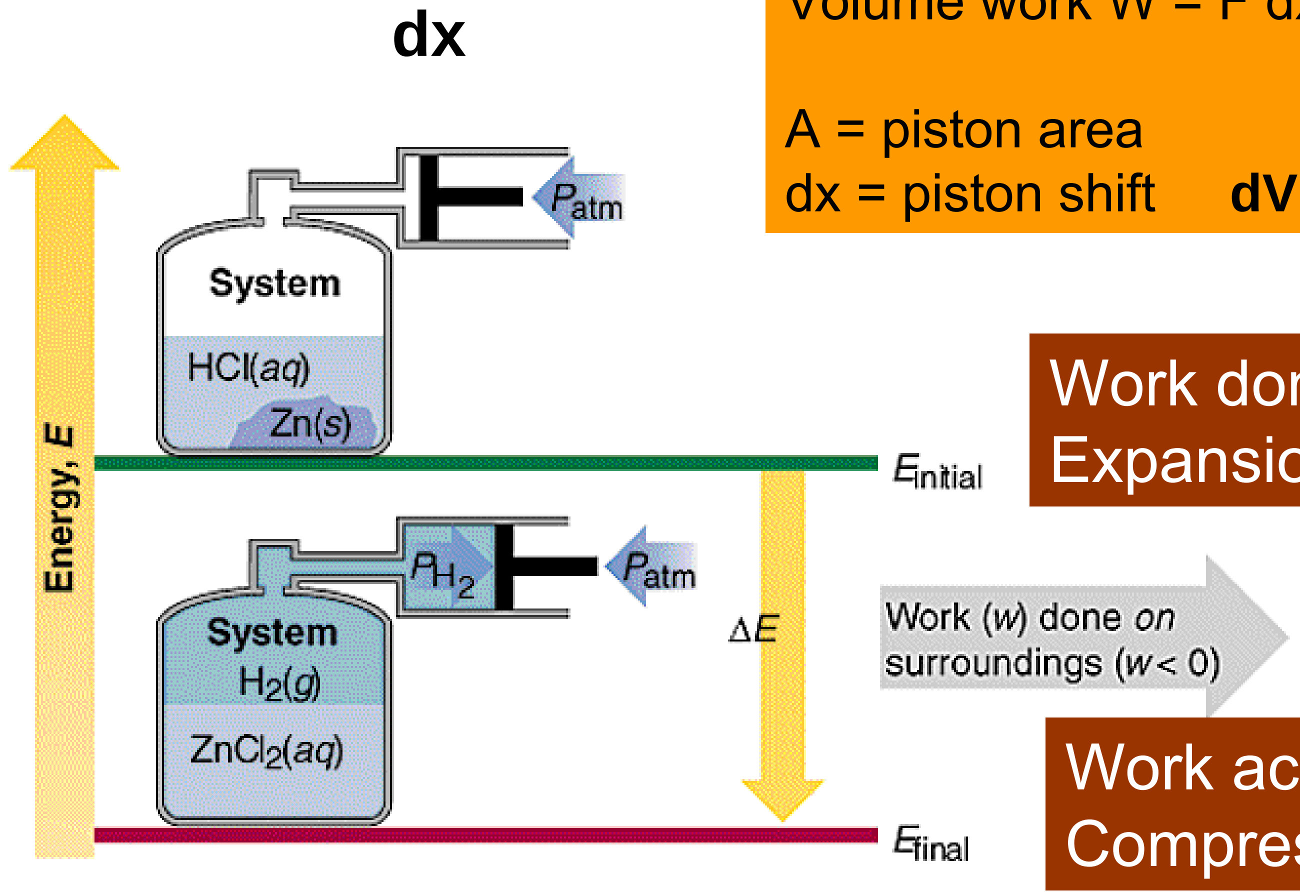


Heat released to surroundings
–Q (Q < 0)

Heat absorbed from surroundings +Q (Q > 0)

