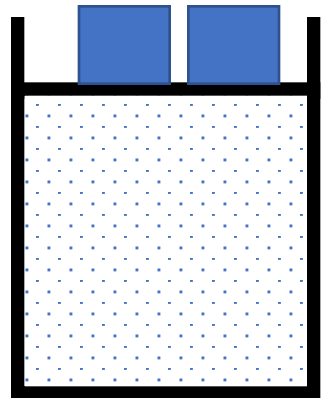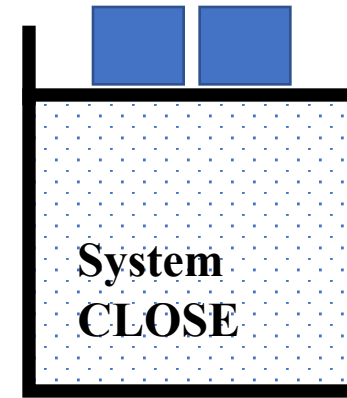# Recap…

System: SYSTEM MUST BE LARGE relative to molecular dimension
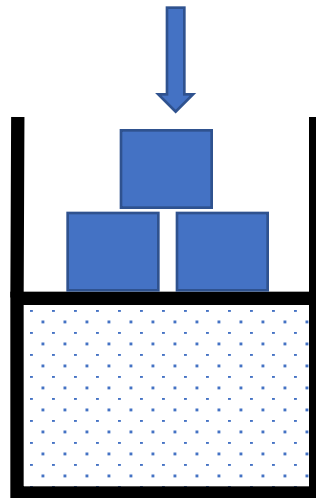
Types of Systems
1. Open
2. Closed
3. Isolated

Properties of the System: at Equilibrium (P, T, V)

System CLOSE

Heat (q)

Work (w)

State function

Path function

1ˢᵗ Law,
$$\Delta U = U2 - U1 = q + w$$

$$W \text{ (PV work)} = -\int_{V_1}^{V_2} P \, dV$$

$PV = n\,R\,T$ **(Experiment)**

n = Number of moles
R = Gas constant = 8.3145 J/mol K

$PV = (N/N_A)\,R\,T$

N = Number of particles
N_A = Avogadro's Number

$$\boxed{PV = N\,K_B\,T}$$

K_B = Boltzmann Constant = R/N_A = 1.38×10^{-23} J/K

Rigorous calculation also end up :
Kinetic energy is a function of "T" only
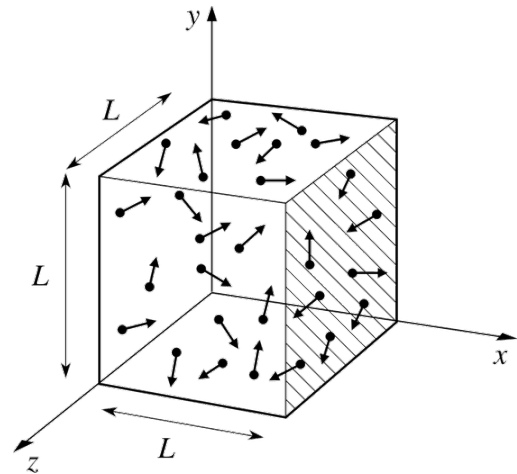

Box of ideal Gas

Target: P ?

Assumptions:
(1) Ideal Gas consist of N point particle
(2) Each particles move with a velocity "v" and mass "m"
(3) N/3 particles moving in each direction

$$F_x = ma = m\frac{dv}{dt} = \frac{d\,(mv)}{dt} = \frac{Change\ in\ momentum}{dt}$$

Change in momentum = 2 mv,
Time for each Collison (dt) = (2L/v)

Force exerted by 1 particle: $\quad F_x = \dfrac{2mv}{\left(\frac{2L}{v}\right)} = \dfrac{mv^2}{L}$

Force exerted by (N/3) particle: $\quad <F_x> = \dfrac{N}{3} * \dfrac{mv^2}{L}$

Pressure: $\quad P = \dfrac{<Fx>}{Area} = \dfrac{\frac{N}{3} * \frac{mv^2}{L}}{L^2} = \dfrac{N}{3} * \dfrac{mv^2}{\boxed{L^3}} = \dfrac{N}{3} * \dfrac{mv^2}{\boxed{V}}$

$$\boxed{P\,V = \frac{N}{3} * mv^2}$$

$$\boxed{\begin{array}{l} \dfrac{N}{3} * mv^2 = N\,K_B\,T \\[2mm] =)\ \dfrac{1}{2}mv^2 = \dfrac{3}{2}K_B\,T \end{array}}$$

Kinetic energy is a function of "T" only
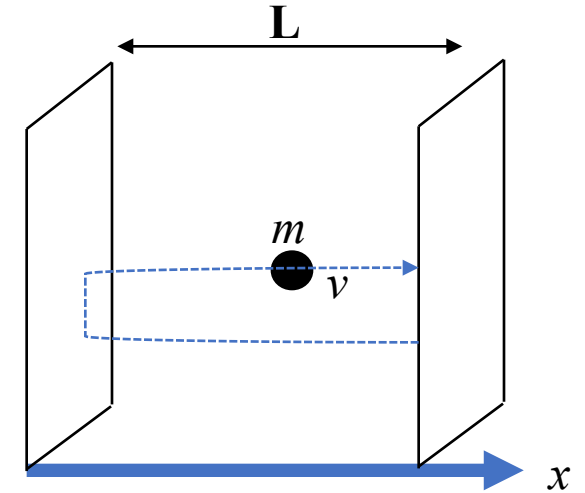
Take home

