Now we talk about **heat:**

**Zeroth Law of Thermodynamics:**
(inserted after the 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.**

Another way to say it: *Energy always flows from hotter object to a colder object when they are in contact.*

Therefore, energy flowing from hot $\rightarrow$ cold is a *spontaneous* process (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.*

Microscopically does this make sense?
Microscopically does this make sense?

We will learn that Temperature is directly proportional to the average energy PER ATOM.

Higher temperature $\rightarrow$ lower temperature simply means fast atoms lose energy to slow atoms during a collision.

(a very common sense result)
We measure $\Delta T$ in surr.

\[
q = C \Delta T
\]

\[
C = q / \Delta T = J/K
\]

so $\Delta T = q/C$

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

(Very pertinent to Problem 1)

Heat Capacity, $C$

$C$ has the units of J/K

molar heat capacity $= C_m \ JK^{-1} \ mol^{-1}$

specific heat capacity $= c \ JK^{-1} \ kg^{-1}$

but sometimes J g$^{-1}$ K$^{-1}$ (You have to check.)
In reality, $C$ is not constant; it always increases with increasing $T$.

We will almost always assume $C$ is constant, however.
Which has the higher heat capacity, water or gold?

<table>
<thead>
<tr>
<th></th>
<th>Molar Heat Cap. $C_m$ (J mol$^{-1}$K$^{-1}$)</th>
<th>Specific Heat Cap. $c$ (J kg$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>25</td>
<td>129</td>
</tr>
<tr>
<td>Water</td>
<td>75</td>
<td>4184</td>
</tr>
</tbody>
</table>

Why?
Example Calculation
From Table 2.2: water has a specific heat capacity of $c = 4.184 \text{ kJ K}^{-1}\text{kg}^{-1}$

What will be the temperature change in 100 kJ of water if 418 kJ of heat is removed?
( Relates to problem 1: hiker with wet clothes in wind loses body heat)

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

$\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.
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.


When $p_{\text{ext}} = p$ 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 can derive: \[\text{kinetic energy of translation} = (3/2) \ nRT\]
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 \textbf{Boltzmann Constant} multiplied by Avogadro’s number.

\(R = 8.3145 \ \text{J K}^{-1} \ \text{mol}^{-1} = 0.082 \ \text{L atm K}^{-1} \text{mol}^{-1} = 0.083145 \ \text{L bar K}^{-1} \text{mol}^{-1}\)
Derive: kinetic energy of translation of an ideal gas = n(3/2) RT

Pressure \( = p = \text{average force per unit area} \) of a billion billion violent collisions

Volume = Area \times length = A \times c

Velocity in z direction = v_z

\( \text{z-Force} = F_z = \text{mass} \times \text{acceleration} \)

\( F_z = m \frac{dv_z}{dt} = m \frac{\Delta v_z}{\Delta t} \)

\( \Delta v_z = \text{change of } v_z \text{ during collision} = 2 v_z \)

\( \Delta t = \text{length} / \text{velocity} = 2c / v_z \)

\( \langle F_z \rangle = m \frac{2 \langle v_z^2 \rangle}{2c} = m \frac{\langle v_z^2 \rangle}{c} \quad (=2KE/c) \)

Pressure = force/Area: \( p = \langle F_z \rangle / A = m \frac{\langle v_z^2 \rangle}{abc} \)

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

\( abc = V \)

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

Therefore \( p = \frac{2U_z}{V} \)

Multiplying by \( V \) gives: \( pV = 2U_z = \frac{2}{3} U \) (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)

\( U_z = \frac{1}{3} U \) (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 \( pV = nRT = \frac{2}{3} U \) or \( U = \frac{3}{2} nRT \)

Dividing both sides by \( n \) gives the molar translational kinetic energy:

\( U_m = \frac{3}{2} RT \)
\[ p = \frac{2U_z}{V} \quad \text{therefore} \quad pV = 2U_z = \frac{2nU_m}{3} = nRT \]

\[ U_m = \frac{3}{2}RT \]

\[ = \frac{1}{2} M\langle v^2 \rangle \]

where \( M \) = molecular weight
C\textsubscript{v} for diatomics atomic solids, and molecular solids

Principle of energy equipartition:

Molar energy = ½ RT per degree of freedom

gas molecules have 3 translational degrees of freedom (DOF)
U_{m,\text{translational}} = (3/2) RT (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\textsubscript{v} = (7/2) R

But, at room temperature C\textsubscript{v} is typically about 5/2 RT (vibration not involved)
at very high temperature C\textsubscript{v} is typically about 7/2 RT (all DOF are involved)
at very low temperature C\textsubscript{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.