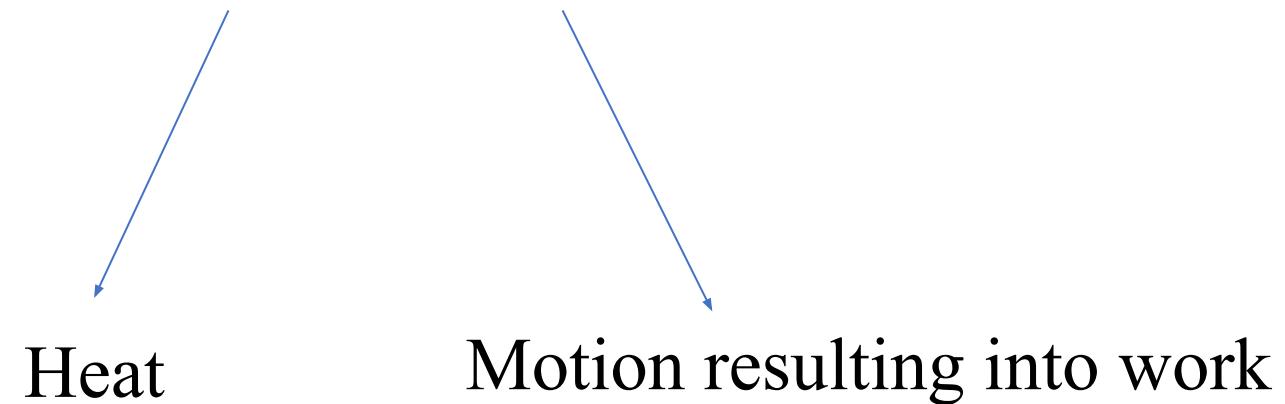


THERMODYNAMICs

Dt. 29-06-2021

Thermo + Dynamics



Thermodynamics deals with the energy changes accompanying all types of physical and chemical Processes

The laws of thermodynamics apply only to matter in bulk (assemblages of a vast number of molecules) and not to individual atoms or molecules

- ❖ Thermodynamics can predict whether a given process including a chemical reaction is feasible under a given set of conditions
- ❖ However, it does not tell anything about the rate at which a given process may proceed
- ❖ For example, thermodynamics predicts that hydrogen and oxygen gases would react to yield liquid water, but it does not tell us whether the reaction will be fast or slow

System and surroundings

System: It may be defined as any specified portion of matter under study which is separated from the rest of the universe with a bounding surface

Surrounding: The rest of the universe which can exchange energy and matter with the system is called the surrounding

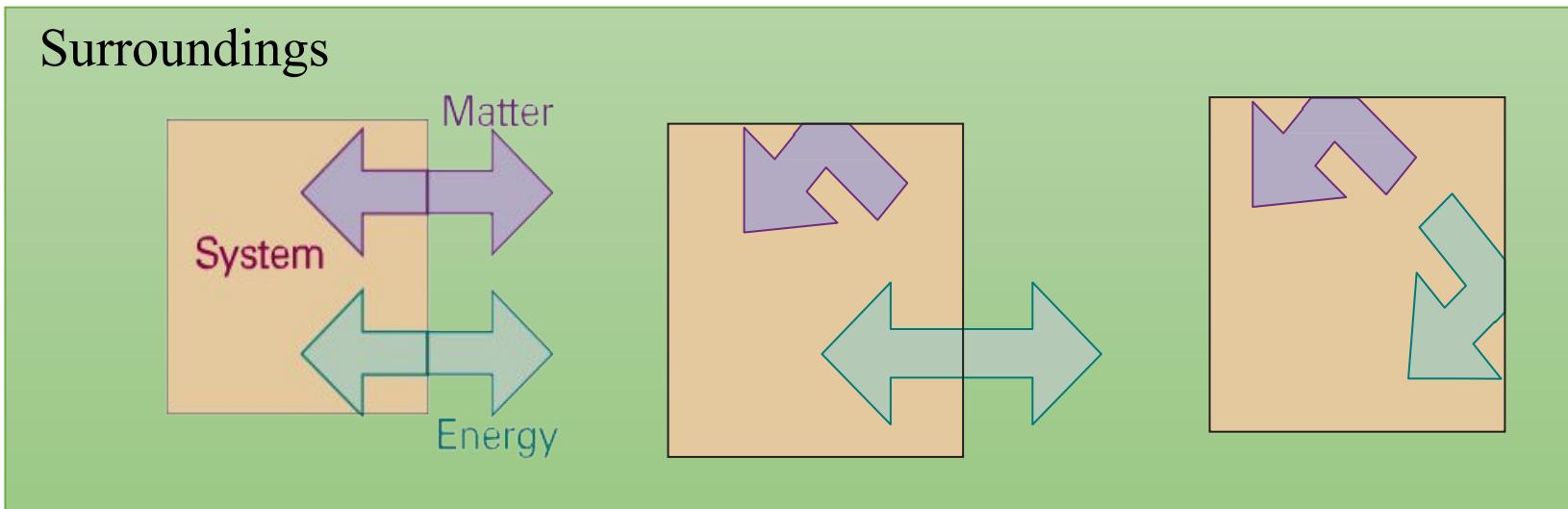
- ❖ **Open system:** A system which can exchange energy as well as matter with its surroundings is called an open system
- ❖ **Closed system:** A system which can exchange energy, but not matter with its surroundings is called a closed system
- ❖ **Isolated system:** A system which can exchange neither energy nor matter with its surroundings is called an isolated system

Different types of systems : Three types

Open

Closed

Isolated



Macroscopic properties: The properties associated with a macroscopic system (consisting of Large number of particles) are called macroscopic properties.

Ex: Pressure, temperature, volume, composition, density, viscosity, surface tension etc.

Extensive properties: Those properties of a system which depends upon the amount of the substance present in the system

Ex: mass, volume, energy, heat capacity

Intensive properties: which are independent of the amount of the substance present in the system

Ex: Pressure, temperature, density, viscosity, surface tension, specific heat etc.

State of a system: When the macroscopic properties of a system have definite values, the system is said to be in a definite state

Whenever there is a change in any one of the macroscopic properties, the system is said to change into a different state.

State variables: As the state of a system changes with change in any of the macroscopic Properties, these properties are called state variables.

Pressure, temperature, volume, mass, composition are important state variables.

THERMODYNAMIC

When we talk about a given system, we say it is in a particular "thermodynamic state."

A particular thermodynamic state is characterized by a few "macroscopic observables," such as

Pressure, temperature, volume, color, altitude, etc.

Differences (Changes) in Macroscopic Observables

Changes in Pressure (P), Volume (V), and Temperature (T):

$$\Delta P = P_f - P_i \quad \Delta V = V_f - V_i \quad \Delta T = T_f - T_i$$

What can we say about all of these?