1. Kinetic energy (KE) of an ideal gas is dependent only on TEMPERATURE
2. Note, U = KE+ PE, but PE = 0 for ideal gas. Internal energy (U) is only "TEMPERATURE DEPENDENT".
3. $\frac{1}{2}mv^2 = \frac{3}{2}K_B\ T$ (ONLY VALID for Kelvin scale)
4. Different gases (DILUTE) have same average kinetic energy irrespective of mass at fixed Temp.
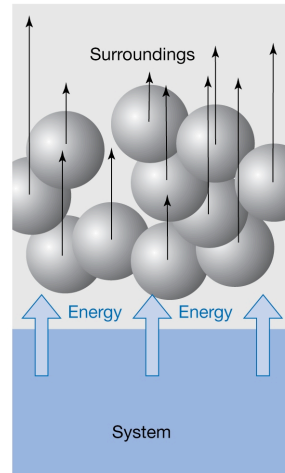
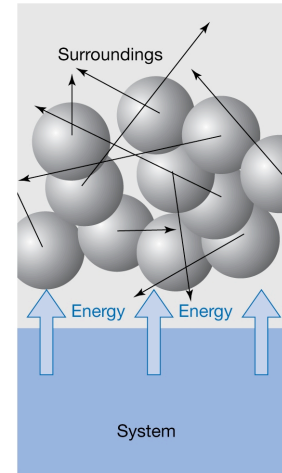# PHYSICAL INTERPRITATION OF HEAT AND WORK

$$\Delta U = Q+W$$

Biological Thermodynamics

Work (W) and Heat (Q)

$$\Delta U = W + Q$$

Work involves the non-random movement of particles

Heat involves the random movement of particles

Energy transfer to the motion of OBJECTS
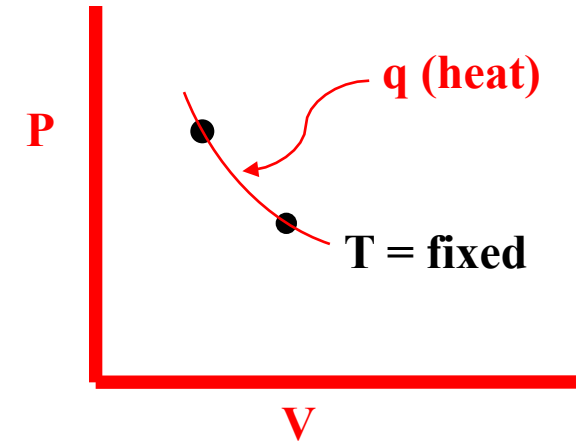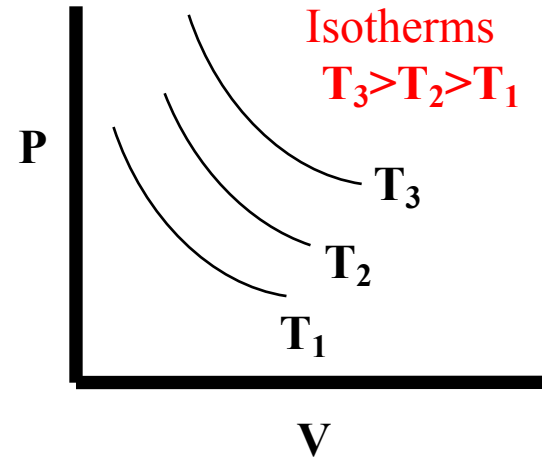
Energy transfer to the motion of ATOMS/
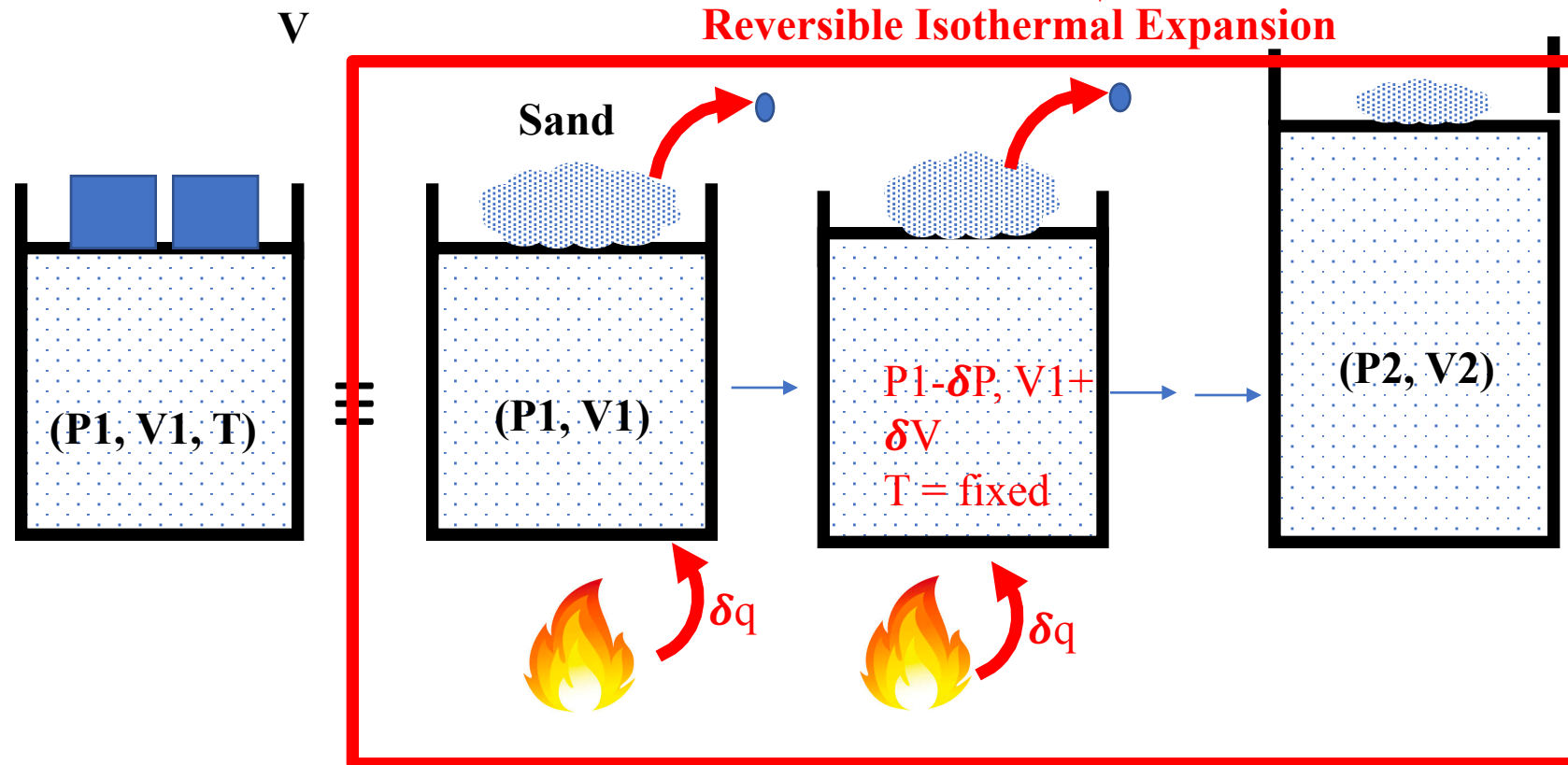
Paths of PV work

