

Now we talk about heat:

## Zeroth Law of Thermodynamics:

(inserted after the 1<sup>st</sup> 3 Laws, and often not mentioned)

If two objects are in thermal equilibrium with a third object, they are in thermal equilibrium with each other.

**Thermal equilibrium** means that the two objects are at the same temperature.

Energy always flows from hotter object to a colder object when they are in contact.

(which is **so obvious to every human** that it goes without saying)  
In other words, we BELIEVE that this will never be violated. Billions of people do that experiment every day without observing a violation. **IT IS THEREFORE A SCIENTIFIC LAW.**

The total **ENTROPY** (total disorder of system + surr) is greater after the transfer of heat from hot to cold.

**Therefore allowed by the 2<sup>nd</sup> Law.**

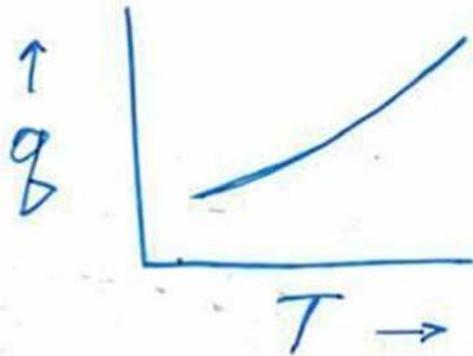
For PURE heating



$q = +$  Surr hot  $w = 0$

System

HEAT CAPACITY  $\equiv C$  J/K



$$C = \frac{dq}{dT} \text{ pure heating}$$

Slope

$$q = \int_{T_1}^{T_2} C(T) dT \approx C (T_2 - T_1)$$

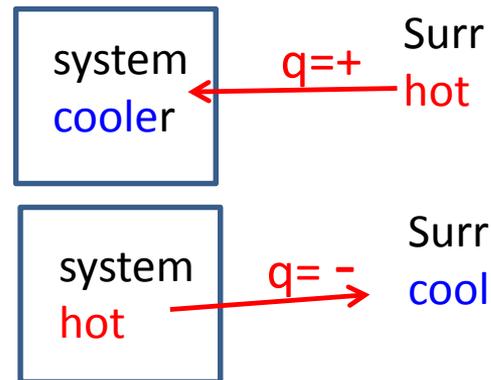
if  $C = C(T)$

or  $C \Delta T$   
if  $C$  constant

# Heat Capacity Units

$$q = C \Delta T$$
$$\text{so } \Delta T = q/C$$

For **PURE**  
heating or  
cooling



*(Very pertinent to Problem 1)*

Therefore a larger heat capacity means a smaller temperature increase for a given amount of heat added.

**C has the units of J/K**

**molar heat capacity =  $C_m$  JK<sup>-1</sup> mol<sup>-1</sup>**

**specific heat capacity =  $c$  J kg<sup>-1</sup> K<sup>-1</sup>**

**or J g<sup>-1</sup> K<sup>-1</sup> (You have to check.)**

Which has the higher heat capacity, **water** or **gold**?

*Molar Heat Cap.*

$$C_m \quad \text{J mol}^{-1} \text{K}^{-1}$$

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**Gold**    **25**

**Water**    **75**

*Specific Heat Cap.*

$$c \quad \text{J kg}^{-1} \text{K}^{-1}$$

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**129**

**4184**

From Table 2.2:

100 kg of water has a specific heat capacity of  $c = 4.184 \text{ kJ K}^{-1}\text{kg}^{-1}$

**What will be its temperature change if 418 kJ of heat is removed?**

( Relates to **problem 1**: hiker with wet clothes in wind loses body heat)

$$q = C \Delta T = c \times \text{mass} \times \Delta T \quad (\text{assuming } C \text{ is independent of temperature})$$

$$\Delta T = q / (c \times \text{mass}) = -418 \text{ kJ} / ( 4.18 \text{ kJ K}^{-1} \text{ kg}^{-1} \times 100 \text{ kg} ) =$$

$$= -418 \text{ kJ} / ( 4.18 \text{ kJ K}^{-1} \text{ kg}^{-1} \times 100 \text{ kg} )$$

$$= -418/418 = -1.0 \text{ K}$$

Note: Units are very important!

