



## **First Law of Thermodynamics:**

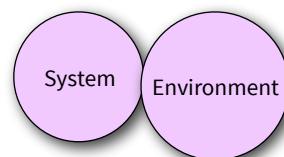
- The principle of the conservation of energy is the fundamental rule underlying all of science.
- The conservation of energy can be expressed using the physics of thermodynamics.
- Recall from last time that the temperature of an object is related to the internal energy per molecule of an object.

$$\overline{KE} = \frac{3}{2}k_B T$$



Temperature is a measure of the concentration of internal energy within an object.

- When a system is in contact with an environment the combined system+environment will come into thermal equilibrium with a uniform temperature.



In thermal equilibrium, both system and environment are at the same temperature.

- Therefore the concentration of energy in the combined system+environment is uniform



Thermal equilibrium is the final state of a system+environment where the internal energy is distributed uniformly

- A system interacting with an environment can increase or decrease its internal energy, and therefore temperature in two different ways:

(I) Heat can flow into, or out of the system into the environment.

(II) The system can do work on, or receive work from the environment.

- Typically heat is labeled as “ $Q$ ”

- If heat goes into the system  $Q > 0$ , if heat leaves the system  $Q < 0$

- If the system does work on the environment then  $W > 0$ , otherwise  $W < 0$

- In terms of the internal energy, heat, and work, the conservation of energy is given by the **first law of thermodynamics**:

$$\Delta U = Q - W$$

- We must be very careful about minus signs when using the first law of thermodynamics.



- Heat is a term used for the flow, or transfer, of internal energy between two objects.

- Heat is not a property of an object. Heat depends on the properties of both the system and the environment.

→ Heat is not a state variable.

- Work is also not a property of an object. It depends on external forces and displacements.

→ Work is not a state variable.

- Therefore, the first law of thermodynamics relates a state variable, the change in internal energy  $\Delta U$  to the sum of two physical processes that are not state variables.

- This is why we do not use  $\Delta Q$  and  $\Delta W$

- If a closed system has no heat flow and no work is done so that  $Q = W = 0$  then the change in internal energy must be zero and the system is called **isolated**.

- In general, the internal energy can change from both heat and work.

- There are four important physical processes that are special cases of the first law that are important.



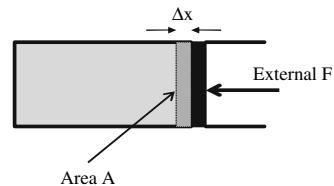
- First we are going to consider the work done by an ideal gas system.

- Suppose we put  $N$  gas molecules into a container with volume  $V$  with one side movable with area  $A$ .

- The pressure of the gas  $P$  exerts a force on the movable wall that can move the wall a distance of  $\Delta x$

- In moving the wall, the gas does work on the container given by:

$$dW = F\Delta x = PA\Delta x = P\Delta V$$



- In general, if a force is applied then there will be acceleration. However, we do not want acceleration because it will break thermal equilibrium

- So we will also consider a external force (friction term) that keeps the velocity of the wall constant and slow. Such a process is call **quasistatic** ("almost static").

- For an ideal gas we know that the state variables  $P$ ,  $V$ , and  $T$  are related via the ideal gas law:

$$PV = Nk_B T$$

- If one of the three variables is fixed, then the others must change to satisfy this equation.



### Four Special Cases:

(I) If the pressure of the gas is fixed, then the process is called **Isobaric** ("one pressure")

- We can add up each term  $dW = P\Delta V$  to get the total work

$$W = P(V_{\text{final}} - V_{\text{initial}}) \quad (\text{Isobaric})$$

- If the final volume is larger, then the work is positive, and the system does work on the environment.

→ The internal energy of the system decreases by the first law

- As the volume varies, the temperature will change since the internal energy is changing

- If the volume decreases, then by the ideal gas law, the temperature must decrease

$$PV = Nk_B T$$

- However, the first law tells us that the internal energy, and therefore temperature must go up.

$$\Delta U = Q - W$$

- This tells us that there must also be heat transfer in an isobaric process.