WRT the System

Volume Work, W



Force on piston $F = p \times A$
Volume work $W = F\,dx = p\,A\,dx = p\,dV$

A = piston area
dx = piston shift **$dV = A \times dx$**

Work done $-W$ ($W < 0$)
Expansion of gas $dV > 0$

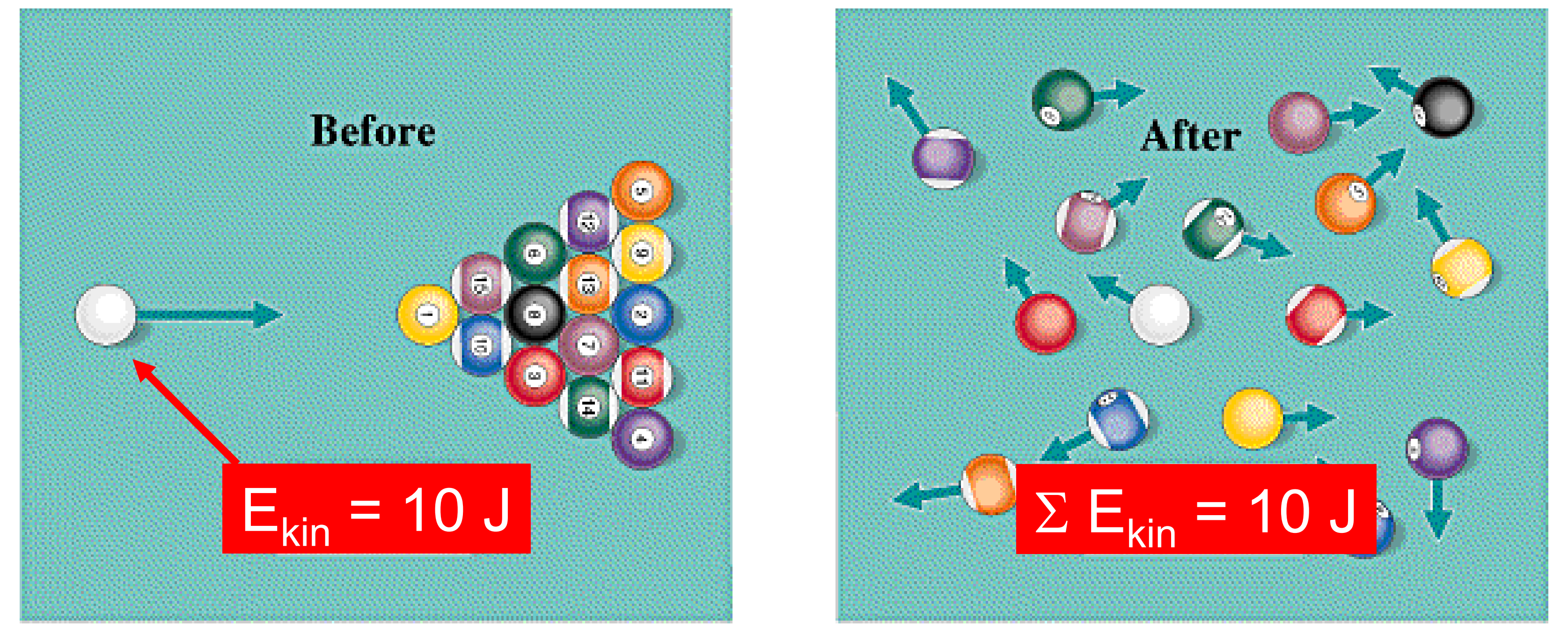
Work accepted $+W$ ($W > 0$)
Compression of gas $dV < 0$

$Zn(s) + 2HCl(aq) \rightarrow H_2(g) + ZnCl_2\,(aq)$

First Law of Thermodynamics

The law of conservation of energy

The energy of an isolated system is constant



E_{kin} = 10 J

ΣE_{kin} = 10 J

First Law of Thermodynamics

The change in internal energy of a closed system is equal to sum of the heat supplied to the system and the work done on it: $\Delta U = Q + W$

Equivalence of work and heat

Work done on surroundings –W (W < 0)
Expansion of gas dV > 0

Heat released
to surroundings –Q (Q < 0)

Work done on system +W
(W > 0)
Compression of gas dV < 0

Heat absorbed from
surroundings +Q (Q > 0)

Reaction Heat at Constant Volume , Q_V

Constant volume V = const.

when $\Delta V = 0$
then $p\,\Delta V = 0$ and $W = 0$

$\Delta U = Q_V$

Reaction Heat at Constant Pressure, Q_p

Constant pressure p = const. Common situation in chemistry.

