## General Physics I

Mechanics, optics, thermal dynamics, and other basic fundamental things.

Timy Che Liu

Lecture VII : measurement Gay-Lussac's law The pressure of a gas of fixed mass and fixed volume is directly proportional to the gas's absolute temperature.

$$
\frac{T}{p}=C \quad \frac{T_{\text {triple }}}{p_{\text {triple }}}=C \quad 1778-1850 \quad \text { Triple point of water }
$$

## Lecture VII : Absolute zero

$$
\frac{273.16 K}{p_{\text {triple }}}=C
$$

Limit to the "degree of cold"
In the SI system, temperature is measured on the Kelvin scale, which is based on the triple point of water (273.16 K). $\frac{T}{p}=C=\frac{273.16 \mathrm{~K}}{p_{\text {riviple }}}$

$$
T=273.16 K\left(\frac{P_{M}}{P_{\text {triple }}}\right)
$$



## Lecture VII : Kelvin scale

## Unit: kelvins

## - K K



## Lecture VII : scale

Temperature is a physical property of matter that quantitatively expresses hot and cold

Celsius \& Fahrenheit

$$
C^{o}=\frac{9}{5} F^{o}+32
$$



## Lecture VII : scale

Temperature${ }^{O} C$${ }^{\circ}{ }^{F}$
Boiling point od water 100 ..... 212Human body37

$$
98.6
$$

Freezing point of water ..... 0 ..... 32
Scales coincide ..... -40

-40

## Lecture VII : measurement

The Constant-Volume Gas Thermometer The temperature of any body in thermal contact with the bulb is then defined to be

$$
T=C p \quad p=p_{0}-\rho g h
$$




## Lecture VII : Zeroth law of thermodynamics

If bodies A and B are each in thermal equilibrium with a temperature T , then A and B are in thermal equilibrium with each other.


## Lecture VII :



## Lecture VII : Thermal expansion



## Lecture VII : Thermal expansion


$\alpha$ coefficient of linear expansion

$$
\begin{aligned}
& A=\left(L_{0}+L_{0} \alpha \Delta T\right)^{2} \\
& A=L_{0}^{2}(1+\alpha \Delta T)^{2} \sim A(1+2 \alpha \Delta T)
\end{aligned}
$$

$$
\beta \equiv 2 \alpha
$$

coefficient of area expansion

## Lecture VII : Thermal expansion

 coefficient of volume expansion$$
\Delta V=\left(L_{0}+L_{0} \alpha \Delta T\right)^{3}
$$

$$
\Delta V=L_{0}^{3}(1+\alpha \Delta T)^{3} \sim V_{0}(1+3 \alpha \Delta T)
$$

$$
\gamma \equiv 3 \alpha
$$

coefficient of volume expansion

## Lecture VII : Thermal expansion



| Substance | $\alpha\left(10^{-6} / \mathrm{C}^{\circ}\right)$ |
| :--- | :---: |
| Ice $\left(\right.$ at $\left.0^{\circ} \mathrm{C}\right)$ | 51 |
| Lead | 29 |
| Aluminum | 23 |
| Brass | 19 |
| Copper | 17 |
| Concrete | 12 |
| Steel | $11-13$ |
| Glass (ordinary) | 9 |
| Glass (Pyrex) | 3.2 |
| Diamond | 1.2 |
| Invar | 0.7 |
| Fused quartz | 0.5 |

## Lecture VII : Example

I have a $10 \mathrm{~cm}^{3}$ steel box that is measured by a steel ruler at room temperature $\left(40^{\circ} \mathrm{C}\right)$ in Taiwan.

1. What is the volume of the same box that measured by the same ruler in Antarctica (233.16 K)?
2. What is volume change when the box moves to Antarctica from Taiwan?


## Lecture VII : Temperature \& heat (Q)

Heat is the energy transferred between two systems because of a temperature difference that exists between them.

$$
T_{A}>T_{B}
$$



The transferred energy is called heat and is symbolized Q

## Lecture VII : Units of heat (Q)

Before scientists realized that heat is transferred energy, heat was measured in terms of its ability to raise the temperature of water. Thus, the calorie (cal) was defined as the amount of heat that would raise the temperature of 1 g of water from 14.5C to 15.5C. In the British system, the corresponding unit of heat was the British thermal unit (Btu), defined as the amount of heat that would raise the temperature of 1 lb of water from 63 F to 64 F . In 1948, the scientific community decided that since heat (like work) is transferred energy, the SI unit for heat should be the one we use for energy - namely, the joule. The calorie is now defined to be 4.1868 J (exactly), with no refer- ence to the heating of water. (The "calorie" used in nutrition, sometimes called the Calorie (Cal), is really a kilocalorie.) The relations among the various heat units are

$$
1 \mathrm{cal}=10^{-3} \mathrm{Cal}=3.968 \times 10^{-3} \mathrm{Btu}=4.178 \mathrm{~J}
$$

## Lecture VII : Specific heat (c)



The transferred energy is called heat and is symbolized Q

$$
Q=\mathrm{c} m \Delta T=\mathrm{C} \Delta T
$$

C : "heat capacity per unit mass" or specific heat Ci: heat capacity

Molar Specific
Specific Heat Heat

$$
1 \mathrm{~mol}=6.02 \times 10^{23} \text { elementary unit }
$$

## "heat capacity of per molar material" or Molar specific heat

Avogadro's Number: $N_{A}=6.02 * 10^{23} \mathrm{~mol}^{-1}$
One mole is the number of atoms in a 12 g sample of carbon-12.