It doesn't matter how the system arrived at the final state from the initial state, the difference (or change) is the same.

Thermodynamic: State Functions

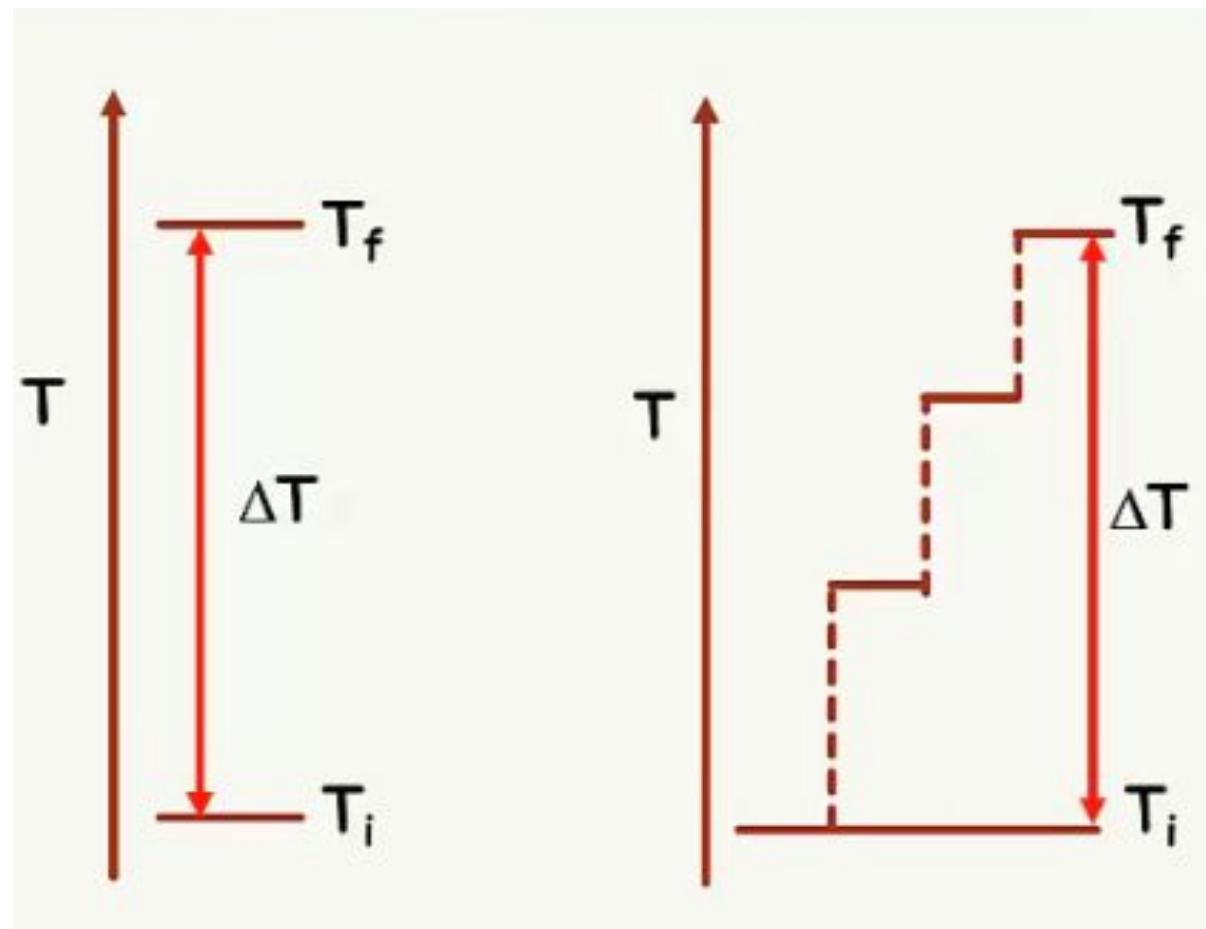
State Functions only depend on the current (thermodynamic) state of the system.

How the system attained that state does not matter!

Example: Compression of a gas inside a piston.



Thermodynamic: State Functions



A State Function is defined as a property of a system that only depends on the initial and final state of the system.

and is independent of the path followed in getting from one to the other.

Examples of State Functions

ΔU is a state function.

Some other state functions...

ΔH (Enthalpy, coming soon...)

ΔP

ΔT

ΔV

Altitude

Mass

chemical composition

Path Functions



A path function does depend on the path followed in getting from the initial to the final state.

Path Functions



Work (w) and heat (q) are path functions.

Two rock climbers of equal mass scale the same cliff. One climbs straight up while the other backslides numerous times on the way up...

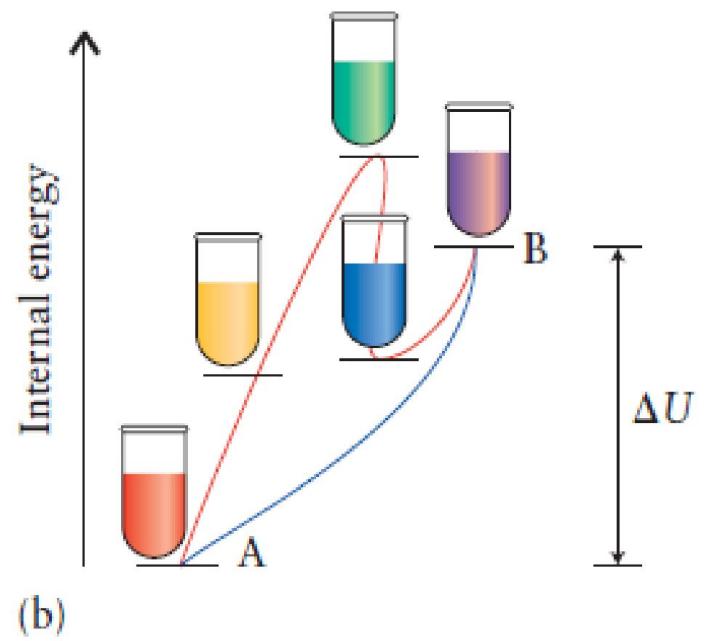
who did more work?