$\Delta U = Q_p - p\,\Delta V$ Volume work done on surroundings

$U_2 - U_1 = Q_p - p\,(V_2 - V_1)$

$Q_p = (U_2 + p\,V_2) - (U_1 + p\,V_1) = H_2 - H_1 = \Delta H$

Enthalpy $H = U + p\,V$ is a state function, H is not heat

Upon absorption of Q_p, heat is partially transformed to U and partially to W

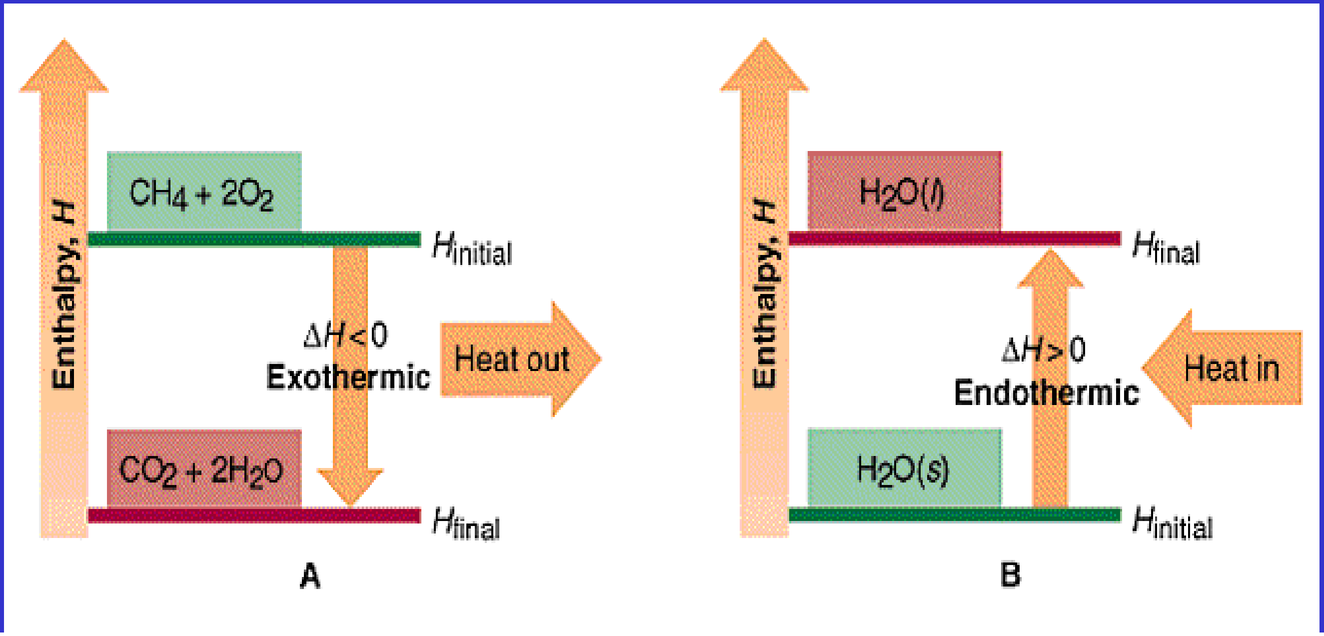
Exothermic and Endothermic Processes

Exothermic Processes

$\Delta H < 0$ System releases heat to surroundings, energy content of the system decreases

Endothermic Processes

$\Delta H > 0$ System absorbs heat from surroundings, energy content of the system increases



Standard State

Values of state functions U, H, G, S depend on T, p, c

Standard State = defined conditions allowing comparison

Agreement, defined for g, l, solutions

T_{st} = 298.15 K
p_{st} = 100000 Pa = 1 bar (formely p_{st} = 1 atm = 101325 Pa)
c_M = 1 M

Marked by superscript zero H^0

Caveat: Standard State is not the same as standard conditions (STP) for gases p = 101.325 kPa T = 273.15 K

Enthalpy of Elements

Enthalpy of elements and compounds H is not known

A convention adopted for elements :

