

Next: Allow a system to interact with its surroundings:

Closed: Can exchange energy, but not matter, w/surroundings

Open: Can exchange energy and matter w/surroundings.

How is energy exchanged? As heat ( $q$ ) or work ( $w$ )

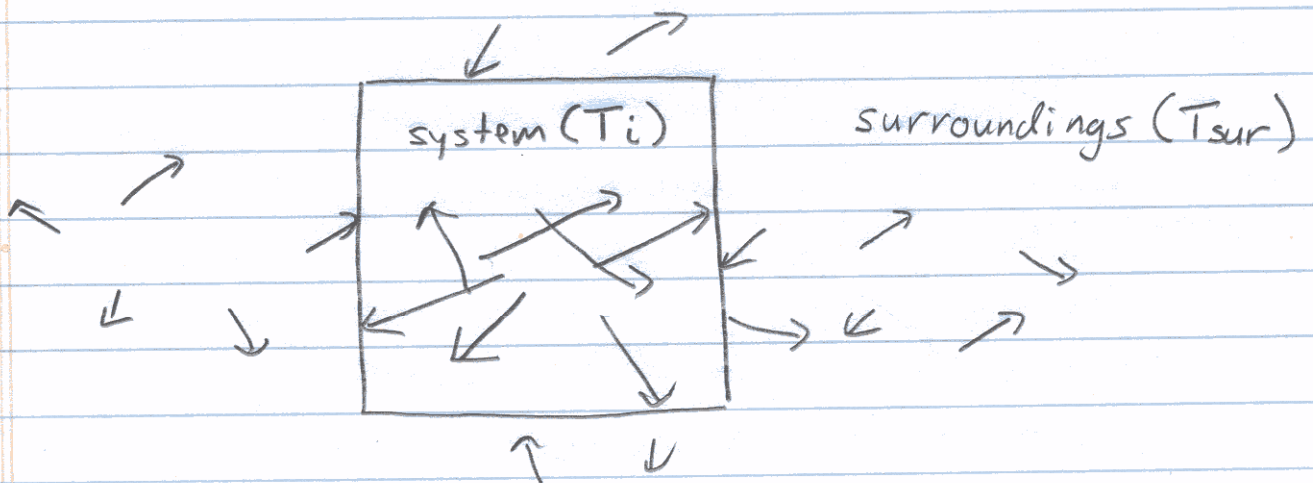
i.e.  $\Delta U_{\text{sys}} = \Delta U = q + w$  (another statement of the 1st Law)

What is  $q$ ?

The transfer of  $E$  due to the random motion of atoms/molecules that causes the  $T$  of a system to match the  $T$  of its surroundings.

(When  $T_{\text{sys}} = T_{\text{surr}}$ , "thermal equilibrium" has been achieved.)

eg Initial state of a system (assumed to be closed)  
(arrows represent average particle velocities)

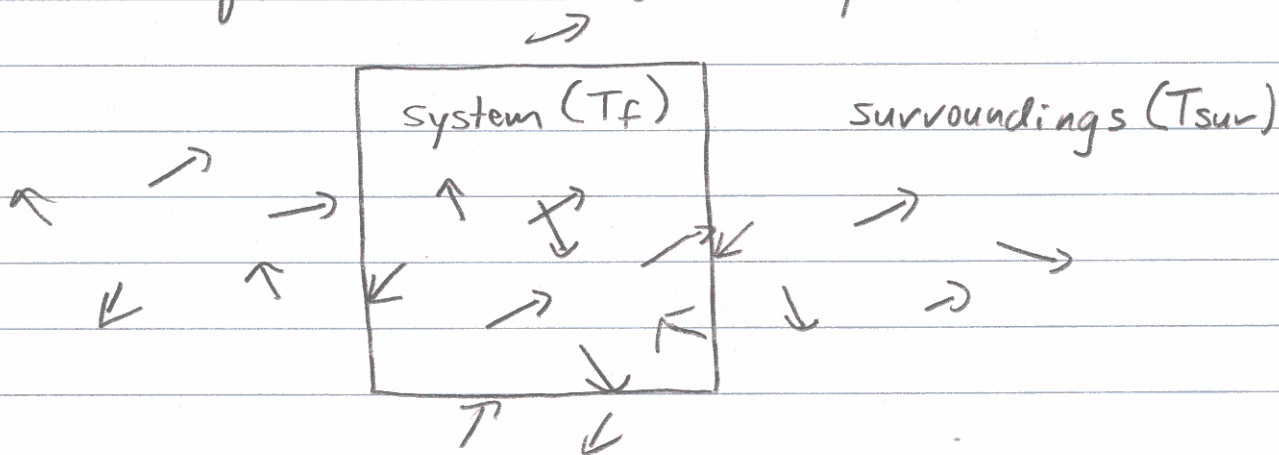


$T_i$  vs.  $T_{sur}$ ?