1. Isothermal
2. Adiabatic

Paths of PV Work (IDEAL GAS)

Isothermal Expansion

Ideal gas, $PV = nRT =$ **constant**

Isotherms
$T_3 > T_2 > T_1$

P

T_3

T_2

T_1

V

P

q (heat)

T = fixed

V
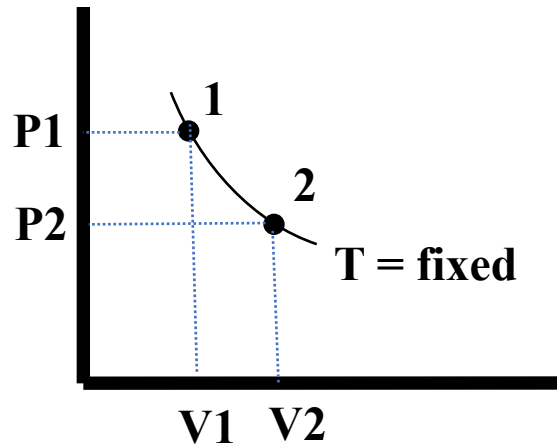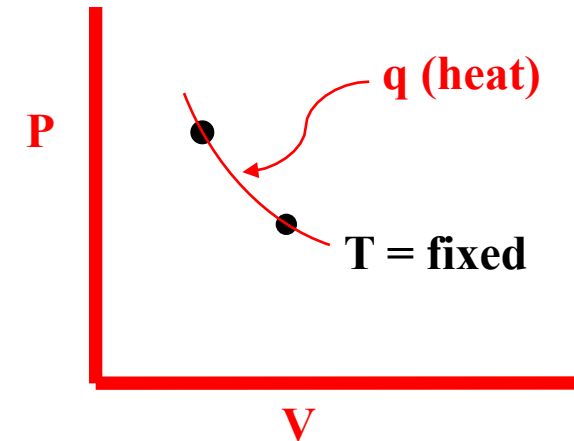
Reversible Isothermal Expansion

Reversible Isothermal Expansion ??

Sand

1

P1

2

P2

T = fixed

V1   V2

(P1, V1, T) $\equiv$ (P1, V1) $\rightarrow$ P1-δP, V1+ δV T = fixed $\rightarrow$ (P2, V2)

δq δq

QUASISTATIC

q (heat)

P

T = fixed

V

Reversible Isothermal Expansion

Sand

REVERSIBLE
(Frictionless Piston)

(P1, V1)

P1-δP, V1+δV
T = fixed

(P2, V2)

δq

δq

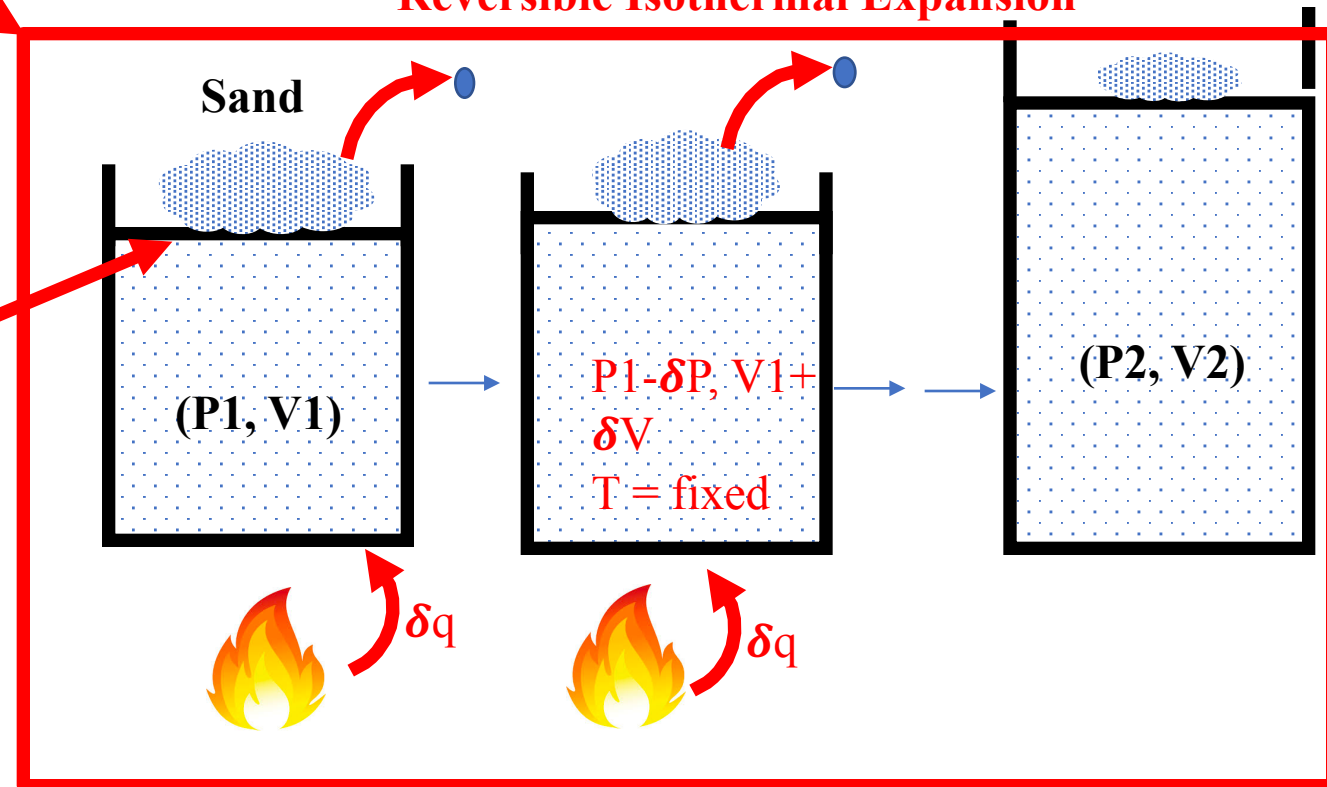Irreversible Isothermal Expansion ??