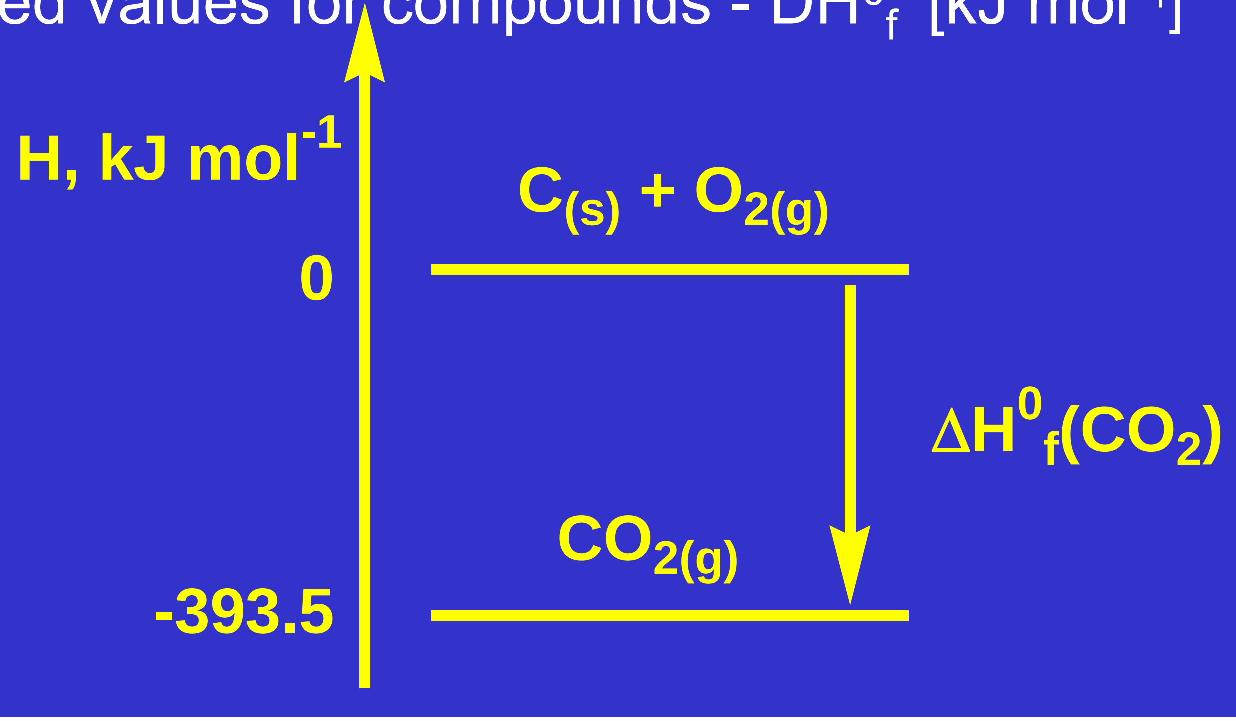
$H^0 = 0$

At Standard State (T = 298.15 K, p = 1 bar)
And in physical state in which an element exists at Standard State conditions

Formation Enthalpy, ΔH^0_f

ΔH^0_f for a reaction in which **1 mol of a compound is formed from elements in standard states** ($H^0 = 0$)
Standard State conditions of p, T

Tabulated values for compounds - DH^0_f [kJ mol^{-1}]



Reaction Enthalpy, ΔH^0_r

ΔH^0_r gives information how much products of a reaction differ in energy from starting compounds

Can be calculated from:

1) Formation enthalpies in reaction

Reactants → Products

$$\Delta H^0_r = \Sigma\, n_{prod}\, \Delta H^0_f\,(\mathrm{Prod}) - \Sigma\, n_{react}\, \Delta H^0_f\,(\mathrm{Reakt})$$

n = stoichiometric coefficients !!!!

Reaction Enthalpy, ΔH^0_r

$$N_2O_4(g) + 4\ H_2(g) \rightarrow N_2(g) + 4\ H_2O(g)$$

$\Delta H^0_{\text{sluč}}$	$N_2O_4(g)$	9.66 kJ mol^{-1}
	$H_2(g)$	0 kJ mol^{-1}
	$N_2(g)$	0 kJ mol^{-1}
	$H_2O(g)$	–241.82 kJ mol^{-1}

$$\Delta H_r = [1\text{mol}(\Delta H(N_2)) + 4\text{mol}(\Delta H(H_2O))] – [1\text{mol}(\Delta H(N_2O_4)) + 4\text{mol}(\Delta H(H_2))]$$

$$\Delta H_r = [1\text{mol}(0\ \text{kJ mol}^{-1}) + 4\text{mol}(-241.82\ \text{kJ mol}^{-1})] – [1\text{mol}(9.66\ \text{kJ mol}^{-1}) + 4\text{mol}(0\ \text{kJ mol}^{-1})]$$