## Lecture VII : Phase Transition

|  | Solid | Liquid | Gas | Plasma |
| :---: | :---: | :---: | :---: | :---: |
| Solid |  | Melting |  |  |
| Liquid | Freezing |  | Vaporization |  |
| Gas | Deposition | Condensation |  | Ionization |
| Plasma |  |  | Recombination |  |



## Lecture VII : Phase Transformation

The amount of energy per unit mass that must be transferred as heat when a sample completely undergoes a phase change is called the heat of transformation L.

$$
Q=L m
$$

When the phase change is from liquid to gas (then the sample must absorb heat) or from gas to liquid (then the sample must release heat), the heat of transformation is called the heat of vaporization. $L_{V}=539 \mathrm{cal} / \mathrm{g}=40.7 \mathrm{~kJ} / \mathrm{mol}$

When the phase change is from solid to liquid (then the sample must absorb heat) or from liquid to solid (then the sample must release heat), the heat of transformation is called the heat of fusion.

$$
L_{F}=79.5 \mathrm{cal} / \mathrm{g}=6.01 \mathrm{~kJ} / \mathrm{mol}
$$

## Lecture VII : The First Law of Thermodynamics

The internal energy $E_{i n t}$ of a system tends to increase if energy is added as heat $Q$ and tends to decrease if energy is lost as work W done by the system.

$$
d E_{i n t}=d Q-d W
$$


change of the total energy


The work done by system
The heat flow into system

## Lecture VII : Start from a Gas System



## Lecture VII : Start from a Gas System



## Lecture VII : Start from a Gas System

$$
\begin{aligned}
& W_{p=\text { constant }}>W_{2}>0 \\
& W_{\Delta V=0}=0 \\
& W_{3}<0
\end{aligned}
$$

Lecture VII : Cycle $\quad W=\int_{V_{i}}^{V_{f}} p d V$


## Lecture VII : The First Law of Thermodynamics

 Special process: Adiabatic processes dQ=0 絕熱
## $\Delta E_{\text {int }}=Q-W$

change of the total energy


## Lecture VII : The First Law of Thermodynamics

 Special process: constant-volume processes dV=0 定容
## $\Delta E_{\text {int }}=Q-W$ <br> The work done by system $p^{*} d V=p^{*} 0$ <br> The heat flow into system

change of the total energy


## Lecture VII : The First Law of Thermodynamics

Cyclical process: dE=0

## $\Delta E_{\text {int }}=Q-W$ <br> The work done by system <br> The heat flow into system

change of the total energy $=0$

$$
Q=W
$$

There are processes in which, after certain interchanges of heat and work, the system is restored to its initial state. In that case, no intrinsic property of the system-including its internal energy-can possibly change.

## Lecture VII : The First Law of Thermodynamics

Free expansion: Q=0, W=0

## $\Delta E_{i n t}=Q-W$ <br> The heat flow into system $=0$

change of the total energy=0


These are adiabatic processes in which no transfer of heat occurs between the system and its environment and no work is done on or by the system. Thus, $\mathrm{Q}=\mathrm{W}=0$

## Lecture VII : Four Special Processes

$$
\text { The Law: } \Delta E_{\mathrm{int}}=Q-W \text { (Eq. 18-26) }
$$

Process
Adiabatic
Constant volume
Closed cycle
Free expansion

Restriction

$$
\begin{array}{cl}
\text { Restriction } & \text { Consequence } \\
Q=0 & \Delta E_{\text {int }}=-W \\
W=0 & \Delta E_{\text {int }}=Q \\
\Delta E_{\text {int }}=0 & Q=W \\
Q=W=0 & \Delta E_{\text {int }}=0
\end{array}
$$

## Lecture VII : Heat transfer



$$
Q=k \frac{\left(T_{H}-T_{C}\right) A}{L} \times t
$$

Conduction rate $P_{\text {cond }}=\frac{Q}{t}$
thermal conductivity $k$

## Lecture VII : Heat transfer

Conduction

Convetion

Radiation

## Lecture VII : Conduction

Substance $\quad k(\mathrm{~W} / \mathrm{m} \cdot \mathrm{K})$

## Metals

Stainless steel 14
Lead 35
Iron 67
Brass 109
Aluminum 235
Copper 401
Silver 428
Gases
Air (dry) 0.026
Helium 0.15
Hydrogen 0.18
Building Materials
Polyurethane foam 0.024
Rock wool 0.043
Fiberglass 0.048
White pine $\quad 0.11$
Window glass $\quad 1.0$

## Lecture VII : Thermal Resistance to Conduction (R-Value)

Conduction rate $P_{\text {cond }}=\frac{Q}{t}=\frac{k}{L} A \Delta T$

$$
R \equiv \frac{L}{k}
$$



Something that has a high R -value is a poor thermal conductor and thus a good thermal insulator.

