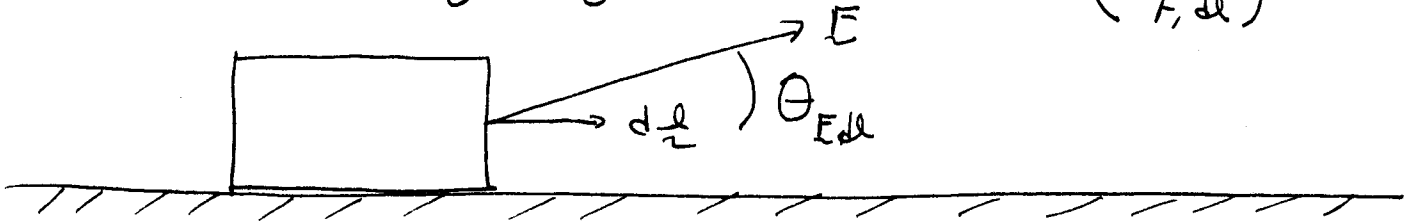


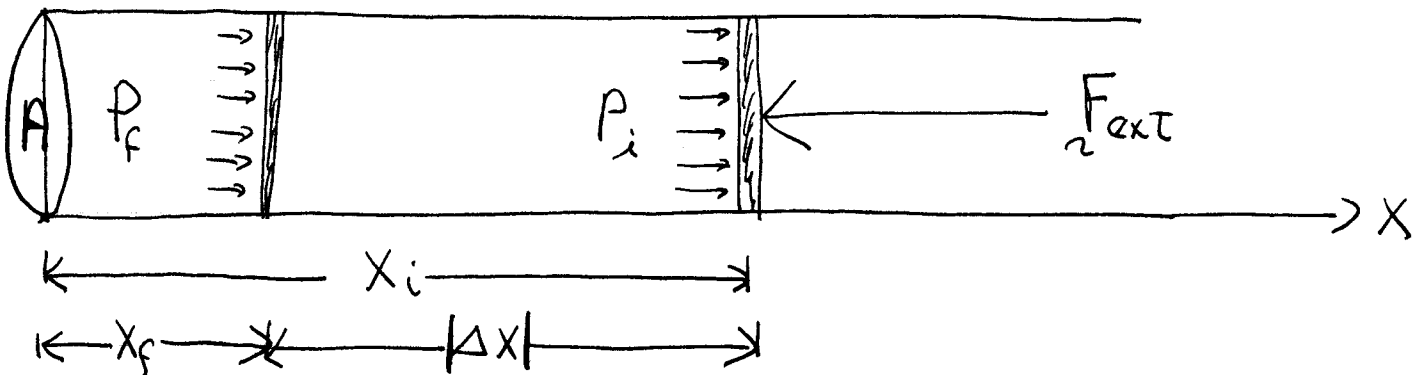
WORK

FROM CLASSICAL MECHANICS, WORK ON A SYSTEM BY A FORCE \vec{F} IS

$$dW \equiv \vec{F} \cdot d\vec{\ell} = |\vec{F}| |d\vec{\ell}| \cos(\theta_{F, d\vec{\ell}})$$



LET US CONSIDER A GAS CONTAINED IN A CYLINDER BY A CONSTANT EXTERNAL FORCE.



IN A COMPRESSION \vec{F}_{ext} IS IN THE SAME DIRECTION AS Δx . THUS

$$\cos(\theta_{F, d\vec{\ell}}) = \cos(0) = 1,$$

AND WE HAVE

$$\Delta W = |F_{ext}| |\Delta x|$$

BUT IN A COMPRESSION $\Delta X < 0$, THUS WE CAN WRITE

$$\Delta W = - |F_{\text{ext}}| \Delta X$$

SINCE $|\Delta X| = -\Delta X$.