$$= –976\ \text{kJ}$$

Reaction Enthalpy, ΔH^0_r

$$2\ KOH(s) + CO_2(g) \rightarrow K_2CO_3(s) + H_2O(g)$$

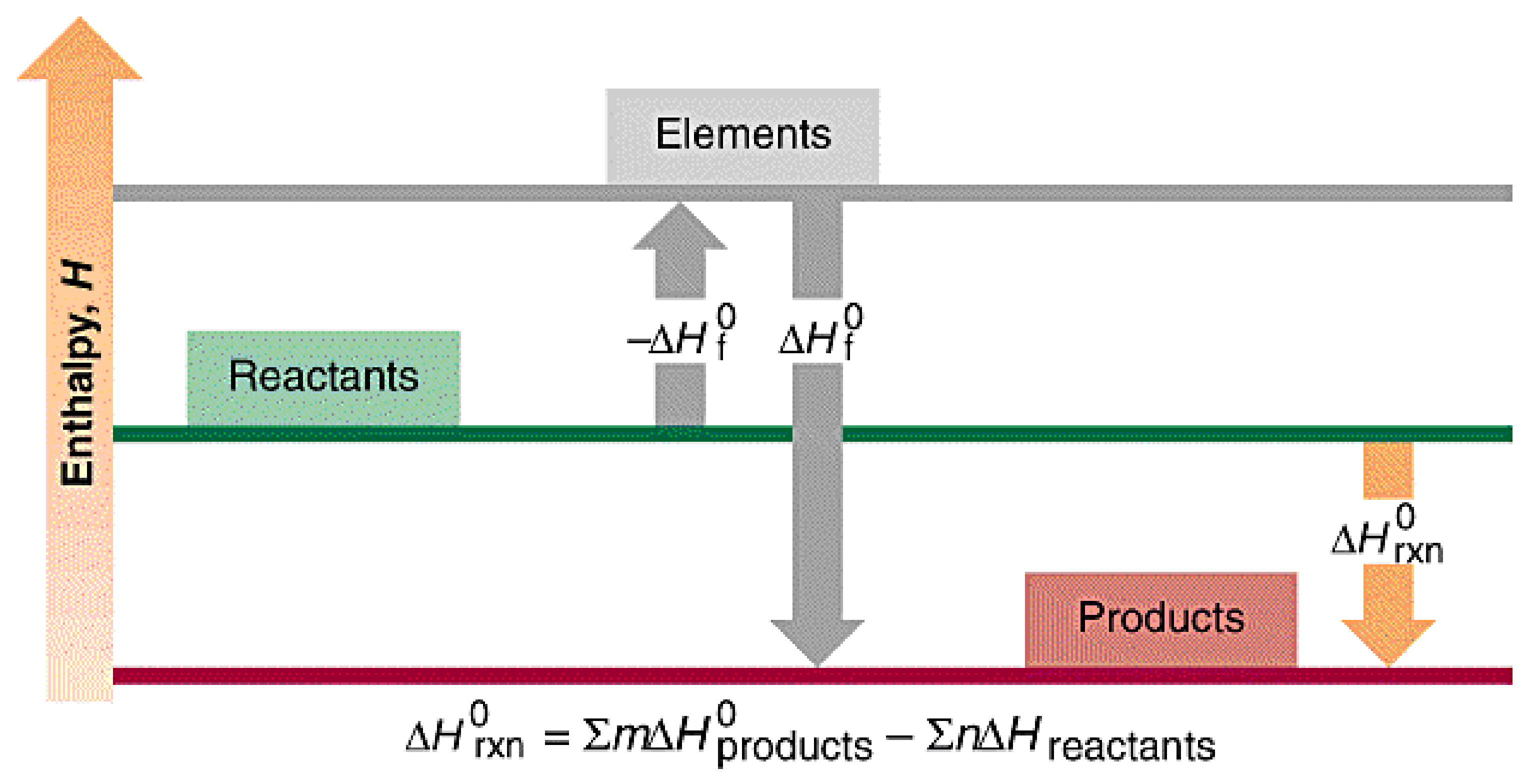
$KOH(s)$	$-424.7\ kJ\ mol^{-1}$
$CO_2(g)$	$-393.5\ kJ\ mol^{-1}$
$K_2CO_3(s)$	$-1150.18\ kJ\ mol^{-1}$
$H_2O(g)$	$-241.82\ kJ\ mol^{-1}$

$$\Delta H = [1mol(\Delta H(K_2CO_3)) + 1mol(\Delta H(H_2O))] - [2mol(\Delta H(KOH)) + 1mol(\Delta H(CO_2))]$$

$$\Delta H = [1mol(-1150.18\ kJ\ mol^{-1}) + 1mol(-241.82\ kJ\ mol^{-1})] - [2mol(-424.7\ kJ\ mol^{-1}) + 1mol(-393.5\ kJ\ mol^{-1})]$$

$$= -149.1\ kJ$$

Reaction Enthalpy, ΔH^0_r



$$\Delta H^0_r = \Sigma\, n_{prod}\, \Delta H^0_f\,(\text{Prod}) - \Sigma\, n_{react}\, \Delta H^0_f\,(\text{Reakt})$$

Reaction Enthalpy, ΔH^0_r

Enthalpy is an extensive variable
(magnitude of ΔH depends on molar amount):

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H = -802\ \text{kJ}$$

$$2CH_4(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g) \qquad \Delta H = -1604\ \text{kJ}$$

Reaction Enthalpy, ΔH^0_r

Reaction enthalpy, ΔH^0_r depends on physical state of reactants and products

$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g) \qquad \Delta H = -802\text{ kJ}$