Lecture VII : Conduction Through a Composite Slab

$$
\begin{gathered}
P_{\text {cond }}=\frac{Q}{t}=\frac{k}{L} A \Delta T \\
P=\frac{k_{2}}{L_{2}} A\left(T_{H}-T_{X}\right)=\frac{k_{1}}{L_{1}} A\left(T_{X}-T_{C}\right) \\
T_{X}=\frac{k_{2} L_{1} T_{H}+k_{1} L_{2} T_{c}}{\left(k_{1} L_{2}+k_{2} L_{1}\right)} \\
P=\frac{A\left(T_{H}-T_{c}\right)}{\left(L_{1} / k_{1}+L_{2} / k_{2}\right)}
\end{gathered}
$$

## Lecture VII : Radiation

$$
P_{\mathrm{rad}}=\sigma \epsilon A T^{4}
$$


$\sigma=5.6704 \times 10^{8} \mathrm{~W} / \mathrm{m}^{2} \mathrm{~K}^{4}$ is called the Stefan-Boltzmann constant
$\epsilon$ represents the emissivity of the object's surface, which has a value between 0 and 1 , depending on the composition of the surface.

## Lecture VII : Kinetic theory of gases

Mole One mole is the number of atoms in a 12 g sample of carbon- 12 .
The number of moles $n, \quad n=\frac{N}{N_{A}}=\frac{M_{\text {sum }}}{M}=\frac{M_{\text {sum }}}{m N_{A}}$
molar mass $M$ (the mass of 1 mol )
molecular mass $m$ (the mass of one molecule):

## Lecture VII : Ideal gas

Our goal in this chapter is to explain the macroscopic properties of a gas such as its pressure and its temperature
$p V=R n T$
$R=8.31 \mathrm{~J} /(\mathrm{mol} \cdot K) \quad \begin{aligned} & R \text { gas constant } \\ & n \text { numbers of moles of gas }\end{aligned}$

$$
n=N / N_{A}
$$

$$
p V=R n T=\frac{R}{N_{A}} N T=k N T
$$

## Lecture VII : Ideal gas

$$
p V=R n T=\frac{R}{N_{A}} R N T=k N T
$$



## Lecture VII : Kinetic theory of gases (pressure)

Considering the single particle hits a wall

$$
\begin{gathered}
\Delta P_{x}=m V_{x}-\left(m V_{x}\right)=2 m V_{x} \\
\text { Finial Initial } \\
\frac{\Delta p_{x}}{\Delta t}=\frac{2 m V_{x}}{2 L / V_{x}}=\frac{m V_{x}^{2}}{L} \\
\text { Presure } p=\frac{F}{L^{2}}=\frac{m V_{x}^{2}}{L^{3}}
\end{gathered}
$$



## Lecture VII : Kinetic theory of gases ( pressure )

Considering N particle system $N=n N_{A}$

$$
\begin{aligned}
& \text { Presure } p=\sum_{i=1}^{N} \frac{F_{i}}{L^{2}}=\sum_{i=1}^{N} \frac{\Delta p_{x, i}}{\Delta t L^{2}}=\sum \frac{m V_{x, i}}{L^{3} / V_{x}}=\sum \frac{m V_{x, i}^{2}}{L^{3}} \\
& \text { Presure } p=\frac{\left.n M N_{A}<V_{x}^{2}\right\rangle}{L^{3}}=\frac{n M<V_{x}^{2}>}{L^{3}} \\
& \text { Pressure } p=\frac{n M<V^{2}>}{3 V^{3}}
\end{aligned}
$$

## Lecture VII : root-mean-square speed

$$
\begin{gathered}
\sqrt{\left\langle V_{x}^{2}\right\rangle} \equiv V_{\text {rms }} \\
\text { Presure } p=\frac{n M\left\langle V^{2}\right\rangle}{3 V}=\frac{n M V_{m s}^{2}}{3 V} \\
p V=\frac{n M V_{\text {rms }}^{2}}{3}=n R T \\
V_{\text {rms }}=\sqrt{\frac{3 R T}{M}}
\end{gathered}
$$

## Lecture VII : Kinetic Energy

$$
\begin{aligned}
K_{\text {average }}=\sum_{i=1}^{N} \frac{m v_{i}^{2}}{2 N} & =\frac{m}{2 N} \sum_{i=1}^{N} v_{i}^{2} & & \\
& =\frac{m}{2} V_{r m s}^{2} & & V_{r m s}=\sqrt{\frac{3 R T}{M}} \\
& =\frac{m}{2}\left(\frac{3 R T}{M}\right) & & n=\frac{N}{N_{A}}=\frac{M_{\text {sum }}}{M}=\frac{M_{s u m}}{m N_{A}} \\
& =\left(\frac{3 k T}{2}\right) & & k=R / N_{A}
\end{aligned}
$$

## Lecture VII : Mean Free Path

Mean free path $\lambda$ is the average distance traversed by a molecule between collisions.


## Lecture VII : Mean Free Path

Considering the molecular first.

A collision occurs when the centers of two molecules come within a distance $d$ of each other, $d$ being the molecular diameter.