IN AN EXPANSION, THE ANGLE BETWEEN \vec{F}_{ext} AND $d\vec{l}$ IS π , AND $\cos(\theta_{\vec{F}, d\vec{l}}) = -1$. MOREOVER, IN THIS CASE $\Delta X > 0$. THUS WE HAVE

$$\begin{aligned} \Delta W &= - |F_{\text{ext}}| |\Delta X| \\ &= - |F_{\text{ext}}| \Delta X. \end{aligned}$$

NOTICE THAT THE FORCE HAS TO CONSTRAIN THE GAS INTO THE PISTON. OTHERWISE, WE DO NOT HAVE A SYSTEM.

WE CAN SAY THAT \vec{F}_{ext} IS A POSITIVE IF CONSTRAINS THE GAS INTO THE CYLINDER AND NEGATIVE IF IT DOES NOT. IN THIS CASE, WE WILL NEVER HAVE A SYSTEM AT EQUILIBRIUM, NO MATTER HOW LONG WE WAIT.

IF WE CONSIDER THE AREA, A , OF THE PISTON

$$\Delta W = - \left(\frac{|F_{\text{ext}}|}{A} \right) A \Delta X.$$

BUT $|F_{\text{ext}}|/A = P_{\text{ext}}$ AND $A \Delta X = \Delta V = V_f - V_i$.
THE FINAL EXPRESSION FOR P-V WORK IS GIVEN BY

$$\Delta W = - P_{\text{ext}} \Delta V.$$

NOTICE THAT $\Delta W > 0$ ON A COMPRESSION ($V_f < V_i$)
AND $\Delta W < 0$ IN AN EXPANSION ($V_f > V_i$).

THE UNITS WILL BE

$$\text{atm} \cdot \text{L} = 1.013 \times 10^5 \text{ newton m}^{-2} (10^{-3} \text{ m}^3)$$

$$\text{atm} \cdot \text{L} = 101.3 \text{ newton m} = 101.3 \text{ J}$$

IF WE NOW CONSIDER INFINITESIMAL DISPLACEMENTS, WE GET AN EXPRESSION FOR INFINITESIMAL WORK

$$dW = - P_{\text{ext}} dV,$$

WHERE dW STANDS FOR AN INCOMPLETE DIFFERENTIAL.

HEAT (FORM OF ENERGY)

FOR A SYSTEM $q > 0 \Rightarrow \Delta T > 0$

$$q < 0 \Rightarrow \Delta T < 0$$

$$1 \text{ g H}_2\text{O} \leftrightarrow 1 \text{ cal} \Rightarrow \Delta T = 1^\circ\text{C}$$

$$1 \text{ cal} = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$$

$$q \equiv C \Delta T$$

$$C = \frac{\Delta q}{\Delta T}$$

$$C = \frac{dq}{dT}$$

$$dq = C dT$$

$$q = \int_{T_i}^{T_f} C(T) dT$$

$C \rightarrow C_p$ CONSTANT P

C_v CONSTANT V

$$C_p = \lim_{\Delta T \rightarrow 0} \left(\frac{q_p}{\Delta T} \right)$$

$$C_v = \lim_{\Delta T \rightarrow 0} \left(\frac{q_v}{\Delta T} \right)$$

$$C_p > C_v$$

AT $P = \text{CONST}$ THE SYSTEM NEEDS TO DO WORK AND INCREASE ITS TEMPERATURE SO

$$q_p > q_v$$

FOR THE SAME FINAL TEMPERATURE.

ALTHOUGH

$$\Delta q \neq q_f - q_i = \int_i^f dq$$

AND

$$\Delta w \neq w_f - w_i = \int_i^f dw$$

THE COMBINATION

$$\begin{aligned}\Delta U &= \Delta q + \Delta w = U_f - U_i \\ &= \int_i^f dU\end{aligned}$$

REVERSIBLE PROCESS \Rightarrow THAT THE SYSTEM

AND ITS SURROUNDINGS ARE

IN THERMAL EQUILIBRIUM

\Leftrightarrow QUASI STATIONARY

STATE FUNCTION OR PATH INDEPENDENT FUNCTION

DEFINITION
IF ΔU DEPENDS ONLY ON THE INITIAL AND FINAL CONDITIONS, U IS A STATE FUNCTION

$$\Delta U = \int_i^f dU = U_f - U_i$$

COROLLARY $\Delta U = 0$ FOR A CLOSED PATH.

$$\Delta U = \oint dU = 0$$

WORK AND HEAT ARE NOT STATE FUNCTIONS

BUT

$$q + w = \Delta U$$

IS A STATE FUNCTION.

