

DO NOT NEED PV DIAGRAM ONLY

COULD MAKE DIAGRAM FOR ANY 2

$$(P, V)$$

$$(P, T)$$

$$(V, T)$$

FOR EXAMPLE $PV^\gamma = \text{CONST}$ → ADIABATIC

USE $PV = NKT \rightarrow P = NK \frac{T}{V}$

SO $PV^\gamma \rightarrow NK \frac{T}{V} \cdot V^\gamma = \text{CONST}$

$\underbrace{NK}_{\text{CONST}} T V^{\gamma-1} = \text{CONST}$

$$\gamma = \frac{f+2}{2}$$

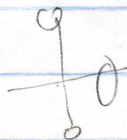
$$TV^{\gamma-1} = \text{CONST}$$

$f=1$ FOR MONATOMIC

$$TV^{\frac{2}{3}} = \text{CONST}$$

$$\gamma = \frac{5}{3}$$

$$(\gamma-1) = \frac{2}{3}$$



ACTUALLY CAN DO DIRECTLY FROM ENERGY

had $U = \frac{3}{2} NKT$

so $\Delta U = \frac{3}{2} Nk \Delta T$

& also $\Delta U = -P \Delta V$

$$\frac{3}{2} Nk \Delta T = -P \Delta V$$

put $P = \frac{NkT}{V}$ in here

$$\frac{3}{2} Nk \Delta T = - NkT \frac{\Delta V}{V}$$

$$\frac{3}{2} \frac{\Delta T}{T} = - \frac{\Delta V}{V}$$

$$\frac{3}{2} \ln T + \ln V = \text{const}$$

← of $\int$ ed.