An equivalent: to think of the moving molecule as having a radius $d$ and all other molecules as being points.

## Lecture VII : Mean Free Path

In time $t$ the moving molecule effectively sweeps out a cylinder of length $v \Delta t$ and radius $d$.
volume $=\pi d^{2} v \Delta t$
$\pi d^{2} v \Delta t N / V$
Since $N / V$ is the number of molecules per unit volume, the number of molecules in the cylinder is $N / V$ times the volume of the cylinder

## Lecture VII : Mean Free Path

Mean free path $\lambda$ is the average distance traversed by a molecule between collisions.

$$
\lambda=\frac{\text { lrngth of path during } \Delta t}{\text { number of the coilions during } \Delta t}
$$



All molecules are moving

## Lecture VII : Maxwell's speed distribution law

$P(v)=4 \pi\left(\frac{M}{2 \pi R T}\right)^{3 / 2} v^{2} e^{-M v^{2} / 2 R T}$
probability distribution function

$$
\int_{0}^{\infty} P(\nu) d \nu \equiv 1
$$

Normalize condition
$\langle x\rangle=\int_{0}^{\infty} x P(\nu) d \nu$
Expected value

$$
\begin{aligned}
& \langle v\rangle=v_{\text {avg }}=\int_{0}^{\infty} v P(\nu) d \nu=\sqrt{\frac{8 R T}{\pi M}} \\
& \left\langle\nu^{2}\right\rangle=\int_{0}^{\infty} v^{2} P(\nu) d \nu=\frac{3 R T}{M} \quad v_{r m s}=\sqrt{\frac{3 R T}{M}} \\
& v_{p}=\sqrt{\frac{2 R T}{M}}
\end{aligned}
$$

## Lecture VII : Maxwell's speed distribution law



Lecture VII : work done by ideal gas (isothermal)

$$
\begin{aligned}
& p V=R n T=\frac{R}{N_{A}} R N T=k N T \\
& W=\int_{i}^{f} p d V=\int_{i}^{f} \frac{k N T}{V} d V \\
& =k N T \ln \left(V_{f}-V_{i}\right)=k N T \ln \left(\frac{V_{f}}{V_{i}}\right)
\end{aligned}
$$

## Lecture VII : work done by ideal gas

Constant V

$$
W=\int_{i}^{f} p d V=0
$$

Constant P

$$
W=\int_{i}^{f} p d V=p\left(V_{f}-V_{i}\right)
$$

## Lecture VII : Kinetic Energy

$$
\begin{aligned}
K_{\text {average }}=\sum_{i=1}^{N} \frac{m v_{i}^{2}}{2 N} & =\frac{m}{2 N} \sum_{i=1}^{N} v_{i}^{2} & & \\
& =\frac{m}{2} V_{r m s}^{2} & & V_{r m s}=\sqrt{\frac{3 R T}{M}} \\
& =\frac{m}{2}\left(\frac{3 R T}{M}\right) & & n=\frac{N}{N_{A}}=\frac{M_{\text {sum }}}{M}=\frac{M_{s u m}}{m N_{A}} \\
& =\left(\frac{3 k T}{2}\right) & & k=R / N_{A}
\end{aligned}
$$

## Lecture VII : internal energy

$$
K_{\text {average }}=\sum_{i=1}^{N} \frac{m v_{i}^{2}}{2 N}=\frac{m}{2 N} \sum_{i=1}^{N} v_{i}^{2}=\left(\frac{3 k T}{2}\right)
$$

The average translational kinetic energy of a single atom depends only on the gas temperature and is given by 3 kT . A sample of $n$ moles of such a gas contains $n N A$ atoms. The internal energy Eint of the sample is then

$$
E_{i n t}=\left(n N_{A}\right) K_{a v g}=\left(n N_{A}\right)\left(\frac{3}{2} k T\right)
$$

$$
E_{\text {int }}=\frac{v}{2} k T \text { Monoatomic ideal gas }
$$

## Lecture VII : internal energy

$$
\begin{aligned}
& E_{i n t}=\left(n N_{A}\right) K_{a v g}=\left(n N_{A}\right)\left(\frac{3}{2} k T\right) \\
& E_{\text {int }}=\frac{3}{2} k T \text { Monoatomic ideal gas }
\end{aligned}
$$

The internal energy Eint of an ideal gas is a function of the gas temperature only; it does not depend on any other variable

## Lecture VII : Molar Specific Heat at Constant Volume

CV is a constant called the molar specific heat at constant volume.

$$
Q=n C_{v} \Delta T
$$

Constant V

$$
\begin{gathered}
W=\int_{i}^{f} p d V=0 \quad \Delta E_{\text {int }}=n C_{v} \Delta T-W \\
\Delta E_{\text {int }}=n C_{v} \Delta T \\
C_{v}=\frac{\Delta E_{\text {int }}}{n \Delta T}
\end{gathered}
$$

## Lecture VII : Molar Specific Heat at Constant Volume

CV is a constant called the molar specific heat at constant volume.

$$
Q=n C_{v} \Delta T
$$

Constant V

$$
\begin{aligned}
C_{v} & =\frac{\Delta E_{\text {int }}}{n \Delta T} \quad E_{\text {int }}=\frac{3}{2} k T \\
C_{v} & =\frac{3}{2} R=12.5 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{~K}
\end{aligned}
$$

Monatomic gas

## Lecture VII : Molar Specific Heat at Constant Volume

$$
\begin{aligned}
& C_{v}=\frac{\Delta E_{\text {int }}}{n \Delta T} \\
& E_{\text {int }}=C_{v} T \quad \text { For any ideal gas } \\
& d E_{\text {int }}=n C_{v} d T \quad \text { For any procoss }
\end{aligned}
$$

A change in the internal energy Eint of a confined ideal gas depends on only the change in the temperature, not on what type of process produces the change.