State function Summary

- The value of state function depends on the initial and final state
- Path independent
- It must be exact differential
- Their cyclic integral is zero

• State function (Z) Summary

- Their cyclic integral is zero
- $Z = P, T, V, U, H, G, A$ etc.
- $Z \neq q$ or w (*path dependent*)
- $\oint dZ = 0$ for example,
- $\oint dU = 0$ $\oint dH = 0$, $\oint dG = 0$
- $\oint dq \neq 0$, $\oint dw \neq 0$



Internal Energy (U)

- State function
- Extensive property
- The value of internal energy of a system depends on the nature of the existence of a system
- In general,
 - if work is done on the system, the internal energy of the system increases
 - If work is done by the system the internal energy of the system decreases

Thermodynamic Function: Internal Energy (U)

temperature

a measure of the average kinetic energy of the particles in a system



This kinetic energy is distributed among



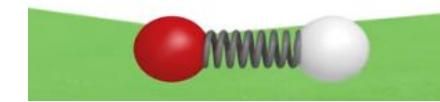
translational motion



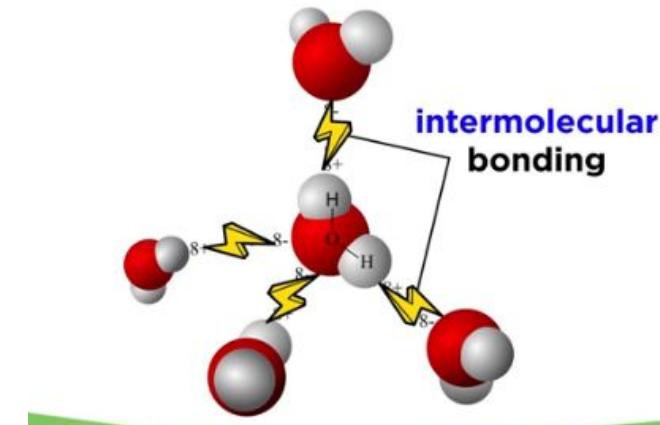
rotational motion



vibrational motion



molecular potential energy



Internal Energy (U)

the sum of all the molecular **kinetic** energies

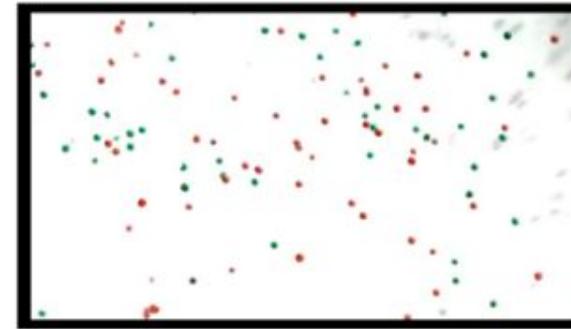
+

the sum of all the molecular **potential** energies

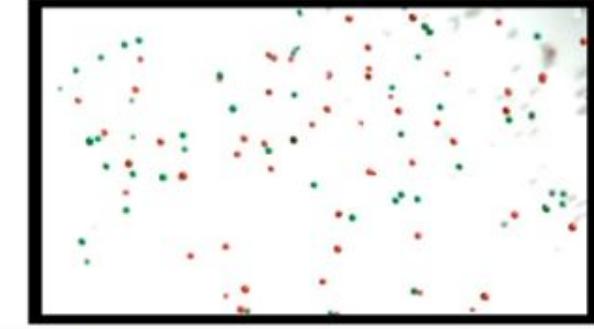
=

internal energy (U)

Energy associated with the atomic motions



higher temperature
more internal energy

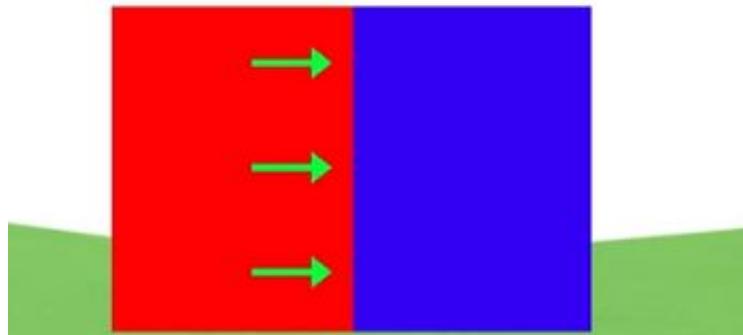


lower temperature
less internal energy

Internal Energy (U)

substances do not
contain heat

heat is a transfer of
internal energy



Thermodynamics

the study of
heat and temperature
and their relation to
energy and work

Internal Energy (U)

**internal energy can
increase due to:**

heat transfer



friction



structural deformation



Internal Energy (U)

**energy is always
conserved**

$$\Delta\text{PE} + \Delta\text{KE} + \Delta\text{U} = 0$$



if any of these quantities
changes then some energy
has been **transferred** from
one form to another

Example

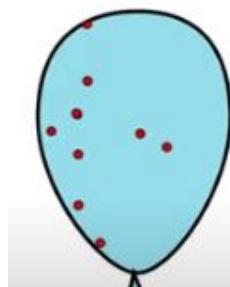
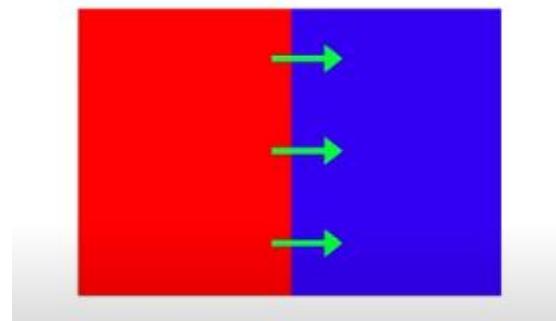
$$\Delta\text{PE} + \Delta\text{KE} + \Delta\text{U} = 0$$



inelastic collision
(kinetic energy is lost)

Internal Energy (U)