CORIC

ISOBARIC PROCESSES

A FOR CONSTANT V PROCESSES, $\Delta V = 0$.
THUS

$$W = 0$$

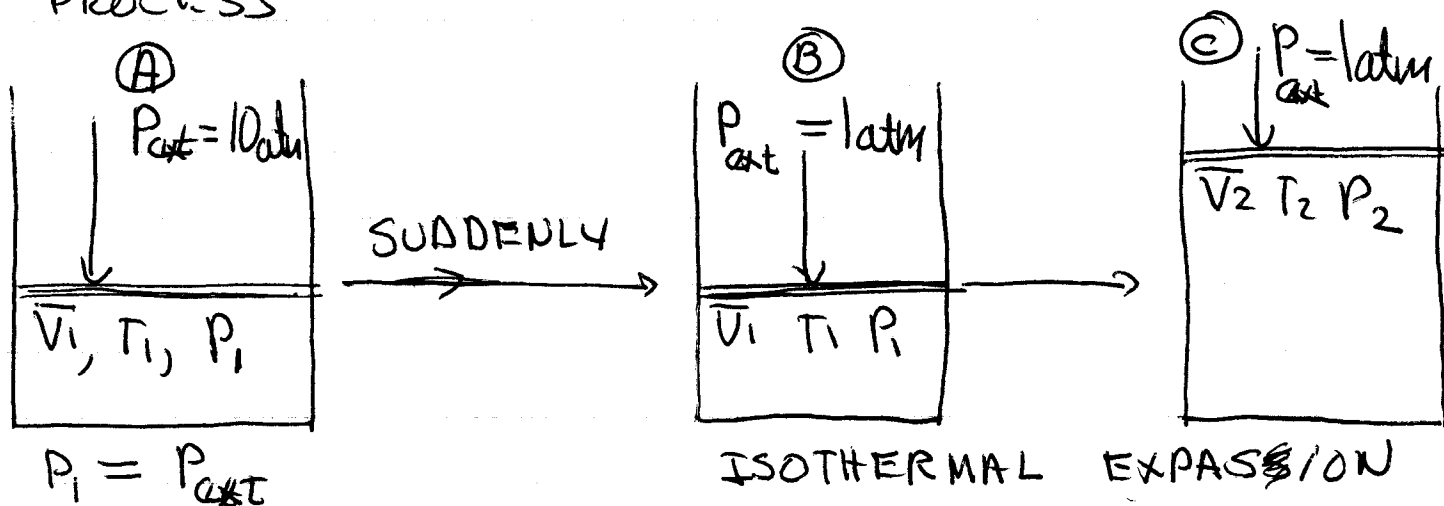
AT CONSTANT VOLUME.

B ISOTHERMAL PROCESSES (T CONSTANT)