- In general both work and heat cause changes in the internal energy.



(II) If the temperature is fixed, then the process is call **isothermal** (“one temperature”)

- The work done for the case of an isothermal ideal gas is

$$W = Nk_B T \ln \left( \frac{V_{\text{final}}}{V_{\text{initial}}} \right) \quad (\text{Isothermal})$$

- Since the temperature is fixed, there can be no change in internal energy

- The heat flow and work must always balance so that  $\Delta U = Q - W = 0$

- If the work is positive, gas expands, then heat must flow into the system  $Q > 0$

- The above equation is only valid for an ideal gas.

- However, for all isothermal process  $\Delta U = 0$



(III) If the volume is fixed, then the process is call **isochoric** (“one volume”)

- Since the volume is fixed, the work must be zero, and the first law reduces to

$$\Delta U = Q$$

- The change in internal energy, and temperature, of the gas is determined by the heat flow.

(IV) If none of the state variables are fixed, but  $Q = 0$  then the processes is called **adiabatic**.

- There is no heat exchange and the first law is

$$\Delta U = -W$$

- The internal energy/temperature change is determined directly by the amount of work.

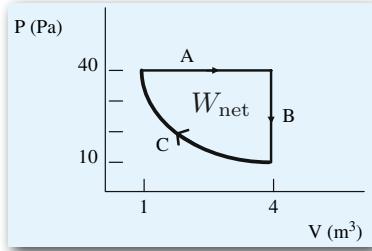
- Most interesting cases are described by one of these 4 processes or as a combination of them.



Ex: Determine the type of each process A, B, C shown in the pressure vs. volume diagram for an ideal gas, and determine the work done by each process and the total work. For process C,  $P \sim 1/V$ .

Solution:

- For process A, the pressure is fixed so the process is isobaric.
- The work done is simply:  $W_A = P\Delta V = (40)(4 - 1) = 120 \text{ J}$ 
  - This is also the area under the A curve.
- For process B, the volume is fixed so the process is isochoric:  $W_B = 0$ 
  - There is no area under the B curve.
- For process C, the process is isothermal as  $PV = \text{constant}$ 
  - The work done during part C is:
$$W_C = Nk_B T \ln(1/4) = PV \ln(1/4) = 40 \ln(1/4) = -55.5 \text{ J}$$
  - This is also the area under the C curve.
- The total work is  $W_{\text{net}} = W_A + W_B + W_C = 64.5 \text{ J}$ 
  - The net work is the area enclosed by the three curves.



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### Thermal Properties of Matter:

- When heat flows out of an object, its internal and temperature will change
  - From experiment it is found that the amount of heat needed to change the temperature by an amount  $\Delta t$  is proportional to the mass of the object and the change in temperature.
- $$Q = cm\Delta t$$
- The constant  $c$  is called the **specific heat** of the material given in units of  $\left[ \frac{J}{\text{kg} \cdot \text{K}} \right]$
  - The specific heat is a measure of how easy or difficult it is to change the temperature of a material via heat flow.
  - Temperature changes indicate changes in the internal energy of an object.
  - For a solid that we can model as a collection of molecules and springs, this change can be seen as a change in the spring constant  $k$  of the springs.

→ The specific heat is related to the potential energy created by the springs



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- Materials with higher specific heats require more heat per mass to increase the temperature.

- Also, these materials will also give off more heat when their temperature drops.

- Water has one of the highest specific heats of all materials.

- This is why it takes so long to boil water!

Material	Specific Heat kcal/kg·°C	Specific Heat J/kg·°C
Aluminum	0.22	900
Copper	0.093	390
Glass	0.20	840
Human body (mean at 37°C)	0.83	3500
Ice (-5°C)	0.50	2100
Iron or steel	0.11	450
Mercury	0.033	140
Silver	0.056	240
Steam (110°C)	0.48	2010
Water	1.00	4186
Wood	0.4	1700

Specific heats of various materials.