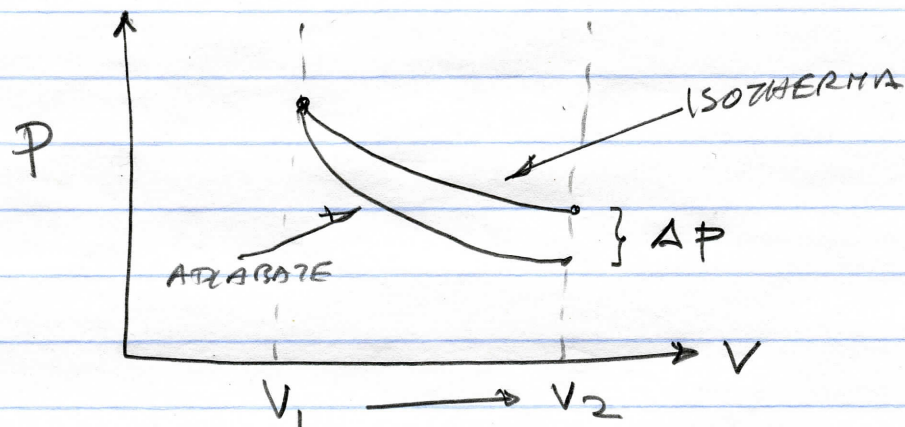
$$\ln T^{3/2} + \ln V = \text{const}$$

Same as
other

$$\Rightarrow T^{3/2} \cdot V = \text{const}$$

$$T V^{2/3} = \text{const.}$$

COMPARISON OF ISOTHERMAL ↓ ADIABATIC

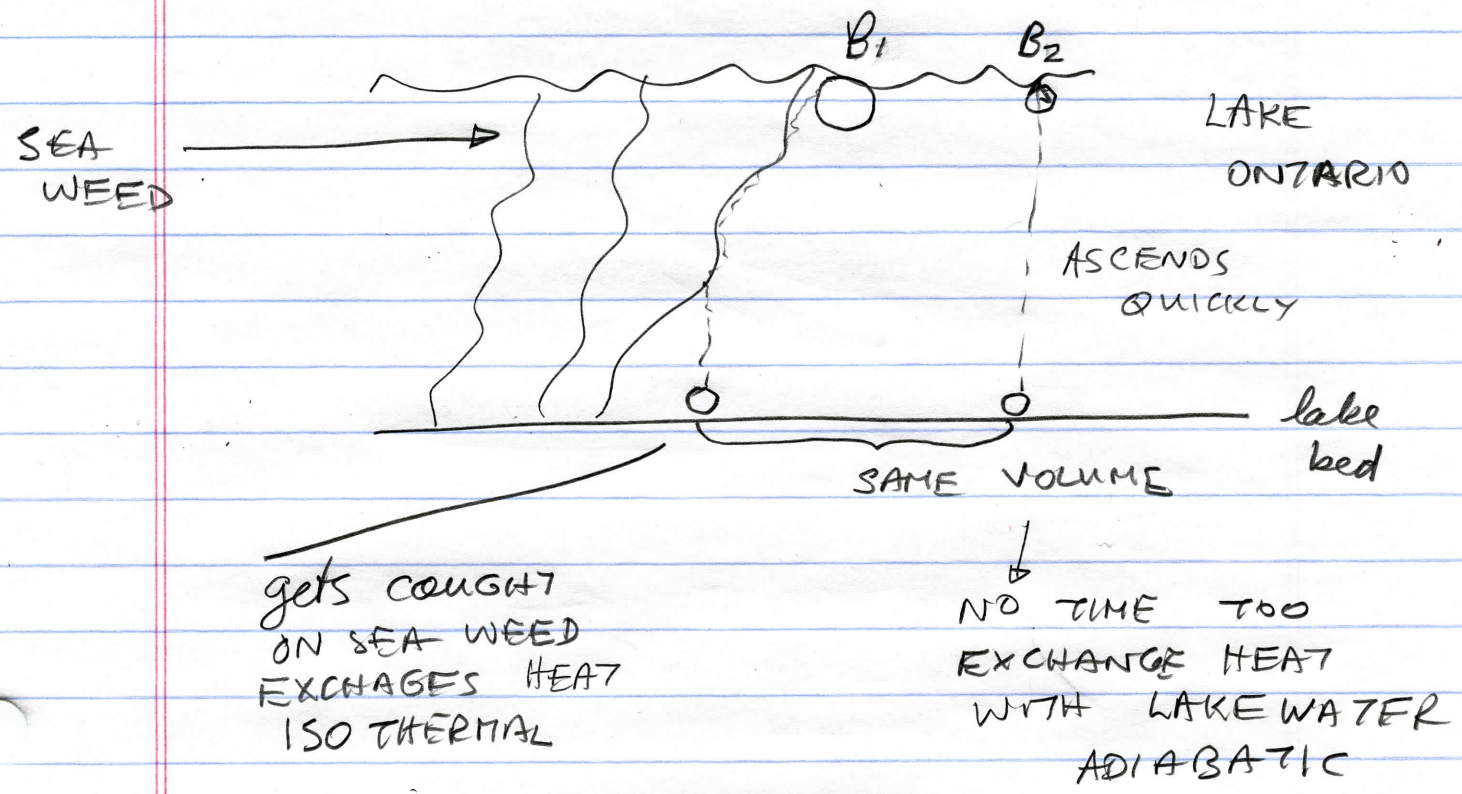


ADIABATE → STEEPER

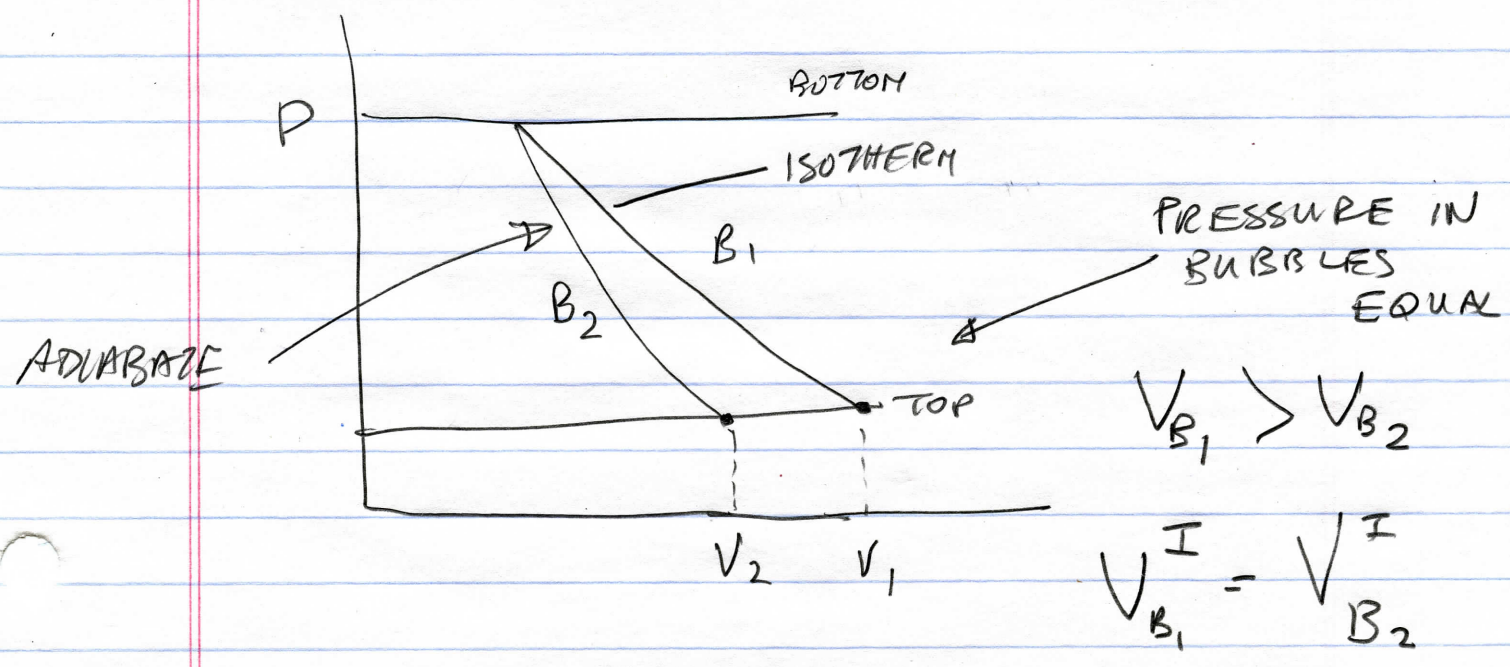


NOTICE PRESSURE
HIGHER AFTER ISOTHERMA

Prob 1.38 in text

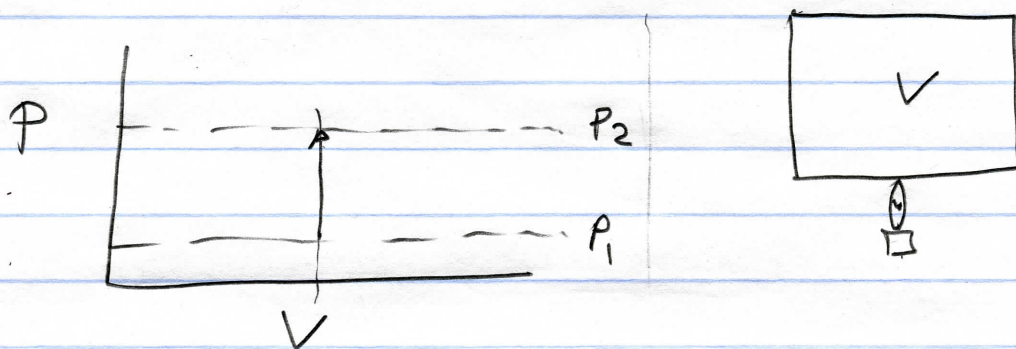


BUBBLES END ON SURFACE → SAME PRESSURE ATMOSPHERIC