**internal energy
can do work**



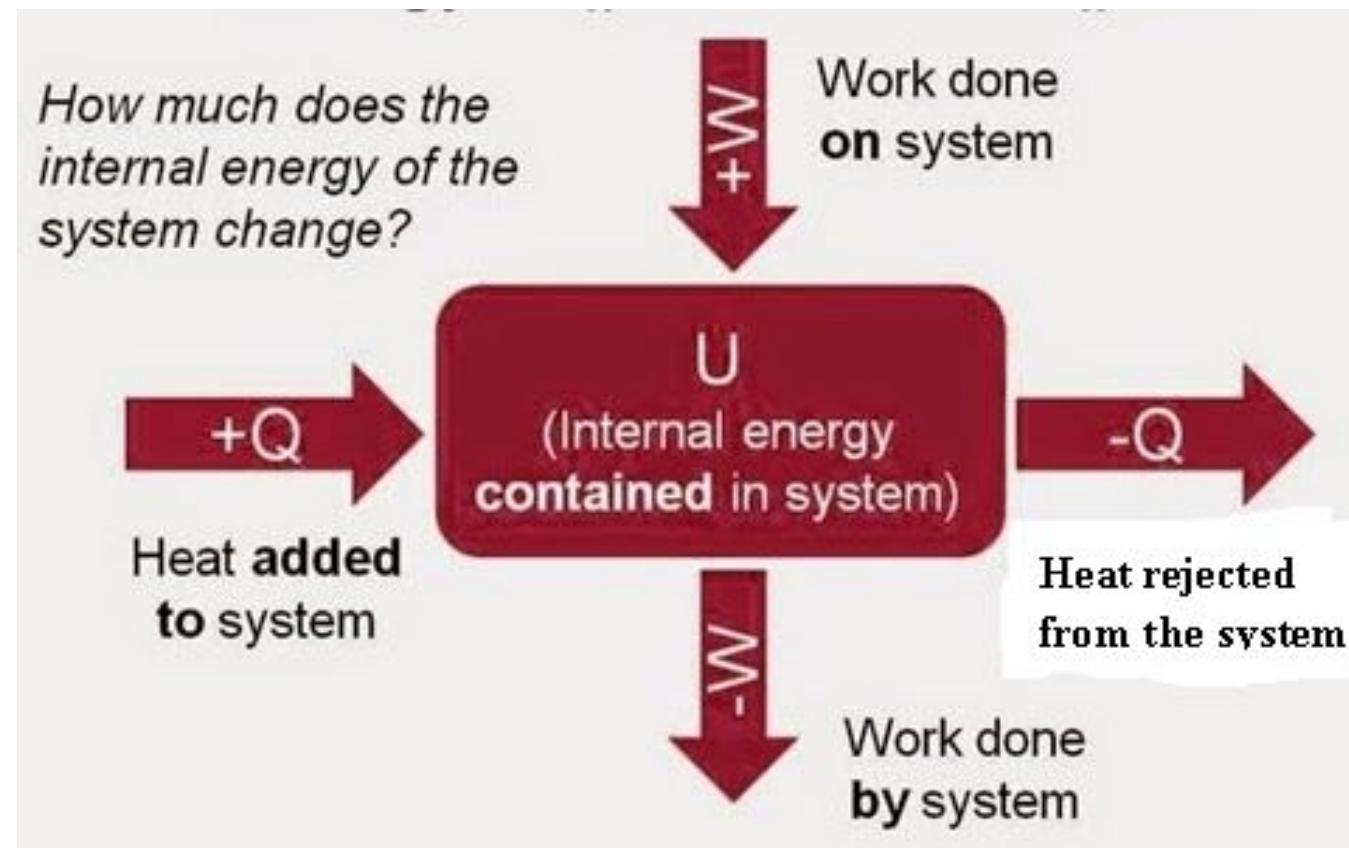
**internal energy
is a state function**

**it depends only
on the state of
the system and not
how it got there**

P and V works for expanding gas

Internal Energy (U)

Sign convention



Enthalpy (H)

When a reaction occurs under constant pressure (which is the usual situation), the energy changes in the reaction are described using Enthalpy (H) instead of the Internal Energy (U).

Enthalpy (H) is the sum of the Internal Energy (U) plus a PV term. The equation used in chemistry is

$$\Delta H_{rxn} = \Delta U_{rxn} + P\Delta V_{rxn}$$

Change in internal
energy of the
system (reaction)

Pressure-volume
work

Difference between Enthalpy and Internal Energies

The big difference between ΔH and ΔU is the little bit of PV work that the reaction does to expand against atmospheric pressure.

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

Enthalpy is a state function.

Constant P and Constant V

ΔH is the heat (of reaction) under constant pressure conditions.
(This means the volume can change).

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

$$\Delta H = q_p$$

$$\Delta H = nC_p dT,$$

$$\Delta U = nC_v dT$$

ΔU is the heat under constant volume conditions. The volume can't change, so no PV work is done during the reaction. ($\Delta V = 0$)

$$\begin{aligned}\Delta H &= \Delta U + P\Delta V \\ &= \Delta U + P(0) = \Delta U\end{aligned}$$

$$\Delta U = q_v$$

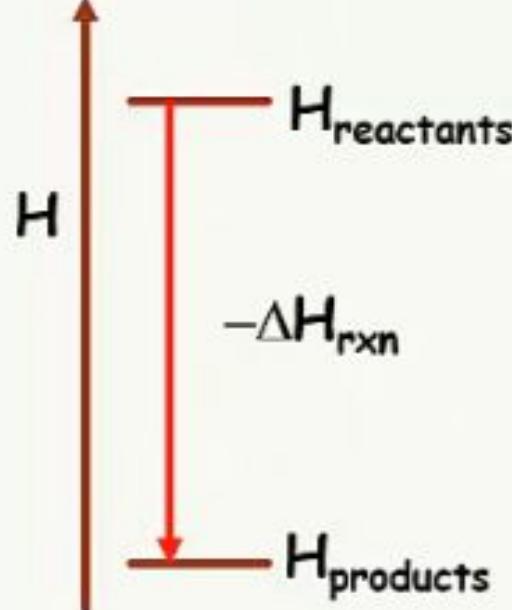
Thermochemistry and Enthalpy

Thermochemistry is the study of heat (q) given off or absorbed during the course of a chemical reaction.

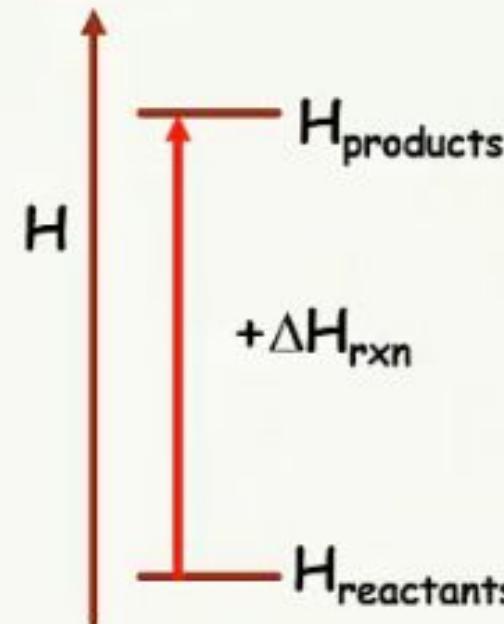
Under constant pressure (the usual situation in a lab)...

$$\Delta H_{rxn} = \Delta U_{rxn} + P\Delta V_{rxn} = q_p$$

Enthalpy of the Reactions (ΔH_{rxn})



When ΔH_{rxn} is negative, heat is released in the reaction.
This is an exothermic reaction.

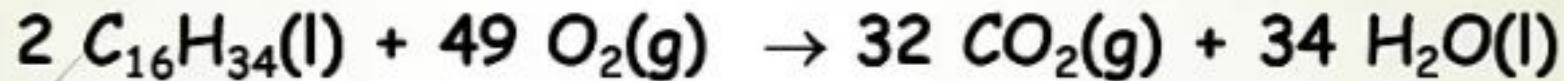


When ΔH_{rxn} is positive, heat is absorbed in the reaction.
This is an endothermic reaction.

Comprehensive

Is the Reaction
Exothermic or Endothermic?

Is this reaction endo or exothermic?