## Lecture VII : Molar Specific Heat at Constant pressure

$$
\begin{gathered}
\text { Start from } Q=n C_{v} \Delta T \quad \text { Constant volume } \\
d E_{\text {int }}=Q-W \\
Q=E_{\text {int }}+W \\
d Q=C_{V} d T+p d V
\end{gathered}
$$

## Lecture VII : Molar Specific Heat at Constant

 pressure$$
\begin{aligned}
& d Q=C_{V} d T+p d V \\
& p V=n R T
\end{aligned}
$$

$$
C_{p}=C_{V}+R
$$

$$
p d V+V d p=R d T
$$

$$
p d V=R d T-V d p
$$

$$
d Q=C_{V} d T+R d T-V d p
$$

$$
d Q=\left(C_{V}+R\right) d T-V d p
$$

$$
d Q=\left(C_{V}+R\right) d T=C_{p} d T
$$

## Lecture VII : Degrees of Freedom and Molar Specific Heats

|  |  | Degrees of Freedom |  |  |
| :--- | :---: | :---: | :---: | :---: |
| Molecule | Example | Translational | Rotational | Total $(f)$ |
| Monatomic | He | 3 | 0 | 3 |
| Diatomic | $\mathrm{O}_{2}$ | 3 | 2 | 5 |


kind of molecule has a certain number $f$ of degrees of freedom, which are independent ways in which the molecule can store energy. Each such degree of freedom has associated with it-on average-an energy of $1 / 2 \mathrm{kT}$ per molecule (or 1/2RT per mole)

$$
\text { Ex } C_{v}=\frac{3}{2} R=\frac{f}{2} R
$$

## Lecture VII : The Adiabatic Expansion of an

 Ideal Gas $p V^{\gamma}=$ constant$$
\begin{aligned}
d E_{i n t} & =Q-W \\
d E_{i n t} & =-W \quad \text { Adiabatic } \\
C_{v} d T & =-W \\
C_{v} d T & =-p d V \\
C_{v} d T+p d V & =0 \\
p_{i} V_{i}^{\gamma} & =p_{f} V_{f \text { Adiabatic }}^{\gamma}
\end{aligned}
$$

## Lecture VII : The Adiabatic Expansion of an Ideal Gas

$$
\begin{aligned}
& p V^{\gamma}=\text { constant } \\
& p_{i} V_{i}^{\gamma}=p_{f} V_{f}^{\gamma} \quad \text { Adiabatic } \\
& p V^{\gamma}=\frac{R T}{V} V^{\gamma}, T V^{\gamma-1}=\text { constant } \\
& T_{i} V_{i}^{\gamma-1}=T_{f} V_{f}^{\gamma-1} \quad \text { Adiabatic }
\end{aligned}
$$

## Lecture VII : free expansion

$$
\begin{aligned}
d E_{\text {int }} & =d Q-d W=0 \\
T_{i} & =T_{f} \\
p_{i} V_{i} & =p_{f} V_{f}
\end{aligned}
$$

## Lecture VII : The Molar Specific Heats of an

 Ideal GasConstant V

$$
W=\int_{i}^{f} p d V=0
$$

Constant P

$$
W=\int_{i}^{f} p d V=p\left(V_{f}-V_{i}\right)
$$

## Lecture VII : Equilibrium

The equilibrium state is defined as the one macroscopic state of a closed system which is automatically attained after a sufficiently long period of time such that the macroscopic state quantities no longer change with time.

All systems which are in thermal equilibrium with a given system are also in thermal equilibrium with each other
-The zeroth law of thermodynamics

## Extensive(additive) state quantities:

 These quantities are proportional to the amount of matter in a system$$
\mathrm{V}, \mathrm{E}, \mathrm{M}, \mathrm{~S}, C_{V}, C_{P} \ldots
$$

## Intensive state quantities

These quantities are independent of the amount of matter in a system

$$
\mathrm{T}, \mathrm{p}, \rho \ldots
$$

## Equalization of Temperature

$$
\begin{array}{c:c}
T_{H} & Q \\
T_{L} \\
d Q_{H}=-Q & d Q_{L}=Q \\
\frac{d Q_{H}}{T_{H}}=-\frac{Q}{T_{H}} & \frac{d Q_{L}}{T_{L}}=\frac{Q}{T_{L}} \equiv d S_{L} \\
Q\left(\frac{1}{T_{L}}-\frac{1}{T_{H}}\right)=d S \geq 0
\end{array}
$$

## Equalization of Temperature



## Irreversible process

The processes do not reserve themselves.
Ex: isothermal process

## Reversible process

The processes only over equilibrium states. Ex: frictionless adiabatic process

isothermal process
V



## Lecture VII : Reversible process

In thermodynamics, a reversible process is a process whose direction can be returned to its original position by inducing infinitesimal changes to some property of the system via its surroundings.