LET US CONSIDER AN IDEAL (PERFECT) GAS
UNDER AN IRREVERSIBLE EXPANSION

B. - ISOTHERMAL PROCESS

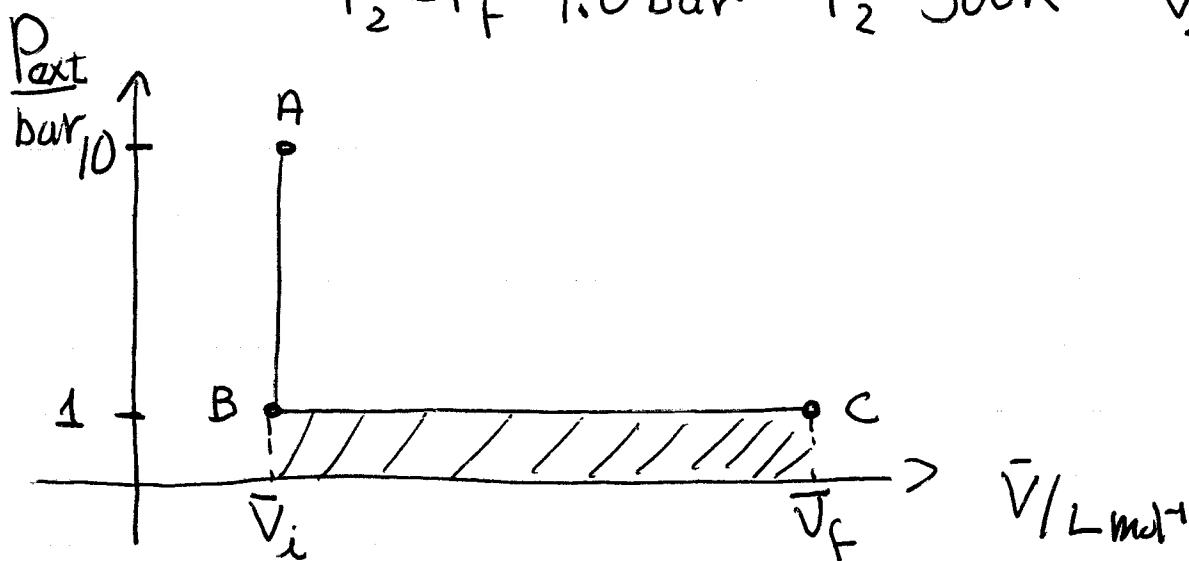
LET US CONSIDER AN IDEAL GAS AN IRREVERSIBLE PROCESS



PATH 1

$$P_i = P_1 = 10 \text{ bar} \quad T_1 = 300 \text{ K} \quad \bar{V}_1 = 2.46 \text{ L mol}^{-1}$$

$$P_2 = P_f = 1.0 \text{ bar} \quad T_2 = 300 \text{ K} \quad \bar{V}_2 = 24.6 \text{ L mol}^{-1}$$



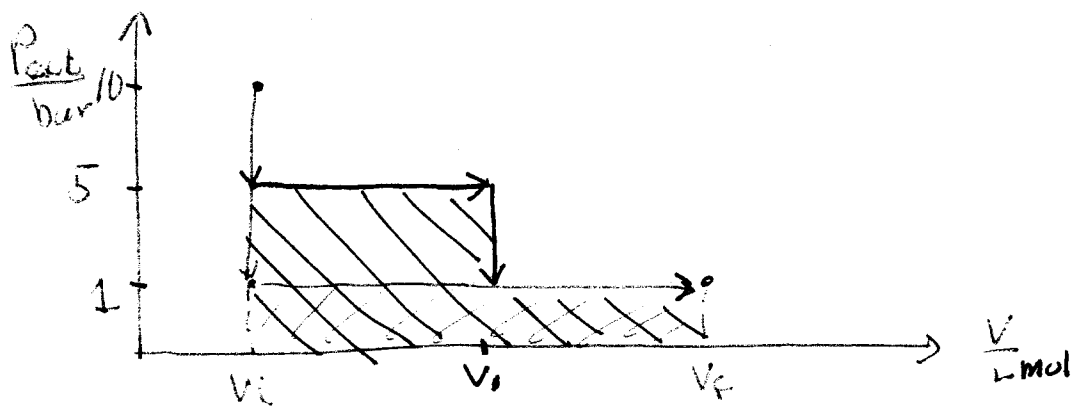
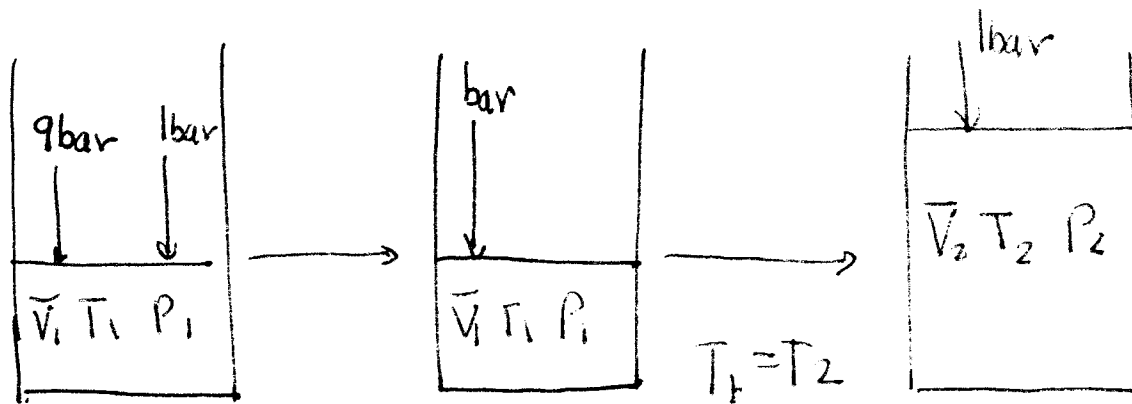
THE GAS EXPANDS AND THE WORK AGAINST THE EXTERNAL PRESSURE