$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H = -890\text{ kJ}$

Reaction Enthalpy, ΔH^0_r

Reversed reaction has opposite sign of ΔH_r
(First Hess Law or Lavoisier-Laplace Law)

$CO_2(g) + 2H_2O(g) \rightarrow CH_4(g) + 2O_2(g)$ $\Delta H = +802$ kJ

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $\Delta H = -802$ kJ

Hess Laws

First Hess Law or Lavoisier-Laplace Law

Thermal effect of a reaction in one direction is equal to the reverse reaction with an opposite sign.

$$\mathrm{C_{(s)} + O_{2\,(g)}} \underset{\Delta H^0_r = +394\ \mathrm{kJ\ mol^{-1}}}{\overset{\Delta H^0_f = -394\ \mathrm{kJ\ mol^{-1}}}{\rightleftarrows}} \mathrm{CO_{2\,(g)}}$$

Germain Henri Hess
(1802 - 1850)

Hess Laws

Ionisation energy of H

Electron affinity of H^+

$$H \underset{EA}{\overset{IE}{\rightleftarrows}} H^+ + e^-$$

Electron affinity of F

Ionisation energy of F^-

$$F^- \underset{EA}{\overset{IE}{\rightleftarrows}} F + e^-$$

Hess Laws

Second Hess Law

If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the individual reactions into which the overall reaction may be divided.

The enthalpy change for a chemical reaction is independent of the pathway or number of steps provided that the final and initial reaction conditions are identical.

Hess Laws

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H^0_f = -393.5\ \mathrm{kJ\ mol^{-1}}$

$2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(g)}$ $\Delta H^0_r = -483.6\ \mathrm{kJ\ mol^{-1}}$

$C_{(s)} + 2\ H_2O_{(g)} \rightarrow CO_{2(g)} + 2\ H_{2(g)}$ $\Delta H^0_r = +90.1\ \mathrm{kJ\ mol^{-1}}$

$\Delta H^0_f\ (H_2O,\ g) = -242\ \mathrm{kJ\ mol^{-1}}$

Reaction Enthalpy, ΔH^0_r

Can be calculated from:

2) bond enthalpies ΔH^0_b of all bonds formed or broken during a reaction

Reactants → Products

$$A\text{-}A + B\text{-}B \rightarrow A\text{-}B + A\text{-}B$$

Energy used for breaking A-A and B-B bonds

Energy released upon formation of A-B bonds

$$\Delta H^0_r = \Sigma\ x\ \Delta H^0_b\ (A\text{-}A) - \Sigma\ y\ \Delta H^0_b\ (A\text{-}B)$$

Bond Energies in Diatomic Molecules

Energy used to separate two atoms to an infinite distance

Energy of bonding electrons is the lowest when atoms are at a bonding distance. Energy used to break the bond is consumed by increasing energy of electrons.

During the bond formation the corresponding energy is released.

$H_{2(g)} + Br^{\bullet}_{(g)} \rightarrow H^{\bullet}_{(g)} + HBr_{(g)}$ $\Delta H^0{}_r = +70\ \text{kJ mol}^{-1}$

$E(H\text{–}H) = 436\ \text{kJ mol}^{-1}$ $E(H\text{–}Br) = 366\ \text{kJ mol}^{-1}$

Bond Energies in Diatomic Molecules

$H_{2(g)} + Br_{2(g)} \rightarrow 2\ HBr_{(g)}$ $\Delta H^0_r = -103\ \text{kJ mol}^{-1}$

$E(H\text{–}H) = 436\ \text{kJ mol}^{-1}$ $E(H\text{–}Br) = 366\ \text{kJ mol}^{-1}$

$E(Br\text{–}Br) = 193\ \text{kJ mol}^{-1}$

$629\ \text{kJ mol}^{-1}$ $732\ \text{kJ mol}^{-1}$

Energy used for breaking bonds

Energy released upon formation of bonds

Bond Energies in Polyatomic Molecules

$2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(g)}$ $\Delta H^0_r = -483.6\ \text{kJ mol}^{-1}$

$H_2O_{(g)} \rightarrow 2\ H^{\bullet}_{(g)} + O^{\bullet}_{(g)}$ $\Delta H^0_r = +926.9\ \text{kJ mol}^{-1}$