## The processes only over equilibrium states.



Adiabatic process


## Lecture VII : Irreversible vs. Reversible

| Isothermal process | Adiabatic process |
| :--- | :--- |
| An isothermal process is defined as one <br> of the thermodynamic processes which <br> occur at a constant temperature | An adiabatic process is defined as one of the <br> thermodynamic processes which occur without any <br> heat transfer between the system and the surrounding |
| Work done is due to the change in the <br> net heat content in the system | Work done is due to the change in its internal energy |
| The temperature cannot be varied | The temperature can be varied |
| There is a transfer of heat | There is no transfer of heat |

## Lecture VII : Irreversible vs. Reversible



Irreversible
Macroscopic
credit: wiki

reversible Microscopic

## Lecture VII : Spontaneous Process

a spontaneous process is the time-evolution of a system in which it releases free energy and it moves to a lower, more thermodynamically stable energy state (equilibrium state)

## Lecture VII : Heat Engine



Energy Reservoir Model


## Lecture VII : Carnot's engine



## Lecture VII : Carnot's engine

## Energy Reservoir Model



## Lecture VII : Carnot's engine

$$
\Delta E_{i n t}=Q-W
$$



## Lecture VII : Carnot's engine (detail) $d E_{i n t}=d Q-d W$



$$
\begin{aligned}
& 1->2: p_{1} V_{1}=p_{2} V_{2}=n K T_{h} \\
& \Delta E_{\text {int }}=0=Q_{1}-W_{1} \frac{V_{2}}{V_{1}}=\frac{p 1}{p 2} \\
& Q_{1}=-W_{1}=N K T_{h} \ln \frac{V_{2}}{V_{1}}
\end{aligned}
$$

This is the amount of heat exchanged with heat bath in 1->2 step. Since $V_{2}>V_{1}, d Q_{1}>0$; the amount of heat $\Delta Q_{1}$ is added to the gas at the expense of the heat bath.

## Lecture VII : Carnot's engine (detail) $d E_{\text {int }}=d Q-d W$



## Lecture VII : Carnot's engine (detail) $d E_{i n t}=d Q-d W$



## Lecture VII : Carnot's engine (detail) $d E_{i n t}=d Q-d W$



## Lecture VII : Carnot's engine (detail) $d E_{i n t}=d Q-d W$



## Lecture VII : Carnot's engine (detail) $d E_{\text {int }}=d Q-d W$



$$
\begin{aligned}
& \frac{V_{2}}{V_{1}}=\frac{V_{3}}{V_{4}} \\
& \frac{Q_{1}}{T_{h}}+\frac{Q_{3}}{T_{c}}=0
\end{aligned}
$$

It is valid for any reversible cyclic process

## Lecture VII : Carnot's engine (detail) $d E_{i n t}=d Q-d W$



$$
\frac{Q_{1}}{T_{h}}+\frac{Q_{2}}{T_{c}}=0 \quad \oint \frac{d Q_{r e v}}{T}=0
$$

$\frac{d Q_{\text {rev }}}{T}$ is for any reversible thermodynamic process
The extensive state function is the entropy
V

$$
d S \equiv \frac{d Q_{r e v}}{T}
$$

## Lecture VII : efficiency of Carnot's engine

$$
\begin{aligned}
& W_{\text {total }}=W_{1}+W_{2}+W_{3}+W_{4} \\
& W_{1}=N K T_{h} \ln \frac{V_{2}}{V_{1}} \quad W_{3}=N K T_{c} \ln \frac{V_{4}}{V_{3}} \\
& \text { Heat extracted } Q_{L} \quad{ }_{3} \quad W_{\text {total }}=N K\left(T_{h}-T_{c}\right) \ln \frac{V_{2}}{V_{1}}=Q_{1}+Q_{3} \\
& V \quad \eta=\frac{W_{\text {total }}}{Q_{1}}=\frac{Q_{1}+Q_{3}}{Q_{1}}=1-\frac{T_{c}}{T_{h}}
\end{aligned}
$$

## Lecture VII : example:

Calculate the total change in entropy if 4000 J of heat transfer occurs from a hot reservoir at $\mathrm{Th}=600 \mathrm{~K}$ to a cold reservoir at $\mathrm{Tc}=250 \mathrm{~K}$, assuming there is no temperature change in either reservoir.
the heat transfer from the hot reservoir,

$$
\Delta S_{H}=\frac{4000 \mathrm{~J}}{600 \mathrm{~K}}=-6.67 \mathrm{~J} / \mathrm{K}
$$

the heat transfer from the hot reservoir,

$$
\Delta S_{C}=\frac{4000 \mathrm{~J}}{250 \mathrm{~K}}=16 \mathrm{~J} / \mathrm{K}
$$