P1

P2

V2

(P1, V1, T)

(P2, V1, T)

NOT IN THE
PV diagram

(P2, V2, T)
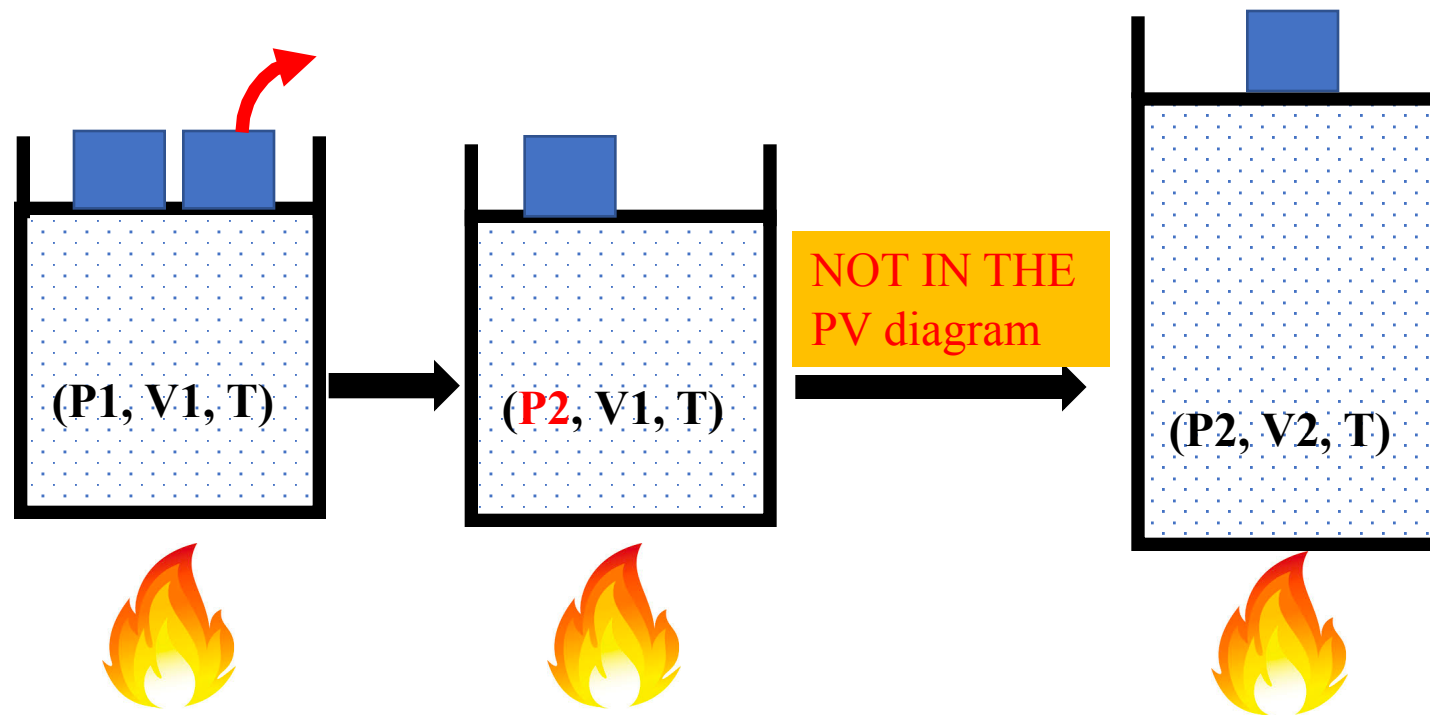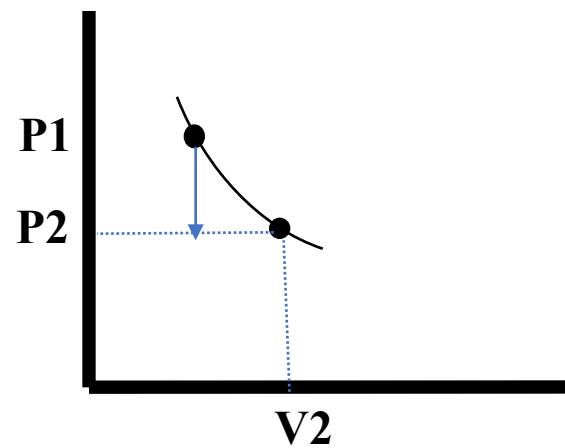
WORK ?

Area Under the PV Curve

P1,V1

P

P2,V2

V

Irreversible

P_1, V_1

P

P_2, V_2

V
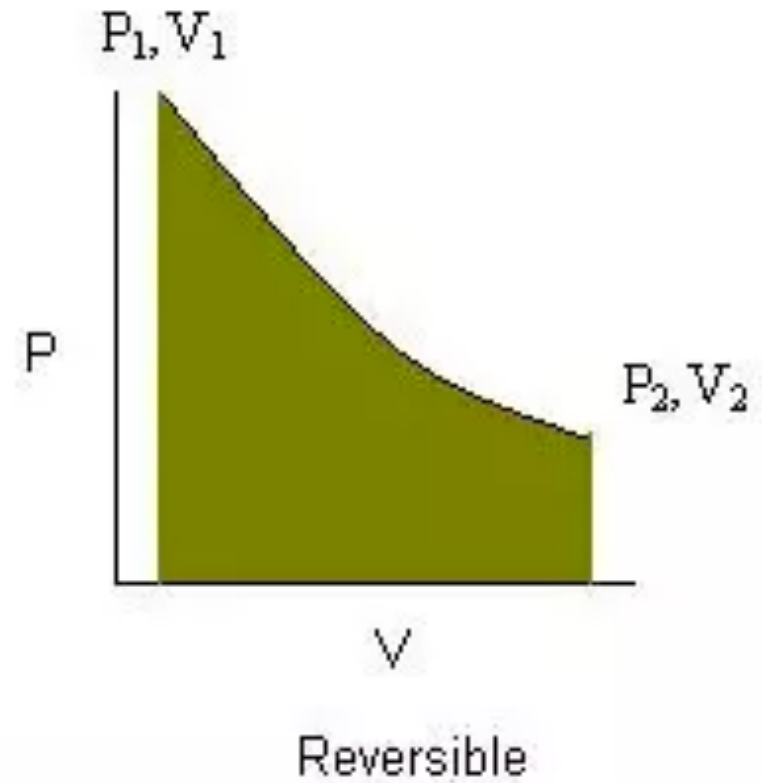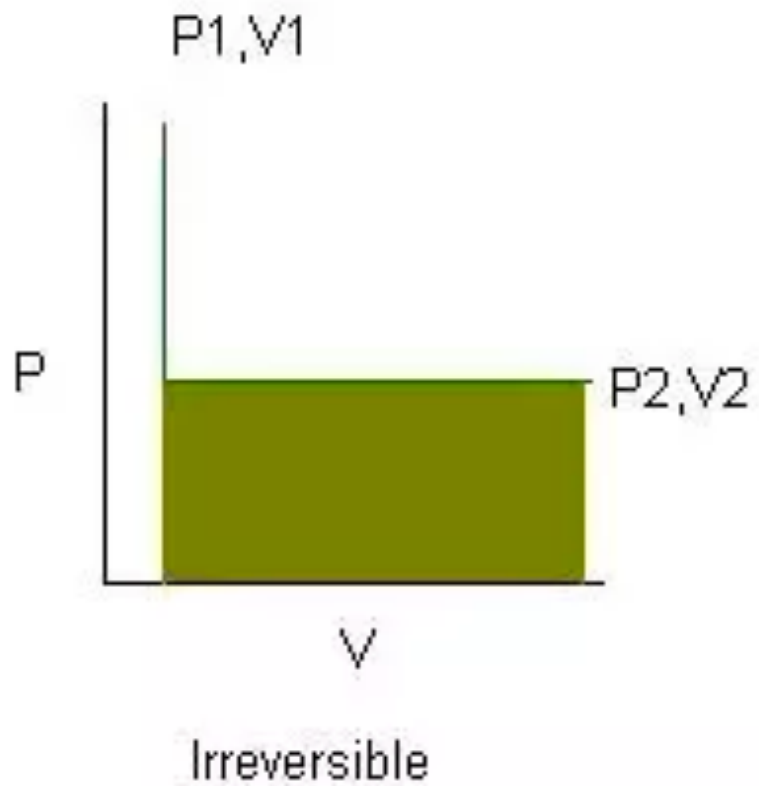
Reversible