Always attach units to each number and make sure they cancel to desired unit

**Problems you can do now (partially): 1b, 15, 16a,f, 19**

## A Detour into the Microscopic Realm

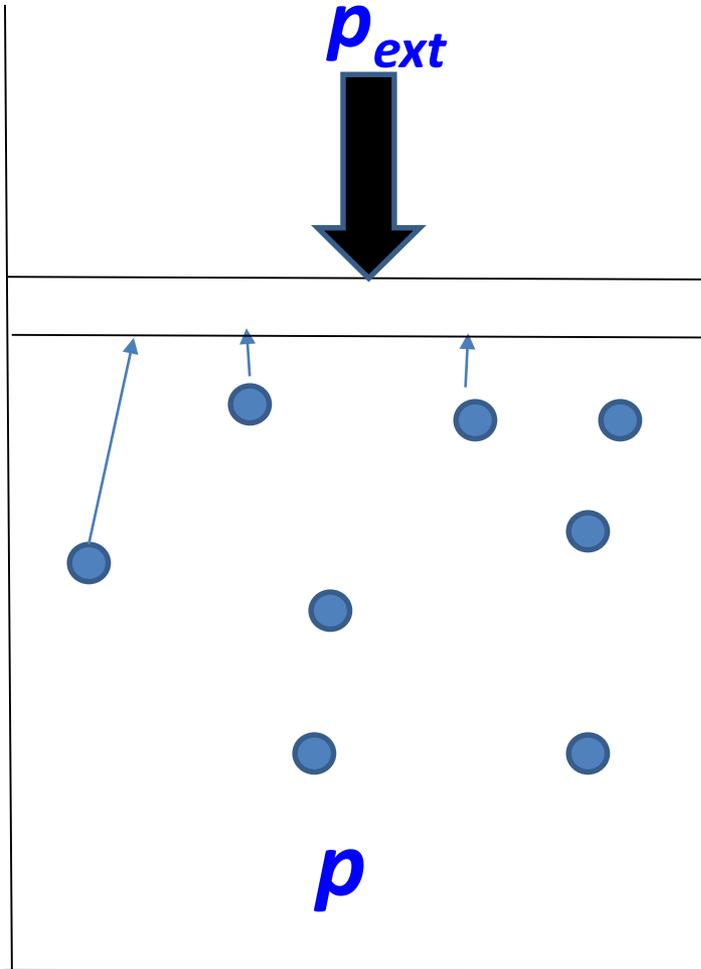
# “Internal Energy of system”: U the relation of **average kinetic energy per molecule and temperature**

Today’s students generally have knowledge of the microscopic nature of things and have a curiosity about what underlies quantities such as pressure,  $\Delta U$ ,  $q$ , and  $w$ .

This section has been inserted to help take some of the mysteries out of quantities that you will be encountering in our study of the First and Second Laws.

It is also the introduction to the important construct known as the “**ideal gas**”. You will **not** be expected to know how to do the complicated looking derivation that follows. It is only meant to help you see that the relationship of temperature and **average kinetic energy per molecule** (average, not total) comes from only a few simple familiar physics principles , and why atoms and molecules have the heat capacity values they do.

# What is PRESSURE?



Pressure of gas,  $p$ , is caused by enormous numbers of collisions on the walls of the container.

See the following link for a dynamic cartoon.  
[http://en.wikipedia.org/wiki/Kinetic\\_theory\\_of\\_gases](http://en.wikipedia.org/wiki/Kinetic_theory_of_gases)

When  $p_{ext} = p$  the external force exactly balances the force exerted by the **molecular collisions** on the piston.

**Ideal gas** = point masses  
with NO INTERACTIONS  
i.e., **NO POTENTIAL ENERGY**,  
**ONLY KINETIC ENERGY**

# Internal Energy of an ideal gas:

the relation of **kinetic energy and temperature**

We will derive: kinetic energy of translation =  $(3/2) nRT$

from: the ideal gas law:  $pV$  =  $nRT$

(where  $n$  = number of moles of gas and  $R$  = the “gas constant”)

We see that by simply multiplying the pressure times the volume times  $3/2$  gives the total translational energy of the molecules in a container !!!

## A Note about $R$ , the “gas constant”

It is unfortunate that  $R$  is called the gas constant.

$R$  should rightly be called the **EVERYTHING CONSTANT!**

Who has heard of the Boltzmann constant?