$2\ H_{2(g)} + O_{2(g)} \rightarrow 4\ H^{\bullet}_{(g)} + 2\ O^{\bullet}_{(g)}$

$4\ H^{\bullet}_{(g)} + 2\ O^{\bullet}_{(g)} \rightarrow 2\ H_2O_{(g)}$

$E(H{-}H) = 436\ \text{kJ mol}^{-1}$

$E(O{=}O) = 498.3\ \text{kJ mol}^{-1}$

$2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(g)}$

$\Delta H^0_r = 2(436) + (498.3) - 2(926.9) = -\ 483.5\ \text{kJ mol}^{-1}$

Total enthalpy – both O-H bond are broken

Bond Energies in Polyatomic Molecules

$H_2O_{(g)} \rightarrow 2\ H^{\bullet}_{(g)} + O^{\bullet}_{(g)}$ $\Delta H^0_r = +926.9\ \text{kJ mol}^{-1}$

$H_2O_{(g)} \rightarrow {}^{\bullet}OH_{(g)} + H^{\bullet}_{(g)}$ $\Delta H^0_r = ?$ $+492\ \text{kJ mol}^{-1}$

$(926.9)/2 = 463.5\ \text{kJ mol}^{-1}$

$CH_3OH_{(g)} \rightarrow CH_3O^{\bullet}_{(g)} + H^{\bullet}_{(g)}$ $\Delta H^0_r = +437\ \text{kJ mol}^{-1}$

Bond Energies in Polyatomic Molecules

$CH_{4(g)} \rightarrow CH_3{}^{\bullet}{}_{(g)} + H^{\bullet}{}_{(g)}$ $\Delta H^0{}_r = +435\ \text{kJ mol}^{-1}$

$CH_{4(g)} \rightarrow C^{\bullet}{}_{(g)} + 4\ H^{\bullet}{}_{(g)}$ $\Delta H^0{}_r = +1663\ \text{kJ mol}^{-1}$

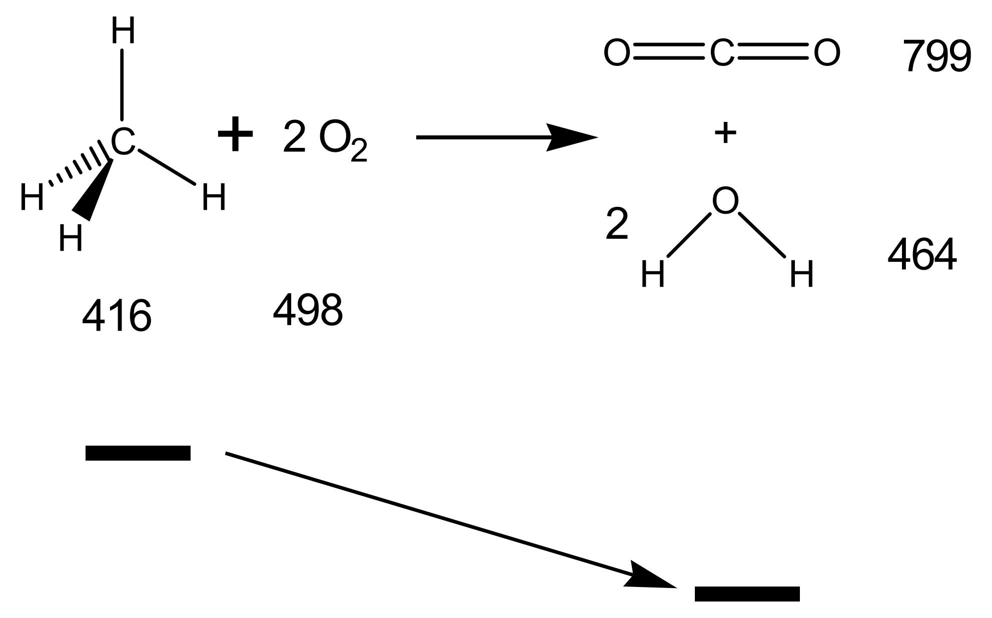
$1663/4 = 416\ \text{kJ mol}^{-1}$

400 kJ mol^{-1}	$HCCl_3$
414 kJ mol^{-1}	H_2CCl_2
422 kJ mol^{-1}	H_3CCl

Average Bond Energy

$CH_{4(g)} + 2\ O_{2(g)} \rightarrow CO_{2(g)} + 2\ H_2O_{(g)}$ $\Delta H^0_r = -790$ kJ mol^{-1}

E(C–H) = 416 kJ mol^{-1}
E(O=O) = 498 kJ mol^{-1}
E(C=O) = 799 kJ mol^{-1}
E(O–H) = 464 kJ mol^{-1}