What type of reaction is it? **A combustion reaction!**

$$\Delta H_{\text{rxn}} = -10700 \text{ kJ/mol}$$

Endo or exothermic?

Combustion Reactions are Exothermic Reactions



First law of thermodynamics

- Law of conservation of energy
- Energy can neither be created nor be destroyed, it can only be transferred from one form to another

$$\Delta U = q + w \text{ (mathematical form) } (\textbf{if work is done on the system})$$

↑ ↑
heat work

Initial internal energy = U_A

If the heat absorbed by the system is q ,

And work done by the system is W ,

then final internal energy, $U_B = U_A + q - W$

Change in internal energy,

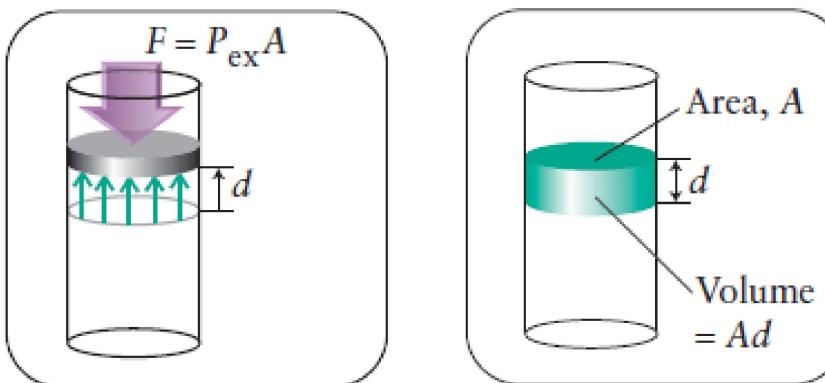
$$\Delta U = U_B - U_A = (U_A + q - W) - U_A$$

or, $\Delta U = q - W \text{ (if work is done by the system)}$

Work done:

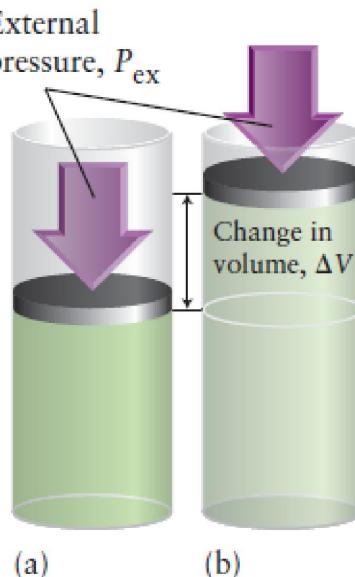
Work = opposing force \times distance moved

$$\text{Work} = P_{\text{ex}}A \times d$$



$$w = -P_{\text{ex}}\Delta V$$

From the sign convention,



Work

- Unit conversions

$$1 \text{ Pa}\cdot\text{m}^3 = 1 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-2} \times 1 \text{ m}^3 = 1 \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-2} = 1 \text{ J}$$

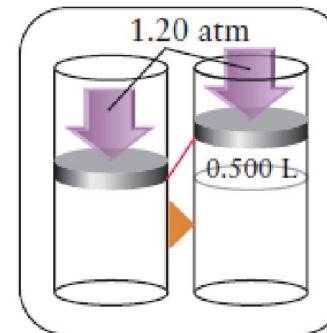
$$1 \text{ L}\cdot\text{atm} = 10^{-3} \text{ m}^3 \times 101\,325 \text{ Pa} = 101.325 \text{ Pa}\cdot\text{m}^3 = 101.325 \text{ J} \text{ (exactly)}$$

EXAMPLE 1 Calculating the work done when a gas expands

- Suppose a gas expands by 500. mL (0.500 L) against a pressure of 1.20 atm and no heat is exchanged with the surroundings during the expansion. (a) How much work is done in the expansion? (b) What is the change in internal energy of the system?

(a) From $w = -P_{\text{ex}}\Delta V$,

$$w = -(1.20 \text{ atm}) \times (0.500 \text{ L}) = -0.600 \text{ L}\cdot\text{atm}$$

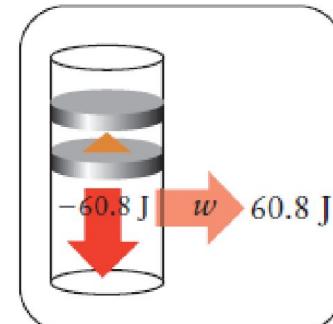


Convert into joules by using $1 \text{ L}\cdot\text{atm} = 101.325 \text{ J}$.

$$w = -(0.600 \text{ L}\cdot\text{atm}) \times \frac{101.325 \text{ J}}{1 \text{ L}\cdot\text{atm}} = -60.8 \text{ J}$$

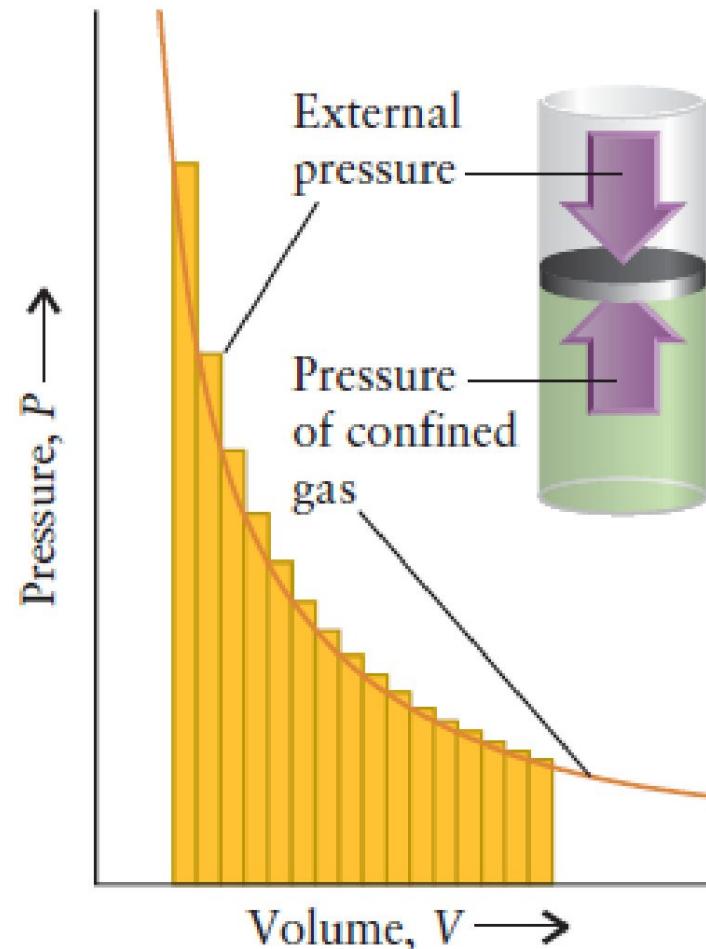
(b) Because no energy is transferred as heat, $w = \Delta U$.