$$
\Delta S_{\text {total }}=\Delta S_{H}+\Delta S_{C}=-6.67 \mathrm{~J} / \mathrm{K}+16 \mathrm{~J} / \mathrm{K}=9.33 \mathrm{~J} / \mathrm{K}
$$

example: $\eta=\frac{W_{\text {total }}}{Q_{1}}=1-\frac{T_{c}}{T_{h}}$
(a) Calculate the work output of a Carnot engine operating between temperatures of 600 K and 100 K for 4000 J of heat transfer to the engine. (b) Now suppose that the 4000 J of heat transfer occurs first from the 600 K reservoir to a 250 K reservoir (without doing any work, and this produces the increase in entropy calculated above) before transferring into a Carnot engine operating between 250 K and 100 K . What work output is produced?
(a) $\eta=1-\frac{100 K}{600 K}=0.833$

$$
W_{\text {total }}=\eta Q_{H}=0.833 \times 4000 \mathrm{~J}=3333 \mathrm{~J}
$$

(b) $\eta^{\prime}=1-\frac{100 K}{250 K}=0.6$

$$
W_{\text {total }}^{\prime}=\eta^{\prime} Q_{H}=0.6 \times 4000 \mathrm{~J}=2400 \mathrm{~J}
$$

$$
W_{\text {unavail }}=W_{\text {total }}-W_{\text {total }}^{\prime}=933 \mathrm{~J}
$$

$$
W_{\text {unavail }}=\Delta S / T_{C}=\Delta S / 100 K=933 \mathrm{~J}
$$

$$
\Delta S=9.33 \mathrm{~J}
$$



## Lecture VII : example: coal-fired power station

A coal-fired power station is a huge heat engine. It uses heat transfer from burning coal to do work to turn turbines, which are used to generate electricity. In a single day, a large coal power station has $2.50 \times 10^{14} \mathrm{~J}$ of heat transfer from coal and $1.48 \times 10^{14} \mathrm{~J}$ of heat transfer into the environment. (a) What is the work done by the power station? (b) What is the efficiency of the power station? (c) In the combustion process, the following chemical reaction occurs: $\mathrm{C}+\mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}$. This implies that every 12 kg of coal puts $12 \mathrm{~kg}+16 \mathrm{~kg}+16 \mathrm{~kg}=44 \mathrm{~kg}$ of carbon dioxide into the atmosphere. Assuming that 1 kg of coal can provide $2.5 \times 10^{6} \mathrm{~J}$ of heat transfer upon combustion, how much $\mathrm{CO}_{2}$ is emitted per day by this power plant?

$$
\begin{aligned}
& W=Q_{H}-Q_{L}=2.50 \times 10^{14} \mathrm{~J}-1.48 \times 10^{14} \mathrm{~J}=1.02 \times 10^{14} \mathrm{~J} \\
& e f f=\frac{W}{Q_{H}}=\left(1.02 \times 10^{14} \mathrm{~J}\right) / 2.50 \times 10^{14} \mathrm{~J} \sim 0.408 \\
& \frac{2.50 \times 10^{14} \mathrm{~J}}{2.5 \times 10^{6} \mathrm{~J}} \operatorname{coal} \frac{44 \mathrm{~g} \mathrm{CO}}{2} \frac{12 \mathrm{~g} \mathrm{Coal}}{}=3.7 \times 10^{8} \mathrm{~kg} \mathrm{coal}
\end{aligned}
$$

## Lecture VII : Otto's cycle



$$
\Delta W_{2}>\Delta W_{1}
$$

## Lecture VII : heat engine



All real heat engines lose some heat to the environment


## $T_{L}$

Extracting heat $Q_{H}$ and using it all to do work W would constitute a perfect heat engine. Forbidden by the second law

## Lecture VII : Refrigerator



All real refrigerators require work to get heat to flow from a cold area to a warmer area.


Spontaneous flow of heat from a
cold area to a hot area would
constitute a perfect refrigerator
Spontaneous flow of heat from a
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constitute a perfect refrigerator forbidden by second law


Real case: work done against friction is lost to cold reservoir

## Lecture VII : Refrigerator



All real refrigerators require work to get heat to flow from a cold area to a warmer area.

## $K=\frac{\left|Q_{L}\right|}{|W|}$, Coefficient of refrigerator performance

Carnot refrigerator is a Carnot engine operating in reverse.

$$
K_{C}=\frac{\left|Q_{L}\right|}{\left|Q_{H}\right|-\left|Q_{L}\right|}
$$

## Lecture VII ：Entropy（熵 尸 九 ）

If an irreversible process occurs in a closed system，the entropy $\mathbf{S}$ of the system always increases；it never decreases．


## Lecture VII ：Entropy（熵 尸 九 ）

## If an irreversible process occurs in a closed system，the entropy $\mathbf{S}$ of the system always increases；it never decreases．

Pressure and volume are state properties，properties that depend only on the state of the gas and not on how it reached that state．Other state properties are temperature and energy．We now assume that the gas has still another state property－its entropy．


## Lecture VII ：Entropy（熵 尸 尤）

The change of the entropy idS：entry of a system during a process that takes the system from a initial state I to finial state f