WORK depends on the path you take (PATH FUNCTION)

Calculate work done

REVERSIBLE ISOTHERMAL EXPANSION

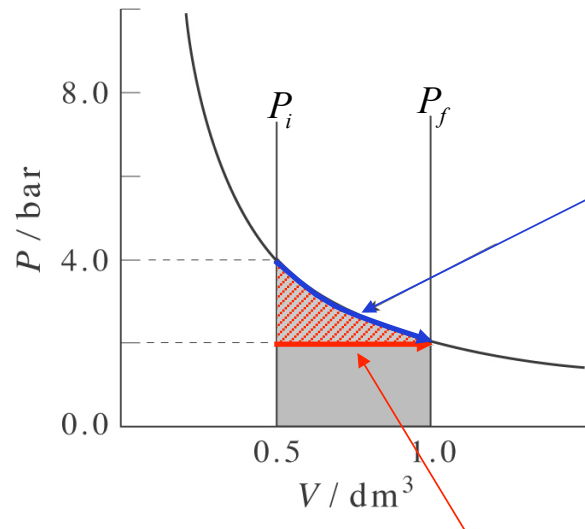For an expansion, *the maximum work is done on the surroundings along the reversible path*. It is the same work (with opposite sign) as that required for compression when traveling in the opposite direction. Thus, it is indeed a *reversible* path.

$$w = -\int_{V_1}^{V_2} P\, dV \quad \text{(Ideal gas, } PV = nRT\text{)}$$

reversible path

$$w_{\text{rev}} = -\int_{V_1}^{V_2} \frac{nRT}{V}\, dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1}$$

$$P_{\text{ext}} = P_f \longrightarrow$$

Constant P_{ext} path with maximum w

Expansion implies $V_2 > V_1$ so work is negative

Irreversible expansion: $W = P_{\text{ext}}(V_2 - V_1)$

REVERSIBILITY AS A LIMIT

Consider three ways to *isothermally* (so $PV = $ constant) expand an ideal gas from 0.5 dm^3 and 4 bar to 1.0 dm^3 and 2 bar.

One step

$w = -100$ J

Two steps

$w = -117$ J

Reversible

$w = -139$ J

1 L.bar = 100 J

HEAT SOURCE NOT SHOWN

REVERSIBLE ISOTHERMAL COMPRESSION

Work *depends on the path* taken from V_1 to V_2. For a compression, *the minimum work is done along the reversible path*. In infinitesimally small steps, P_{ext} is made infinitesimally larger than P_{gas}. Thus, at every step P_{ext} is *equal* to the *equilibrium* gas pressure P_{gas},

$$P_{ext} = P_f \implies$$ Constant P_{ext} path with minimum w

$$w_{rev} = -\int_{V_1}^{V_2} P_{gas}\,dV$$

$$\left(\text{ideal gas}: P_{gas} = \frac{nRT}{V} \right)$$

reversible path

$$w_{rev} = -\int_{V_1}^{V_2} \frac{nRT}{V}\,dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$w_{rev} = -nRT \ln \frac{V_2}{V_1}$$