$$\Delta U = -60.8 \text{ J}$$



Expansion against changing external pressure

- Reversible process
(infinitesimal change in external pressure)
- Irreversible process
(finite change or measurable change)



Work done for reversible isothermal expansion of a gas

Work done for a small change in volume

$$dw = -P_{ext} dV$$

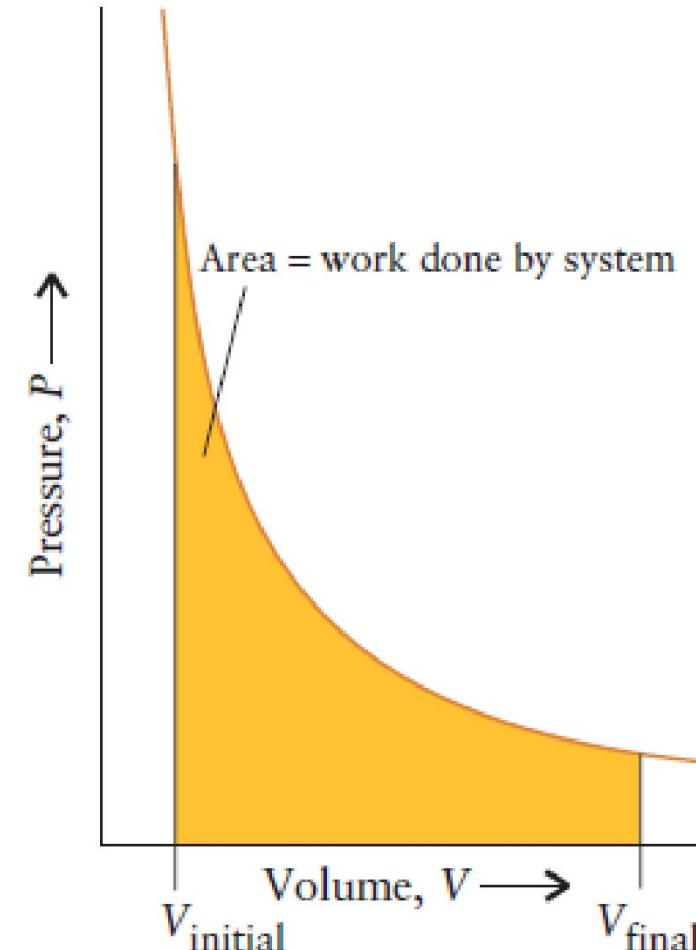
$$dw = -P dV$$

For the ideal gas case $P = \frac{nRT}{V}$

$$dw = -\frac{nRT}{V} dV$$

$$\text{Total work done} = -nRT \int_{V_{initial}}^{V_{final}} \frac{1}{V} dV$$

$$= -nRT \ln \frac{V_{final}}{V_{initial}}$$



Enthalpy

The state function that allows us to keep track of energy changes at constant pressure is called the enthalpy, H

$$H = U + PV$$

$$dH = dU + d(PV)$$

at constant
pressure

at constant
volume

$$dH = dU + PdV$$

$$= dq_P$$

$$dH = dU + VdP$$

Change in Enthalpy

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + \Delta(nRT)$$

For a reaction at constant temperature

$$\Delta H = \Delta U + \Delta n(RT)$$

(Or)

$$\Delta H = \Delta U + \Delta n_g(RT)$$

For a reaction at const.
T and fixed no. of moles

$$\Delta n(RT) = 0$$

$$\Delta H = \Delta U = 0$$

Hess's Law of constant heat summation

The energy changes accompanying chemical processes are governed by a general principle, known as Hess's law.

- ❖ According to this law, the amount of heat evolved or absorbed in a process including a chemical change, is the same whether the process takes place in one or several steps

Process-1: Suppose a system changes from state A to state B in one step and the heat exchanged is q .

Process-2: Now the same system changes from state A to state B in three steps involving a change from state A to state C, from C to D and then D to B. If q_1 , q_2 and q_3 are the heats exchanged in the 1st, 2nd and 3rd step, respectively, then according to Hess's law:

$$q = q_1 + q_2 + q_3$$

This implies that the enthalpy of reaction depends only on the initial reactants and final products and **independent of the path** in which the change is brought about

Application of Hess's Law

1. Calculation of enthalpies of reactions:

Hess's law is useful to calculate the enthalpies of many reactions which can not be determined Experimentally.

Ex: It is difficult to measure the heat evolved when carbon burns in oxygen to form CO



However, it can be determined if the heat evolved in the combustion of one mole of carbon to form CO_2 and the conversion from CO to CO_2 are known



Or,



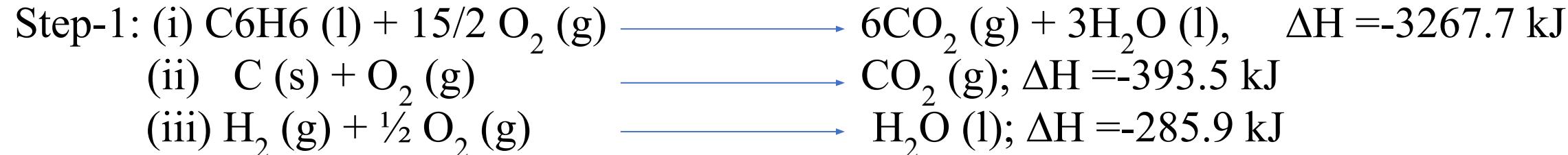
According to Hess's law: $x + (-282) = -395.5$ or $x = -395.5 + 282 = -111.5 \text{ kJ}$

Thus, ΔH for the combustion of C to form CO is -111.5 kJ .

2. Calculation of enthalpies of formation:

Hess's law is useful to calculate the enthalpies of formation of compounds when it is not possible to determine Experimentally.

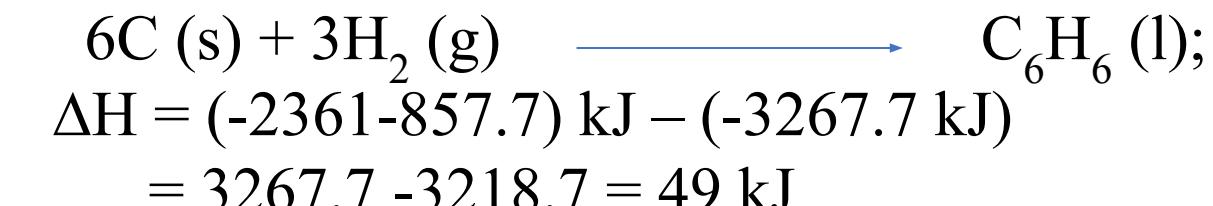
Ex: It is impossible to determine experimentally the enthalpy of formation of benzene from its Elements. However, it can be calculated from the enthalpy of combustion of benzene and the Enthalpy of formation of water and CO₂.