$$\int dW = - \int_{\bar{V}_i}^{\bar{V}_f} P_{ext} d\bar{V} = - P_{ext} (\bar{V}_f - \bar{V}_i)$$

WORK

$$W = \int \delta w = - \int_{V_i}^{V_f} P_{\text{ext}} dV$$

ISOTHERMAL EXPANSION



PATH 1

$$V_i = 2.46 \text{ L}$$

$$V_f = 24.6 \text{ L}$$

$$V_o = 4.92 \text{ L}$$

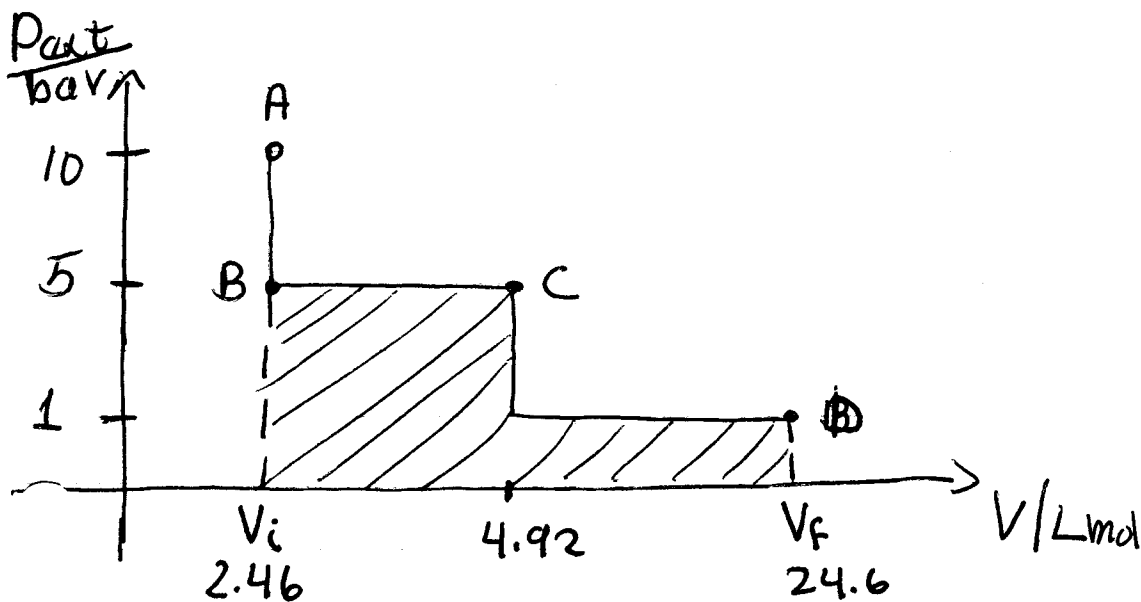
$$W_1 = - P_{\text{ext}} (V_f - V_i)$$

$$W_2 = - 5 \text{ bar} (4.92 - 2.46) \frac{\text{L}}{\text{mol}} - 1 \text{ bar} (24.6 - 4.92) \frac{\text{L}}{\text{mol}}$$