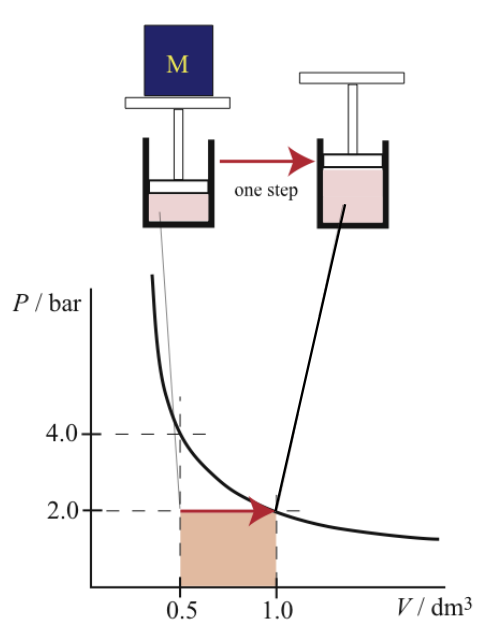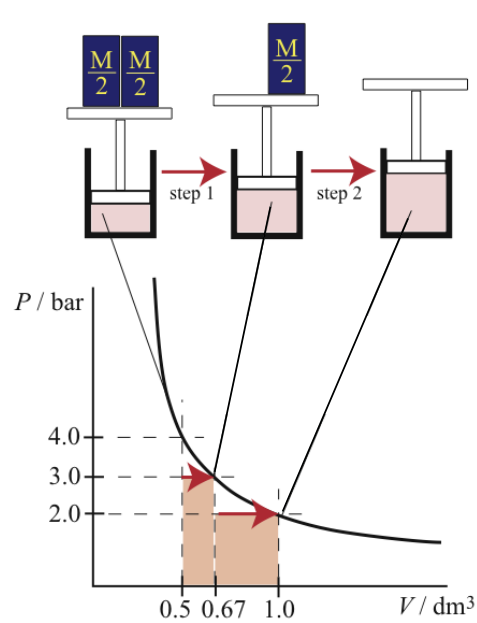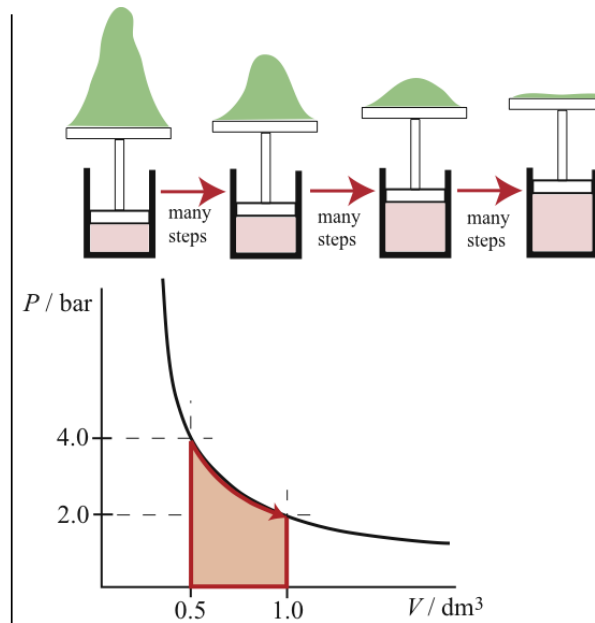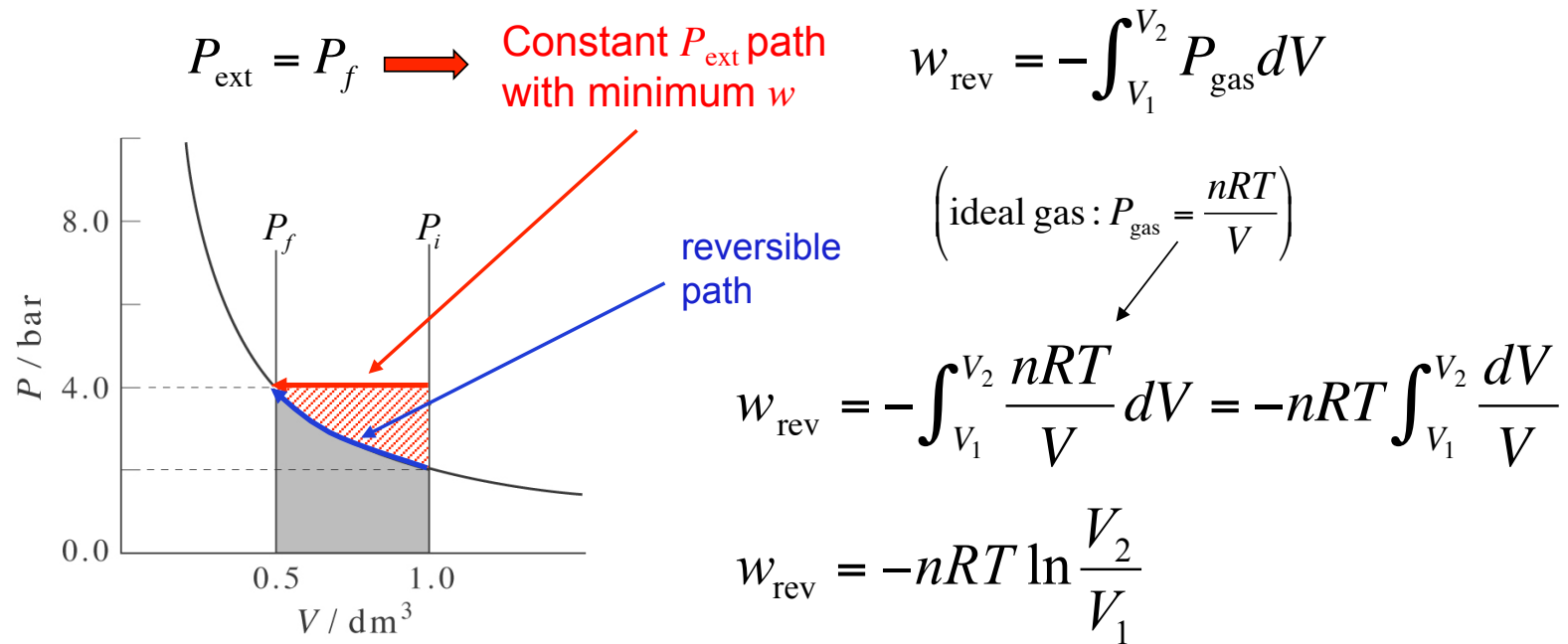Compression implies $V_2 < V_1$ so work is positive, as it should be

First Law and Isothermal expansion (Ideal gas)
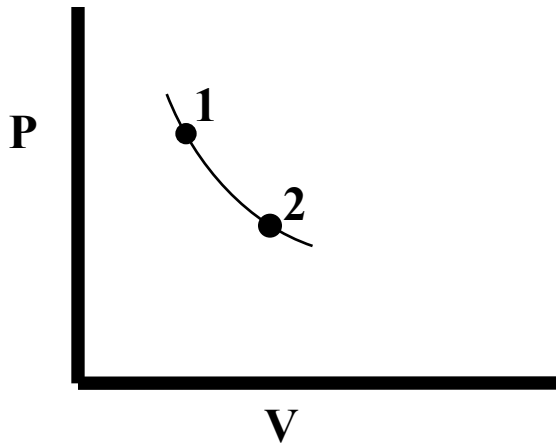
$\Delta U = q + w$ **(No non-mechanical work)**

Isothermal reversible Expansion

IDEAL GAS (Internal energy is a function of Temperature only)

$\Delta U = 0$

=) $0 = q + w$
=) $q = - w$
=) $q = - [-nRT \ln (V2/V1)]$

Makes sense, q = +Ve (heat added)
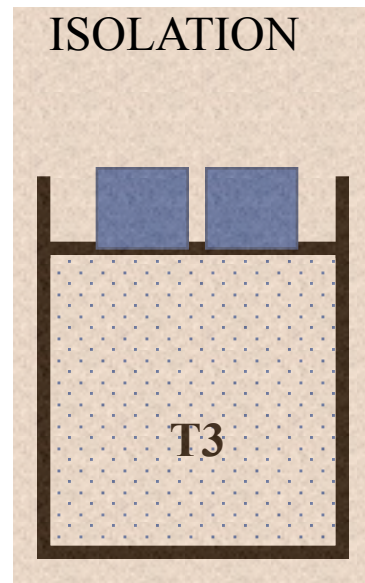   **w = Negative (work is done by the gas)**

What about blooming of flower (Reversible or Irreversible)?