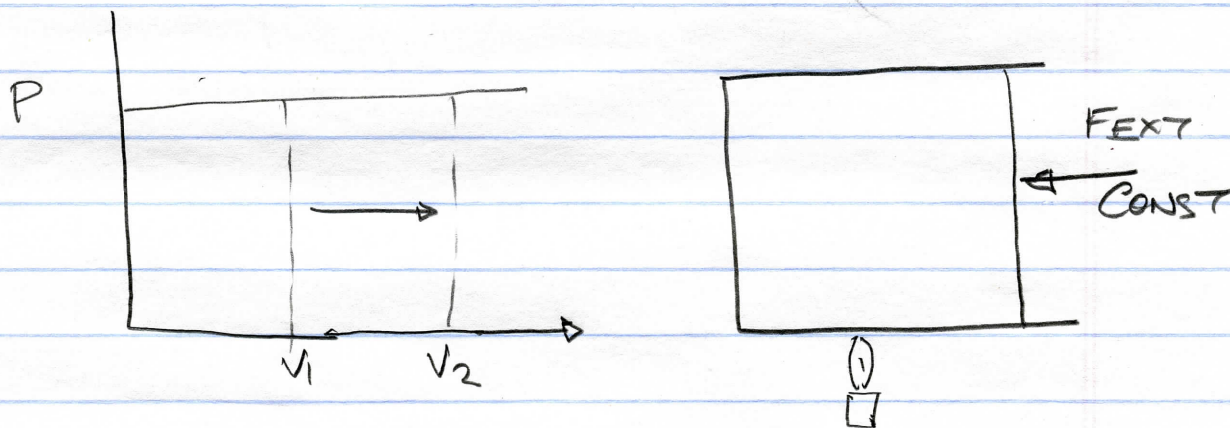


OTHER PROCESSES

ISOCORIC $\longrightarrow$ FIXED VOLUME



ISOBARIC $\longrightarrow$ FIXED PRESSURE

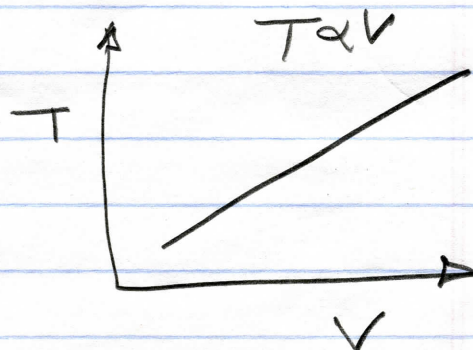


TRANSFORM ISOBARIC TO TV PLOT

$$PV = NkT$$

$$P = \frac{NkT}{V}$$

$\uparrow$ $\uparrow$
 Const Const



6

THERMODYNAMIC EQUILIB $\longrightarrow$ MACROSCOPIC
CHARACTERISE
SYSTEM

P, V, T, N

Other macroscopic quantities

$\hookrightarrow$ HEAT CAPACITY

At first sight $\longrightarrow$ Amount of Heat
Needed to raise T
of system by $1K$

$\downarrow$
Example of ECONOMIC RELEVANCE

HEATING WATER IN A BOILER
costs Money

$$C = \frac{Q}{\Delta T} \quad \leftarrow \text{depends on Mass or Size of body}$$

Specific Heat of N particles $\frac{C}{N}$

SPECIFIC HEAT of mass m $\frac{C}{m}$

For Water — 1 gram

$$C = 4.2 \frac{\text{J}}{^{\circ}\text{C}} = \frac{1 \text{ CALORIE}}{^{\circ}\text{C}}$$