$$W_2 = - 32.0 \frac{\text{bar L}}{\text{mol}}$$

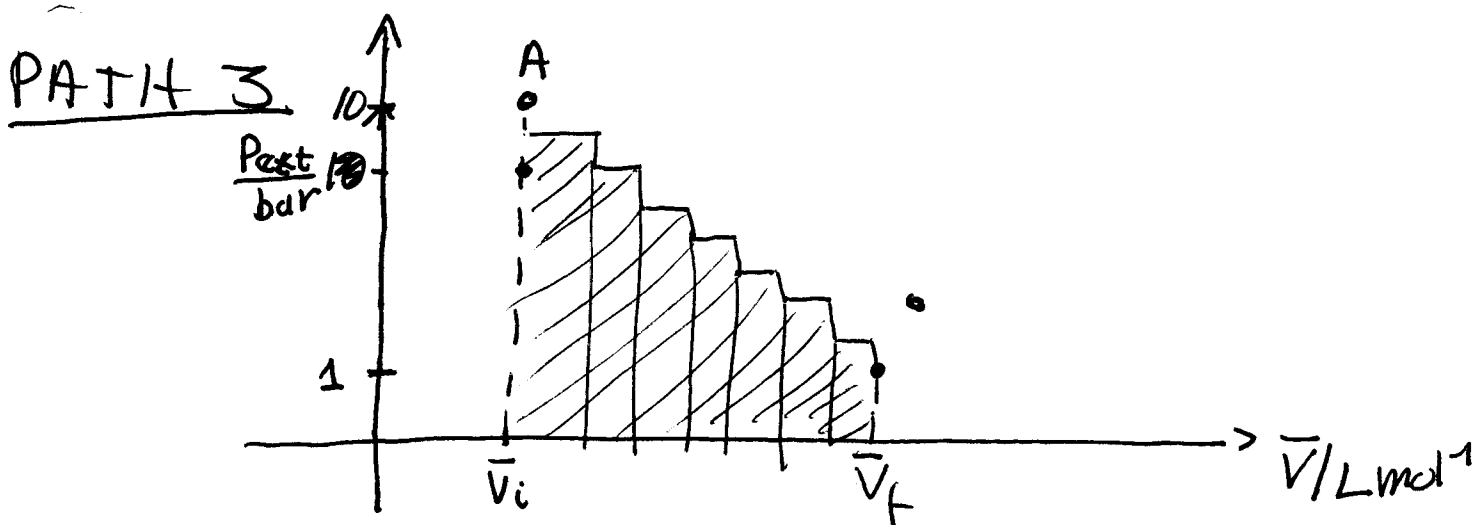
$$\int dw = -1 \text{ bar} (24.6 - 2.46) \frac{\text{L}}{\text{mol}} = -22.1 \text{ bar L mol}^{-1}$$

PATH 2



$$\int dw = w = -5 \text{ bar} (4.92 - 2.46) \text{ L mol}^{-1} \\ - 1 \text{ bar} (24.6 - 4.92) \frac{\text{L}}{\text{mol}} = -32.0 \text{ bar L mol}^{-1}$$