As the gas rushes to fill the entire container，the pressure，temperature，and volume of the gas fluctuate unpredictably．In other words，they do not have a sequence of well－defined equilibrium values during the intermediate stages of the change from initial state i to final state f．Thus，we cannot trace a pl path for the free expansion on the p－V plot（right plot），and we cannot find a relation between Q and $T$ that allows us to integrate as Eq．（1）requires．

$$
\begin{equation*}
\left.\Delta S=S_{f}-S_{i}=\int_{i}^{f} \frac{d Q}{T}(1) \quad \operatorname{lP}_{i}, V_{i}\right) \tag{1}
\end{equation*}
$$

## Lecture VII : Entropy

Adiabatic process

$$
p_{i} V_{i}^{\gamma}=p_{f} V_{f}^{\gamma}
$$

$$
\Delta S=S_{f}-S_{i}=\int_{i}^{f} \frac{d Q}{T}
$$

$$
\int^{f} d O=O \quad \begin{aligned}
& \text { where } Q \text { is the total energy } \\
& \text { whens }
\end{aligned}
$$ transferred as heat during the process

$$
\Delta S=S_{f}-S_{i}=\frac{Q}{T}
$$

To find the entropy change for an irreversible process, replace that process with any reversible process that connects the same initial and final states. Calculate the entropy change for this reversible process


## Lecture VII ：The second law of thermodynamics

## Clausius statement

Heat can never pass from a colder to a warmer body without some other change， connected therewith，occurring at the same time．

不可能把熱量從低溫物體傳遞到高溫物體而不產生其他影響

Kelvin statement
It is impossible for a self－acting machine，unaided by any external agency，to convey heat from one body to another at a higher temperature．It is impossible，by means of inanimate material agency，to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects．

不可能從單一熱源吸收能量，使之完全變為有用功而不產生其他影響

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> The entropy of any isolated system increases in any spontaneous process and remains unchanged in an equilibrium（reversible）process．

> 孤立熱力學系統從一個平衡㮩到另一平衡㮩的過程中，其摘永不減少：若過程可逆，則摘不變；若不可逆，則摘增加。

## Lecture VII ：The second law of thermodynamics

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For isolated system in equilibrium it holds that

$$
d S=0, \quad S=S_{\max }
$$

For irreversible process it holds that

$$
d S>0
$$



Which one has bigger entropy?

Lecture VII : example $\Delta S \equiv \frac{Q}{T}$
Find the increase in entropy of 1.00 kg of ice originally at 273.15 K that is melted to form water at 273.15 K .
latent heat of fusion= $334 \mathrm{~kJ} / \mathrm{kg}$


Order


Disorder

$$
\begin{aligned}
\Delta S & \equiv \frac{Q}{T} \\
& =\frac{1 \mathrm{~kg} 334 \mathrm{~kJ} / \mathrm{kg}}{T}
\end{aligned}
$$

$$
=\frac{334 \mathrm{~kJ}}{273.16 \mathrm{~K}}
$$

$$
=1.22 \times 10^{3} \mathrm{~J} / \mathrm{K}
$$

## Lecture VII : Entropy Summary



Total number of microstates: 36
Total number of macrostates: 11
MultiPlicity $=\Omega$

$$
\text { Entropy }=S=k \ln \Omega
$$

K: Boltzmann's constant

## Lecture VII ：Normal distribution（bell curve）

## Microstate Most possible macrostate



## MultiPlicity $=\Omega$

$\Omega$ ：
the number of possible microstates available to a system in a given macrostate

$$
S=k \ln \Omega
$$

系統微觀䊉子的無序程度的度量

Suppose you toss 100 coins starting with 60 heads and 40 tails, and you get the most likely result, 50 heads and 50 tails. What is the change in entropy?

$$
\begin{aligned}
\Delta S & =S f-S_{\mathrm{i}}=k \ln \Omega_{f}-k \ln \Omega_{i} \\
& =1.38 \times 10^{-23} \mathrm{~J} / \mathrm{K}\left(\ln 10^{29}-1.4 \times \ln 10^{28}\right) \\
& =2.7 \times 10^{-23} \mathrm{~J} / \mathrm{K}
\end{aligned}
$$

| Heads | Tails | N of microstates |
| :---: | :---: | :---: |
| 100 | 0 | 1 |
| 99 | 1 | 100 |
| 95 | 5 | $7.5^{\star} 10^{\wedge} 7$ |
| 90 | 10 | $1.7^{\star} 10^{\wedge} 13$ |
| 75 | 25 | $2.4^{\star} 10^{\wedge} 23$ |
| 60 | 40 | $1.4^{\star} 10^{\wedge} 28$ |
| 55 | 45 | $6.1^{\star} 10^{\wedge} 28$ |
| 51 | 49 | $9.9^{\star} 10 \wedge 28$ |
| 50 | 50 | $10^{\wedge} 29$ |

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孤立系統的自發過程總是從熱力學機率小的宏觀狀態向熱力學機率大的宏觀狀態轉變

## Lecture VII : Entropy Summary

- a state variable whose change is defined for a reversible process at T where Q is the heat absorbed.
- a measure of the amount of energy which is unavailable to do work.
- a measure of the disorder of a system.
- a measure of the multiplicity of a system.