Heat Balance of Reactions

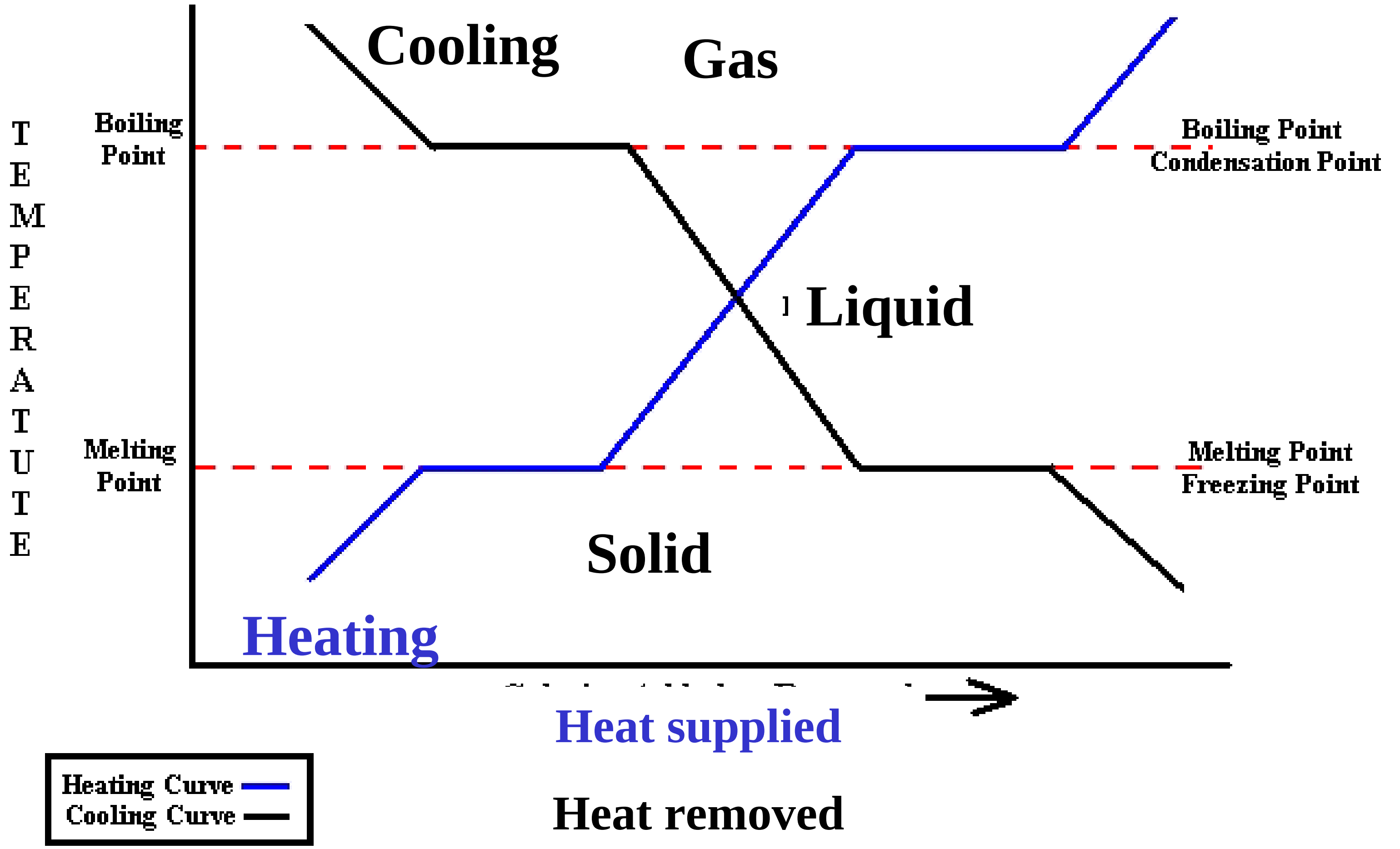
$CH_{4(g)} + 2\ O_{2(g)} \rightarrow CO_{2(g)} + 2\ H_2O_{(g)}$ $\Delta H^0_r = -775\ \text{kJ mol}^{-1}$

ΔH^0_f kJ mol^{-1}

$CH_4(g)$: –102
$O_2(g)$: 0
$CO_2(g)$: –393
$H_2O(g)$: –242

$$\Delta H^0_r = [\ (-\ 393) + 2\ (-\ 242)\ ] - [-\ 102 + 0] = -\ 775\ \text{kJ}$$

Enthalpy at Phase Transitions



Enthalpy at Phase Transitions

Endothermic		Exothermic	
Sublimation	$\Delta H_{subl} > 0$	Depozition	$\Delta H_{dep} < 0$
Evaporation	$\Delta H_{vap} > 0$	Condensation	$\Delta H_{con} < 0$
Melting	$\Delta H_{melt} > 0$	Solidification	$\Delta H_{sol} < 0$

Enthalpy at Phase Transitions