REMEMBER, PV WORK IS THE AREA UNDER THE CURVE IN A P vs V PLOT



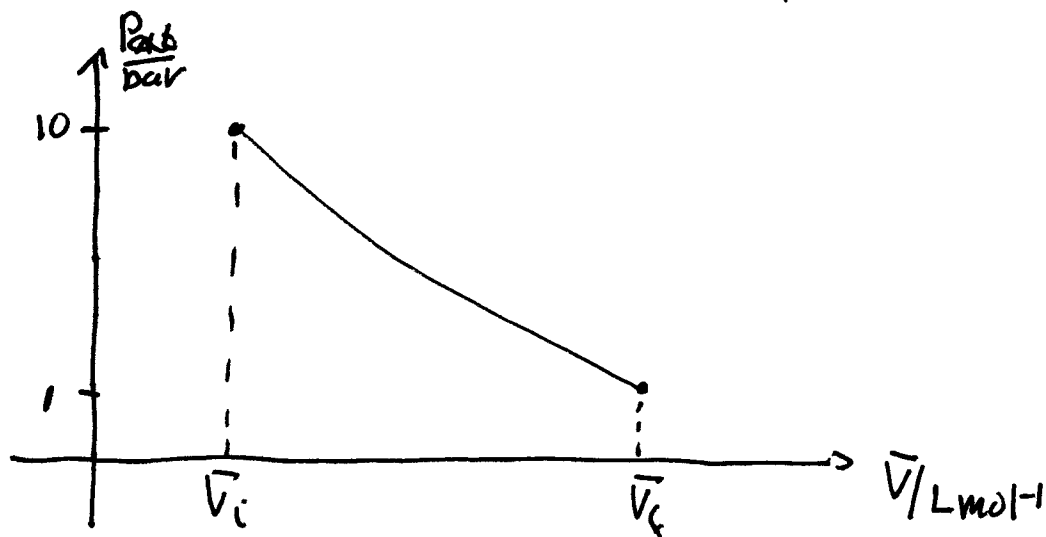
$$W = \sum P_{\text{ext},i} \Delta \bar{V}_i$$

PATH 4

ISOTHERMAL REVERSIBLE EXPANSION

$$\delta W = -P_{\text{ext}} d\bar{V} = -P d\bar{V}$$

WHERE P IS THE GAS PRESSURE.



WE CHANGE P_{ext} VERY SLOWLY
 $P_{\text{ext}} \rightarrow P_{\text{gas}} - \delta P$
 $\bar{V}_i \rightarrow \bar{V}_i + \delta \bar{V}$

CONSIDER A BUCKET FULL OF SAND, AND NOW REMOVE A GRAIN OF SAND AT THE TIME.

$$W_{\text{REV ISO}} = - \int_{V_i}^{V_f} P_{\text{ext}} dV = - \int_{V_i}^{V_f} P dV = - RT \int_{V_i}^{V_f} \frac{dV}{V}$$