Ex: One liter of coffee at 100C is poured into a glass bottle at room temperature (20C). If the glass bottle has a mass of 0.2kg, find the final temperature of the coffee in the closed bottle.

Solution:

- Heat will flow from the coffee (water) into the glass until both are at the same temperature.
- Therefore we can write  $Q_{\text{loss from coffee}} = Q_{\text{gained glass}}$
- These can be written mathematically as:

$$c_{\text{water}}m_{\text{water}}(100 - T) = c_{\text{glass}}m_{\text{glass}}(T - 20)$$

↖ This includes an extra minus sign since heat is lost  $Q < 0$

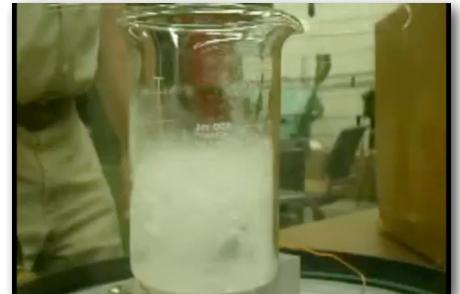
- Plugging in the values for the specific heat and masses:  $T = 97 \text{ C}$



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### Phase Changes:

- What we have discussed so far applies to solids, liquids, and gases.
- But what happens if you have a material that changes phases?
- The thermodynamic properties of material depend strongly on what phase the material is in
- When a material goes from one phase to another (ex. liquid  $\rightarrow$  gas) the system is said to go through a **phase transition**.



Phase transitions of nitrogen in vacuum

- During a phase transition, the temperature of the material remains constant.
- All of the heat goes into breaking or forming bonds between molecules in the object.

- The heat required to change the phase of a unit mass of a material is called the **heat of transformation**:

$$Q_{\text{trans}} = Lm$$



The temperature of melting ice is always 0C until all of the ice is melted

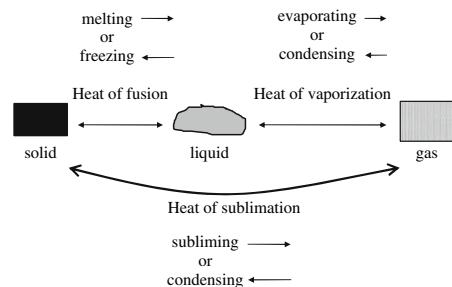


- The constant L is called the **latent heat**, and depends on the material and type of phase transition.

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- There are three different kinds of phase transitions, each with a different latent heat  $L$ :

- Melting or freezing -> **heat of fusion**
- Evaporation or condensation -> **heat of vaporization**
- Sublimation -> **heat of sublimation**



Kinds of phase transitions and their names

Material	Melting Point (°C)	Heat of Fusion (kJ/kg)	Boiling Point (°C)	Heat of Vaporization (kJ/kg)	Heat of Vaporization (kcal/kg)
Helium	—	—	—269	25	6.0
Nitrogen	-210	25.7	6.1	-195.8	200
Ethyl alcohol	-114	104	24.8	78	854
Mercury	-39	11.3	2.7	357	204
Water	0	333	79.7	100	2260
Carbon dioxide	-79	Sublimes	—	578	138
Aluminum	660	399	95.3	2467	10550
Tungsten	3410	184	44	5660	2520

Latent heats of various materials

- The amount of heat required to change phases does not depend on which direction you go (liquid->gas , gas->liquid)
- The amount of heat required to melt a block of ice is the same as the amount of heat released when water forms to ice.



Sublimation of iodine (solid directly to gas)



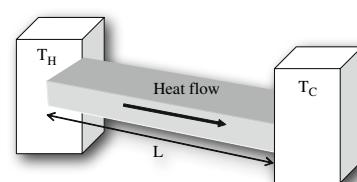
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## Heat Transfer Mechanisms:

- There are three ways in which heat can be transferred from one object to another: convection, conduction, and radiation.

### Conduction:

- Suppose we have a rod of length  $L$  and a perpendicular area  $A$  with the two ends of the rod at different temperatures.



- The hotter molecules in the material will oscillate more rapidly

- The hotter molecules collide with the colder molecules and transfer some of their energy.