Step-2: Multiply eq. (ii) by 6 and eq. (iii) by 3



Adding (iv) and (v) and then subtracting (i), we get



Thus, ΔH for the formation of benzene is 49 kJ.

Entropy (S)

- Entropy = Disorderness
- Measure of the disorder of a system
- Entropy comes from the **second law of thermodynamics**, which states that all systems tend to reach a state of equilibrium.

The significance of entropy is that when a spontaneous change occurs in a system, it is found that the total entropy change for everything involved is a positive value.

$$\Delta S = S_{\text{final}} - S_{\text{initial}} \text{ or } \Delta S = S_{\text{(products)}} - S_{\text{(reactants)}}$$

ΔS is change in entropy

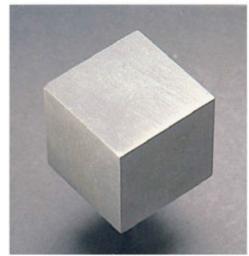
S_{final} and S_{initial} are the final and initial entropies, respectively

Entropy (S)

- Entropy is a thermodynamic property, it is the measure of energy not used to perform work but is dependent on temperature as well as volume.
- Entropy is directly proportional to spontaneity.
- Comparison of entropies: **Gases > liquids > solids** (bromine gas has greater entropy than when in liquid state)
- Entropy is greater for larger atoms (as we move down in groups in periodic table) and molecules with larger number of atoms.
- Entropy is a measure of the number of ways particles as well as energy can be arranged.
- More configurations (different geometries), more will be the entropy.
- Entropy of an irreversible system always increases.

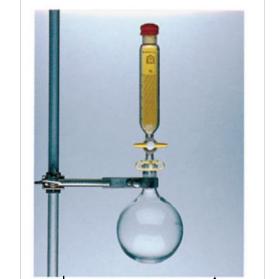


Spontaneous ↓ Not Spontaneous ↑

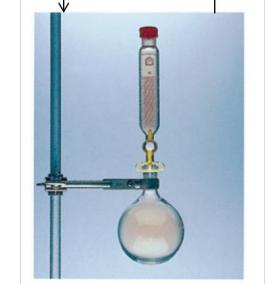


Entropy and Disorder

- In the language of thermodynamics, this simple idea is expressed as the **entropy**, **S**, a measure of disorder.



Spontaneous ↓ Not Spontaneous ↑



- Low entropy means little disorder; high entropy means great disorder.

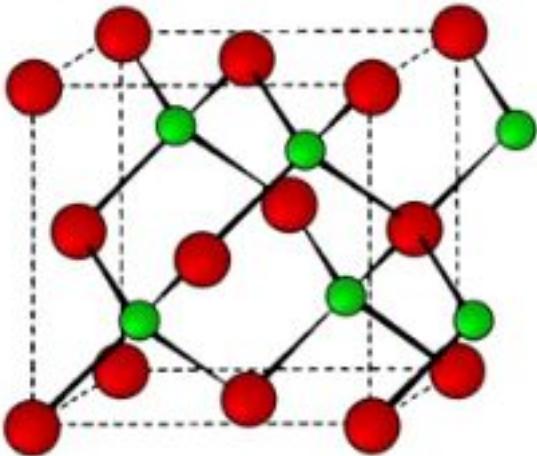
- "The entropy of an isolated system increases in the course of any spontaneous change"-*

The second law of thermodynamics

Entropy Example

- Geometry of the lattice
- Intermolecular distance
- The precise configuration of the every molecules
- And many other parameters

lower entropy



```

SKNode* _sizes;
BOOL _canRestart;
SKLabelNode* _scoreLabelNode;
NSInteger _score;
}

@implementation Lattice

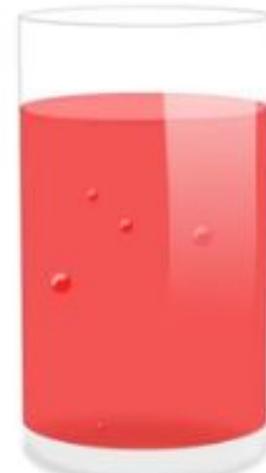
static const uint32_t solidCategory = 1 << 0;
static const uint32_t worldCategory = 1 << 1;
static const uint32_t sizeCategory = 1 << 2;
static const uint32_t scoreCategory = 1 << 3;

static NSInteger const kVerticalSizeGap = 100;

-(id)initWithSize:(CGSize)size {
    if (self = [super initWithSize:size]) {
        _movingMolecule = [SKNode node];
        _canRestart = NO;
    }
    return self;
}

```

greater entropy



```

SKNode* vesselSize = [SKNode node];
vesselSize.position = CGPointMake(
self.frame.size.width + _sizeLocation1.size.width,
0 );
vesselSize.zPosition = -10;

CGFloat y = arc4random() % (NSInteger)(self.frame.size.height / 3 );

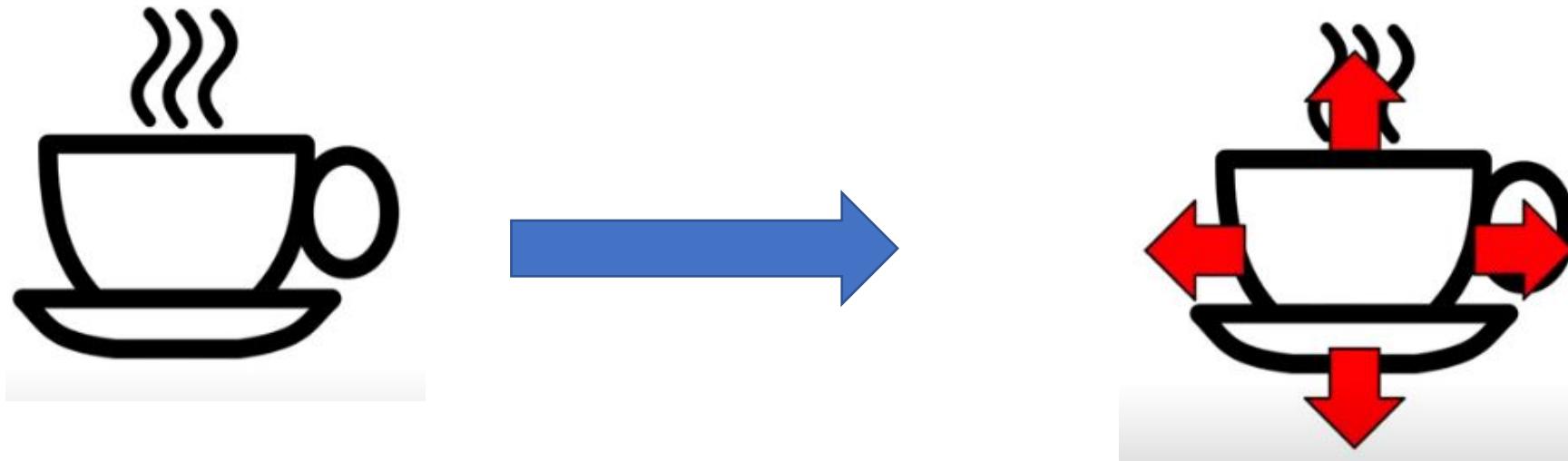
SKVolumeNode* size1 = [SKVolumeNode
VolumeNodeWithLocation:_sizeLocation1];
[size1 setScale:2];
size1.position = CGPointMake( 0, y );
size1.physicsBody = [SKPhysicsBody
bodyWithRectangleOfSize:size1.size];
size1.physicsBody.dynamic = NO;
size1.physicsBody.categoryBitMask =
sizeCategory;
size1.physicsBody.contactTestBitMask =
liquidCategory;