Ans- Irreversible

- Adiabatic Processes
- Enthalpy

Adiabatic Processes

Isotherms
$T_3 > T_2 > T_1$

P

V

T_3

T_2

T_1

T3

ISOLATION

T3
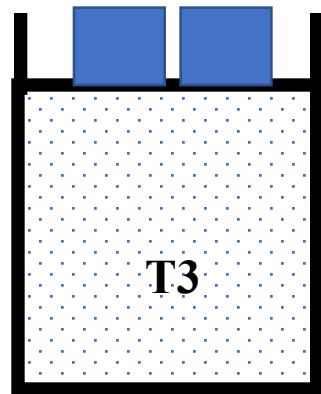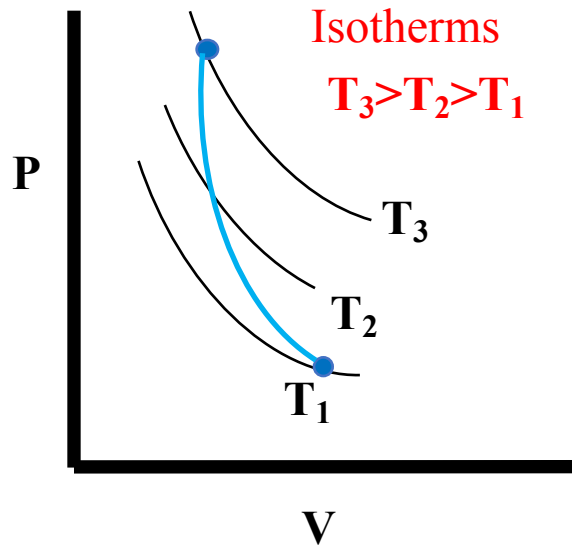
Fly off PV plane
Irreversible

T1

T3

Reversible

1 grain at a time
No heat source

T1
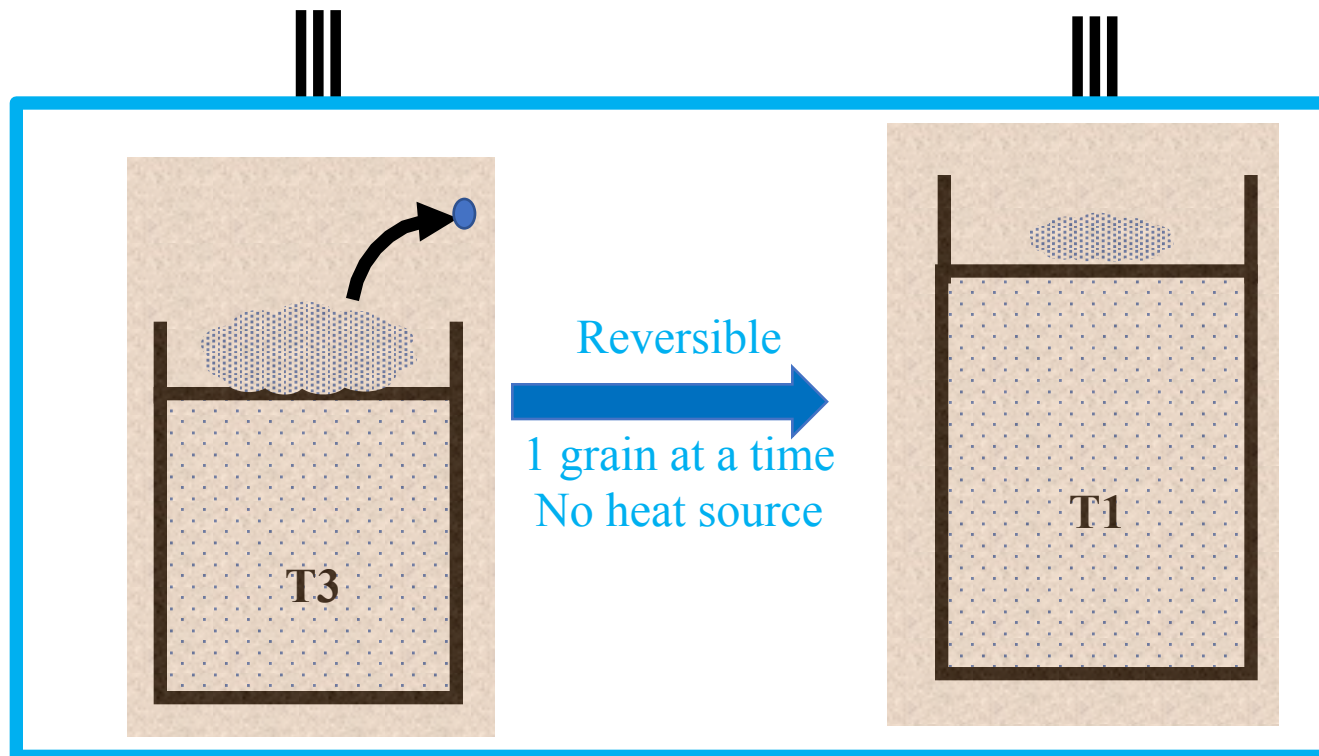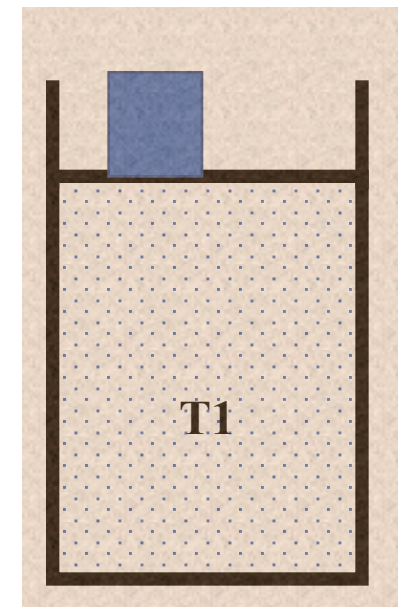
Lets calculate the work done (Adiabatic Processes)
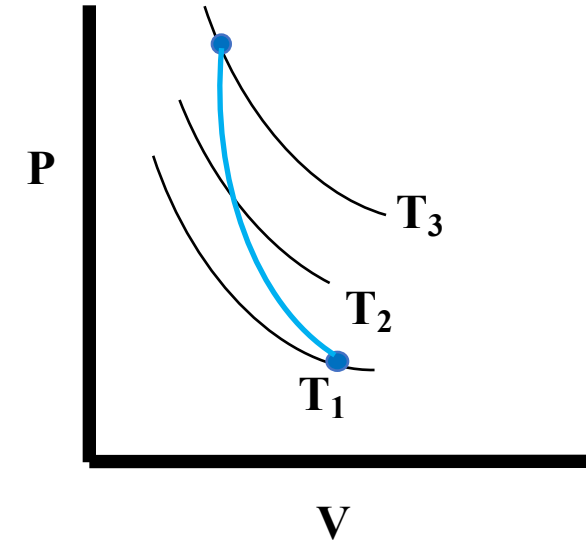
$$w = -\int_{V_1}^{V_2} P \, dV$$