- In the steady state, the temperature along the rod will not change, but will vary linearly along the length  $L$



Color indicates temperature for this liquid crystal

- The rate at which heat is transferred depends on the following:

- The cross-sectional area  $A$
- The variation in temperature along the rod:  $\Delta T / \Delta L$
- The kind of material that the rod is made out of.



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- The ability of a material to transfer heat is a property called the **thermal conductivity**  $\kappa$

- The rate of thermal conduction for a rod is given by:

$$\text{heat/time} \rightarrow \frac{Q}{t} = \kappa A \left( \frac{T_H - T_C}{L} \right)$$

Thermal Conductivity of Common Materials (at 25° C)

Material	Conductivity (Watts/meter·°C)
Acrylic	0.200
Air	0.024
Aluminum	250.000
Copper	401.000
Carbon Steel	54.000
Concrete	1.050
Glass	1.050
Gold	310.000
Nickel	91.000
Paper	0.050
PTFE (Teflon)	0.250
PVC	0.190
Silver	429.000
Steel	46.000
Water	0.580
Wood	0.130

### Convection:

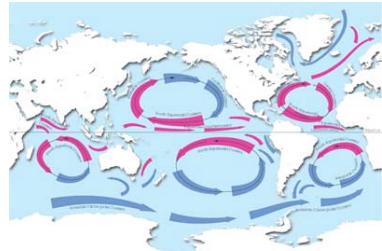
- Fluids that are not at a uniform temperature due to non-uniform heating or cooling, will flow due to differences in the density of the fluid as a function of temperature.

- If you heat a fluid, it expands, and the density goes down.

- Therefore, the fluid is more buoyant and hot fluids will rise to the top of a container.

- **Thermal convection** is the flow of heat via the flow of a fluid with non-uniform temperature.

- The best examples are the wind and the currents in the ocean.



Map of ocean currents



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### Radiation:

- Heat can also be transferred from one object to another via **thermal radiation**

- Radiation is an electromagnetic effect where electric+magnetic waves transfer energy

- This energy can be transferred even if the two materials are not actually in contact.

- For example, light from the sun feels warm

- The hotter the object, the more thermal radiation it releases

- An object will glow red when the temperature is around 1000K

- At around 1700K, the object glows bright white corresponding to more radiation energy



After being placed in a fire, metal glows red

- The rate of energy emission (power) due to radiation is given by the **Stephan-Boltzmann Law**

$$P = \sigma AT^4$$

- Here  $\sigma$  is the Stephan-Boltzmann constant  $\sigma = 5.67 \times 10^{-8} \text{ W}/(\text{m}^2 \cdot \text{K}^4)$

- The emitted power increases extremely fast as the temperature is increased



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- Objects that emit radiation also absorb radiation
- If an object with temperature  $T_1$  is in an environment that is at a temperature  $T_2$ , then the net rate of energy emission is given by:

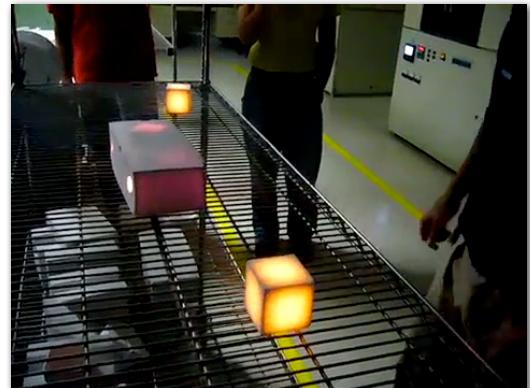
$$P = \sigma A(T_1^4 - T_2^4)$$

- If  $T_2 > T_1$ , then the net power is negative because the object absorbs more power than it emits.

- In general, the amount of heat transferred via radiation is much less than conduction.

- An object can glow white (1700K) but your temperature will not change by much unless you touch it.

- Special materials have thermal conductivities that are so low that even if they glow, you can still pick them up!



Ceramic material used to protect the space shuttle during reentry.

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