$R$  *IS* the **Boltzmann Constant** multiplied by Avogadro’s number.

$$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} = 0.083145 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

Derive: kinetic energy of translation of an ideal gas =  $n(3/2) RT$

Pressure =  $p$  = **average force per unit area**  
of a billion billion violent collisions

[http://en.wikipedia.org/wiki/Kinetic\\_theory\\_of\\_gases](http://en.wikipedia.org/wiki/Kinetic_theory_of_gases)

Volume = Area x length =  $A \times c$

Velocity in z direction =  $v_z$

Force =  $F_z$  = mass x acceleration

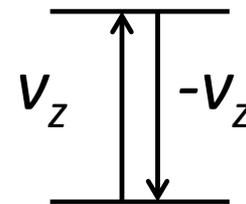
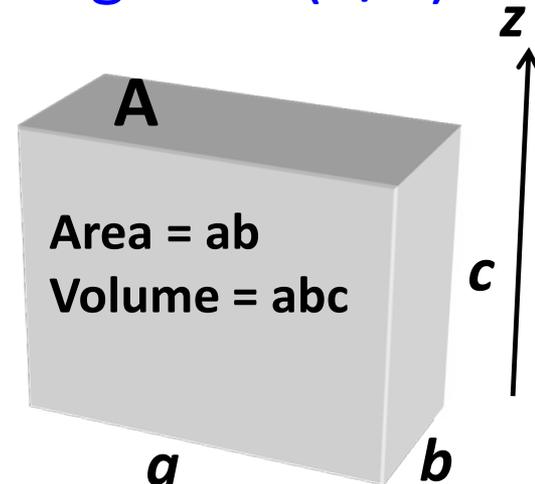
$F_z = m \, dv_z/dt = m \Delta v_z / \Delta t$

$\Delta v_z$  = change of  $v_z$  during collision =  **$2 v_z$**

$\Delta t$  = length/velocity =  $2c / v_z$

$\langle F_z \rangle = m \, 2 \langle v_z^2 \rangle / 2c = m \langle v_z^2 \rangle / c$  (=2KE/c)

pressure = force/Area:  $p = \langle F_z \rangle / A = m \langle v_z^2 \rangle / abc$   
=  $\langle v_z^2 \rangle / V$  (because  $abc = V$ )



pressure = force/Area:  $p = \langle F_z \rangle / A = m \langle v_z^2 \rangle / abc$

$abc = V$

$\frac{1}{2} m \langle v_z^2 \rangle = U_z$  (the kinetic energy due to  $m$  and  $v_z$ )

therefore  $p = 2U_z/V$

multiplying by  $V$  gives:  **$pV = 2U_z = (2/3) U$**  (where  $U$  = total kinetic energy)

(this is because  $U = U_x + U_y + U_z$  and that  $U_x = U_y = U_z$  by symmetry)

$U_z = 1/3 U$  (the total kinetic energy)

$2U_z = (2/3) U$

but  **$pV = nRT$**  (the ideal gas law established by experiments at low pressure)

( $n$  is the number of mols of ideal gas,  $T$  is temperature in Kelvin, and  **$R$  is the universal gas constant**)

giving  $pV = nRT = (2/3) U$  or  **$U = (3/2) nRT$**

Dividing both sides by  $n$  gives the **molar translational kinetic energy:**

$$U_m = (3/2) RT$$

$$p = 2U_z/V \quad \text{therefore } pV = 2U_z = 2U_m/3 = nRT$$

$$U_m = (3/2) nRT$$
$$= \frac{1}{2} M \langle v^2 \rangle$$

# $C_v$ for diatomics atomic solids, and molecular solids

Principle of energy equipartition:

**Molar energy =  $\frac{1}{2} RT$  per degree of freedom**

gas molecules have 3 translational degrees of freedom (DOF)

$$U_{m,\text{translational}} = (3/2) RT \text{ (if ideal; very close to experiment)}$$

Diatomic gases have 2 rotational DOF and 2 vibrational DOF in addition  
(1 bond has vibrational kinetic energy and potential energy)

Expect  $U = (3 + 2 + 2)RT/2 = (7/2) RT$  and therefore  **$C_v = (7/2) R$**

But, at room temperature  $C_v$  is typically about  **$5/2 RT$  (vibration not involved)**  
at very **high temperature**  $C_v$  is typically about  **$7/2 RT$**  ( all DOF are involved)  
at very **low temperature**  $C_v$  is typically about  **$3/2 RT$**  (only translation is involved)

In ~1912 this was one of the mysteries that pointed to the need for quantum mechanics.

Similar considerations pertain to solids. With just a few simple quantum concepts + the Boltzmann distribution we can understand this behavior later in the semester.