(Ideal gas, PV = nRT, ISOTHERM)

I do not know how "P" vary with "V" along the **blue line** ?

Target : Find the PV relation

We will revisit this soon !

- Enthalpy
- Heat Capacity

Constant Pressure Conditions

For a *reversible* process where the work is restricted to pressure-volume work:

$$\Delta U = q + w = q - \int_{V_1}^{V_2} PdV$$

- At *constant volume* $V_1 = V_2$: $\Delta U = q_V$

  constant volume

> ΔU is the heat at *constant volume* (can be measured using bomb calorimetry)

- However, in chemistry it is often more convenient to work at *constant pressure*, for which the heat is,

$$q_P = \Delta U + P_{\text{ext}} \int_{V_1}^{V_2} dV = \Delta U + P\Delta V$$

So q_P is not equal to ΔU.

constant pressure (not a function of V)

Lay's Classic Potato Chips

Ingredients: Potatoes, Vegetable Oil (Sunflower, Corn and/or Canola Oil), and Salt.

Nutrition Facts
Serving Size 1 oz (28g/About 15 chips)
Amount Per Serving
Calories 160   Calories from Fat 90

Enthalpy: A State Function

At *constant volume*, $q_V = \Delta U$; q_V is a state function

At *constant pressure*, $q_P = \Delta U + P\Delta V$ is also a state function

Define the *enthalpy*: $$H = U + PV \quad \text{(general)}$$

$$dH = dU + PdV + VdP \quad \text{(general)}$$

At *constant pressure*: $$\Delta H = \Delta U + P\Delta V$$

confirming that the more general enthalpy *is* equal to the heat at *constant pressure*, $\Delta H = q_P$

H has the same role at constant P that U has at constant V

ENTHALPY VS INTERNAL ENERGY

Ice (H_2O) melting at 273 K and one atm, q_P = 6.01 kJ•mol^{-1}, so

$$\Delta \overline{H} = q_P = 6.01 \, \text{kJ} \bullet \text{mol}^{-1}$$

273 K molar volumes are solid: $\overline{V}_s = 0.0196 \, \text{L} \bullet \text{mol}^{-1}$ ⎤ *rare*
liquid: $\overline{V}_l = 0.0180 \, \text{L} \bullet \text{mol}^{-1}$ ⎦ *and important!*

What is $\Delta \overline{U}$? $\Delta \overline{U} = \Delta \overline{H} - P\Delta \overline{V}$ (at constant pressure)

$$\Delta \overline{U} = \left(6.01 \, \text{kJ} \bullet \text{mol}^{-1}\right) - \left(1 \, \text{atm}\right)\left(0.0180 \, \text{L} \bullet \text{mol}^{-1} - 0.0196 \, \text{L} \bullet \text{mol}^{-1}\right)$$

$$\Delta \overline{U} = \left(6.01 \, \text{kJ} \bullet \text{mol}^{-1}\right) + \left(1.60 \times 10^{-3} \, \text{L} \bullet \text{atm} \bullet \text{mol}^{-1}\right)\left(\frac{0.008314 \, \text{kJ}}{0.08206 \, \text{L} \bullet \text{atm}}\right) \approx 6.01 \, \text{kJ} \bullet \text{mol}^{-1}$$

$$\Delta \overline{U} \approx 6.01 \, \text{kJ} \bullet \text{mol}^{-1}$$

Because ΔV is *very* small, $P\Delta V$ is also very small, and so
there is neglibgible difference between ΔH and ΔU

ENTHALPY VS INTERNAL ENERGY

Water (H_2O) boiling at 373 K and one atm, q_P = 40.7 kJ•mol^{-1}, so

$$\Delta\overline{H} = q_P = 40.7 \text{ kJ} \bullet \text{mol}^{-1}$$

373 K molar volumes are   gas: $\overline{V}_g = 30.6 \text{ L} \bullet \text{mol}^{-1}$

liquid: $\overline{V}_l = 0.0180 \text{ L} \bullet \text{mol}^{-1}$

What is $\Delta\overline{U}$? $\Delta\overline{U} = \Delta\overline{H} - P\Delta\overline{V}$ (at constant pressure)

$$\Delta\overline{U} = \left(40.7 \text{ kJ} \bullet \text{mol}^{-1}\right) - \left(1 \text{ atm}\right)\left(30.6 \text{ L} \bullet \text{mol}^{-1} - 0.0180 \text{ L} \bullet \text{mol}^{-1}\right)$$

$$\Delta\overline{U} = \left(40.7 \text{ kJ} \bullet \text{mol}^{-1}\right) - \left(30.58 \text{ L} \bullet \text{atm} \bullet \text{mol}^{-1}\right)\left(\frac{0.008314 \text{ kJ}}{0.08206 \text{ L} \bullet \text{atm}}\right) = 37.6 \text{ kJ} \bullet \text{mol}^{-1}$$

$$\Delta\overline{U} = 37.6 \text{ kJ} \bullet \text{mol}^{-1}$$

The ΔU term relates to the energy to overcome *intermolecular forces* in the liquid, the ΔH term is *larger* as it includes the $P\Delta V$ expansion work on going from liquid to vapor

Take Home

- $\Delta \overline{U} \sim \Delta \overline{H}$.   (Liquid/Solid phase)
- $\Delta \overline{U} \neq \Delta \overline{H}$.   (if Gas is involved. CAREFUL)
- Measure Heat of a process and assign the value of $\Delta \overline{U}$ and $\Delta \overline{H}$

Next: Heat Capacity, Adiabatic Workdone Thermochemistry , Standard Enthalpy