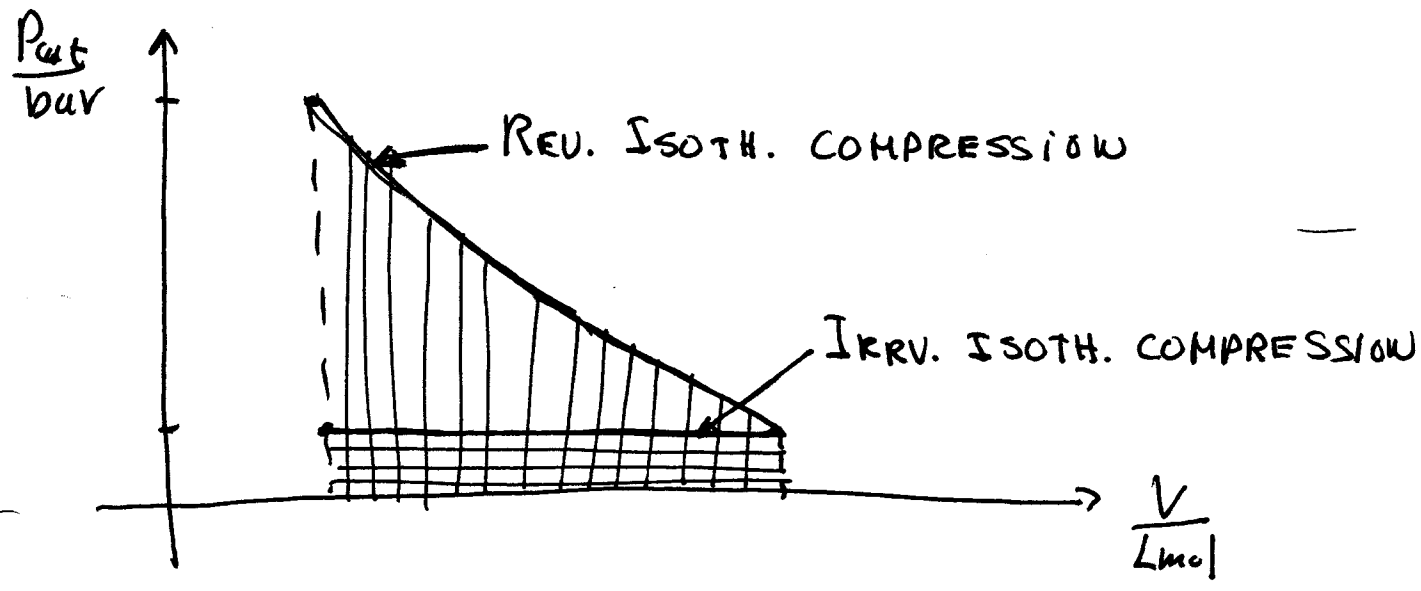
↑ REVERSIBLE
↑ ISOTHERMAL

$$W_{\text{REV ISO}} = - RT \ln(V_f/V_i)$$

$$W = - 0.082 \frac{\text{bar L}}{\text{mol K}} 300 \text{ K} \ln(10) = - 56.6 \frac{\text{bar L}}{\text{mol}}$$

$$-W_{\text{REV}} > -W_{\text{IRREV}}$$

THE MAXIMUM WORK ON THE SURROUNDINGS IS REVERSIBLE WORK.



A REVERSIBLE PROCESS IS ONE IN WHICH THE SYSTEM THROUGHOUT THE PROCESS IS NEVER MORE THAN INFINITESIMALLY REMOVED FROM A STATE OF THERMODYNAMIC EQUILIBRIUM

IN OUR EXAMPLE

$$P_{\text{ext}} \rightarrow P_{\text{gas}} - \delta P.$$

SINCE THE SYSTEM IS ALWAYS IN EQUILIBRIUM WITH ITS SURROUNDINGS, WE HAVE

$$P_{\text{ext}} = P_{\text{system}} = P.$$

THE REVERSIBLE CONDITION FACILITATES THE CALCULATION OF WORK

$$W = - \int_{V_i}^{V_f} P_{\text{ext}} dV = - \int_{V_i}^{V_f} P_{\text{sys}} dV \equiv W_{\text{REV.}}$$

$$= -R \int_{V_i}^{V_f} T \frac{dV}{V} = -RT \int_{V_i}^{V_f} \frac{dV}{V} = -RT \ln \left(\frac{V_f}{V_i} \right)$$

IDEAL GAS
FOR AN REVERSIBLE ISOTHERMAL EXPANSION

$$W_{\text{REV}} = -RT \ln \left(\frac{V_f}{V_i} \right).$$

IN A P vs V PLOT THE AREA UNDER THE CURVE IS EQUAL TO $-W$. THEREFORE

$$-W_{\text{REV}} > -W_{\text{IRREV}}$$

A REVERSIBLE PROCESS IS A SEQUENCE OF EQUILIBRIUM STATES, AND AN INFINITESIMAL CHANGE COULD MOVE THE SYSTEM EITHER FORWARD AND BACKWARDS.