a microscopic description of  $q$

{ Energy (on average!) is first transferred from the system atoms/molecules to the box's atoms/molecules, which then vibrate with greater amplitude. The surrounding's atoms/molecules then collide with the box, drawing off the extra vibrational energy

Final (equilibrium) state of the system:



At equilibrium,  $T_f = T_{sur}$

$T_{sur}$  is unchanged! The surroundings are assumed to be big enough that the energy it gains from the system causes no measurable increase in temperature.

(energy dispersal! the 2nd Law of Thermo!)

Assume ① no work ( $w=0$ ) and ② no chem rxn ( $\Delta U_c=0$ )

Then  $\Delta U = C \Delta T = q$

Since  $\Delta T = T_f - T_i < 0$ ,  $\Delta U < 0$  and  $q < 0$

(in this e.g.; obviously,  $q > 0$  is also possible)

What is w?

Transfer of  $E$  due to the change in the volume of a system ( $\Delta V_{\text{sys}}$ )

So, why should changing volume have any effect on  $E$ ?

(i) Microscopic / quantum mechanical view:

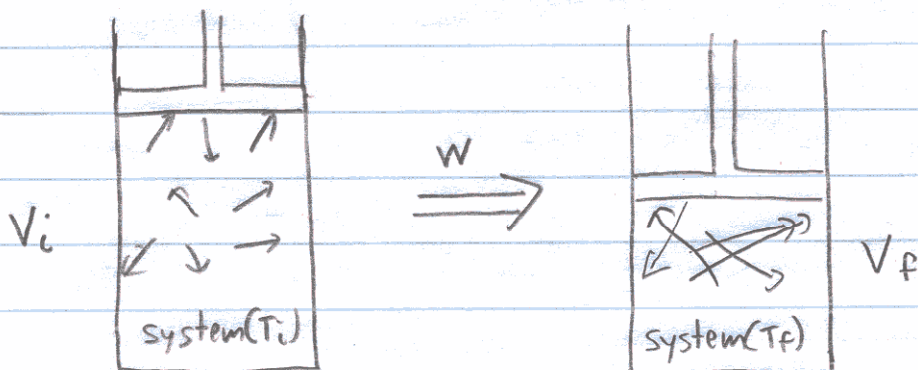
$$E_{\text{trans}} = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8} \left( \frac{1}{mV^{2/3}} \right)$$

(if a particle is a wave, confining it to a smaller volume increases its energy)

(ii) Macroscopic view:

$$w = -P\Delta V \quad (P \text{ is pressure})$$

eg. If  $\Delta V < 0$  (i.e. system gets smaller), the surroundings had to push against the atoms/molecules of the system, giving them more energy in the process:



Assume (1) no heat ( $q=0$ ) (2) no chem rxn ( $\Delta U_c=0$ ).

$$\text{Then } \Delta U = C \Delta T = w = -P \Delta V$$

In above e.g.,  $\Delta V < 0 \Rightarrow w > 0$

$$\Rightarrow \Delta U > 0 \text{ and } \Delta T > 0$$

(consistent w/microscopic view)

## DEMO

Calculating  $w$

- $w = -P \Delta V$  must have units of energy  
 $\begin{matrix} \uparrow & \uparrow \\ \text{bar} & \text{L} \end{matrix}$

$$(1 \text{ atm} = 1.013 \text{ bar})$$

$$\boxed{1 \text{ bar} \cdot \text{L} = 100 \text{ J}} \quad (\text{exactly})$$

- $PV = nRT$  (ideal gas law; Silberberg Chap. 5)

i.e.  $\Delta(PV) = \Delta(nRT)$

$$\boxed{R = 0.08315 \text{ L} \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}$$

In Chem 112, we will always assume  $P$  is constant.

so  $\Delta(PV) = P \Delta V = \Delta(nRT) = \dots ?$