```

- The volume of the liquid
- Shape of the vessel

less information to encode
more thermodynamically favorable

Entropy Example



**The heat energy will be more disorder if more dispersed
this is why heat spontaneously flow from hot to cold**

Entropy (S)

$$\Delta S_{\text{univ}} > 0 \quad (\text{Universe} = \text{system} + \text{surrounding})$$

for any spontaneous process

**an increase in entropy
corresponds with a greater
dispersal of matter/energy**

Entropy

- Thermodynamic definition of entropy

$$dS = \frac{dq_{rev}}{T}$$

$$\Delta S = \int_i^f \frac{dq_{rev}}{T}$$

For isothermal expansion of an ideal gas

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} = \frac{q_{rev}}{T}$$

Measuring Change in Entropy

For **isothermal expansion** of an ideal gas

$$\Delta U = q + w$$

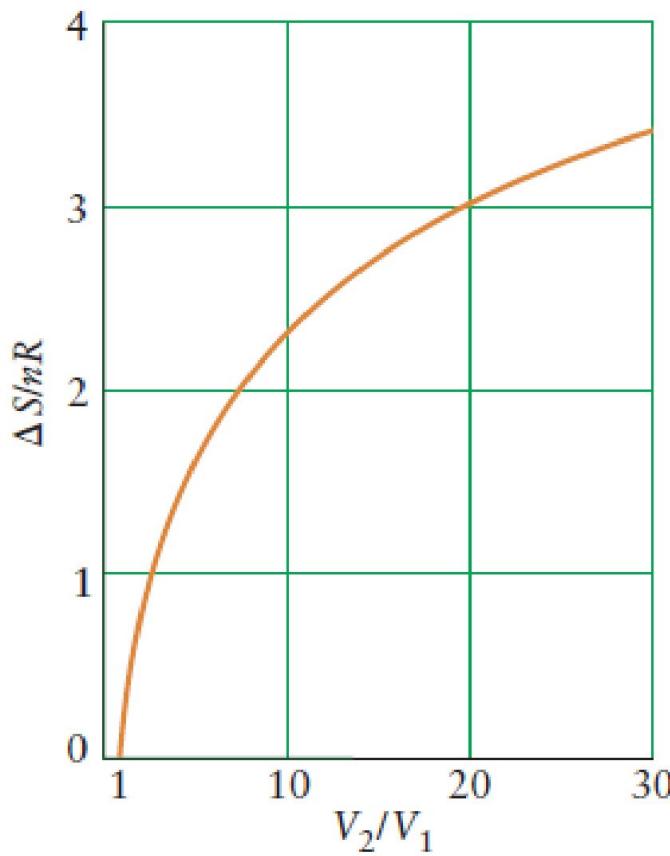
$$\text{or, } 0 = q + w \quad \text{as } \Delta U = 0$$

$$\text{or, } q = -w$$

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} = \frac{q_{rev}}{T}$$

$$q_{rev} = -w_{rev} = nRT \ln \frac{V_f}{V_i}$$

$$\Delta S = \frac{q_{rev}}{T} = nR \ln \frac{V_f}{V_i}$$



Entropy change of an ideal gas

Case-1: When T and V are two variables

From 1st law of thermodynamics,

$$\Delta U = q + w$$

$$\text{or, } dq_{\text{rev}} = dU - dw$$

$$= C_v dT + P dV$$

$$= C_v dT + RT (dV/V)$$

$$\text{or, } dq_{\text{rev}}/T = dS = C_v (dT/T) + R (dV/V)$$

For a finite change of state of a system, the entropy change

$$\Delta S = C_v \int_{T_1}^{T_2} dT/T + R \int_{V_1}^{V_2} dV/V$$

$$\text{or, } \Delta S = C_v \ln(T_2/T_1) + R \ln(V_2/V_1)$$

$$\text{For } n \text{ moles, } \Delta S = nC_v \ln(T_2/T_1) + nR \ln(V_2/V_1)$$

In an isochoric process, volume of gas remains constant, i.e., $V_1 = V_2$

$$\text{Hence, entropy change } \Delta S_v = nC_v \ln(T_2/T_1)$$

Case-2: When T and p are two variables

$$\Delta S = C_v \ln(T_2/T_1) + R \ln(V_2/V_1)$$

$$= C_v \ln(T_2/T_1) + R \ln [(T_2/T_1)/(P_2/P_1)] \quad (\text{as } P_2 V_2 / P_1 V_1 = T_2/T_1)$$

$$= C_v \ln(T_2/T_1) + R \ln(T_2/T_1) - R \ln(P_2/P_1)$$

$$= (C_v + R) \ln(T_2/T_1) - R \ln(P_2/P_1)$$

$$= C_p \ln(T_2/T_1) - R \ln(P_2/P_1)$$

For n moles of an ideal gas,

$$\Delta S = nC_p \ln(T_2/T_1) - nR \ln(P_2/P_1)$$

In an isobaric process, the pressure remains constant, i.e., P₁=P₂

Hence, $\Delta S_p = nC_p \ln(T_2/T_1)$

Ex: One mole of an ideal mono-atomic gas expands reversibly from a volume of 10 dm³ and temperature 298 K to a volume of 20 dm³ and temperature 250 K. Assuming that C_v = 3/2 R, calculate the entropy change for the process.

Ans: Given that T₁ = 298 K, V₁ = 10 dm³
T₂ = 250 K, V₂ = 20 dm³

We know that $\Delta S = C_v \ln(T_2/T_1) + R \ln(V_2/V_1)$

$$\begin{aligned} &= (3/2) \times 8.314 \ln(250/298) + 8.314 \ln(20/10) \\ &= (-2.19 + 5.76) \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 3.57 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$