ACTUALLY this is specific heat at a
FIXED VOLUME

→ C depends on DETAILS OF PROCESS
by which temperature is raised

→ If T raised at fixed V

— $C_V \leftarrow$ FIXED

1ST LAW

$$\Delta U = Q - P\Delta V \quad \xrightarrow{\quad} 0$$

$$Q = \Delta U$$

$$C_V = \left(\frac{Q}{\Delta T} \right)_V = \left(\frac{\Delta U}{\Delta T} \right)_V$$

↑
CONST

$$\left(\frac{\Delta u}{\Delta T} \right)_V \xrightarrow[\text{DERIVATIVE}]{\text{PARTIAL}} \left(\frac{\partial u}{\partial T} \right)_V$$

IDEAL GAS — constant V makes NO DIFFERENCE

$$u = \frac{f}{2} N k T$$

↑
FIXED

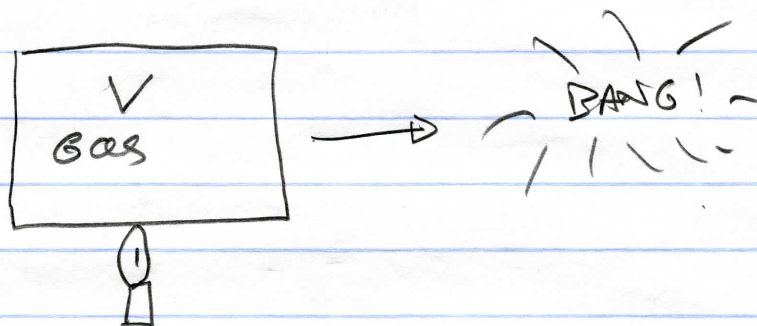
FOR NON IDEAL GAS $u \equiv u(V)$

$$C_{V \text{ IDEAL GAS}} = \left(\frac{\partial u}{\partial T} \right)_V = \frac{\partial \left(\frac{f}{2} N k T \right)}{\partial T}$$

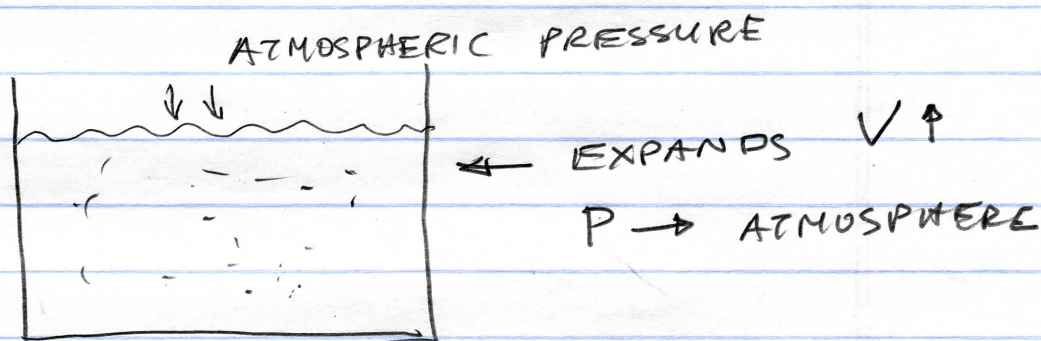
$$= \frac{f}{2} N k.$$

$$\text{or } \left. \frac{C_V}{N} \right|_{\text{IDEAL GAS}} = \frac{f}{2} \cdot k.$$

IN PRACTICE HARD TO KEEP V CONST.



EASY TO KEEP PRESSURE CONST.



$$C_p = \left(\frac{Q}{\Delta T} \right)_P$$

$$Q = \Delta U + P \Delta V \rightarrow 1^{st} \text{ LAW}$$

$$C_p = \left(\frac{\Delta U + P \Delta V}{\Delta T} \right)_P$$

$$C_P = \left(\frac{\Delta u}{\Delta T} \right)_P + \left(\frac{P \Delta V}{\Delta T} \right)_P$$

$$= \left(\frac{\partial u}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

COMPARE

$$C_V = \left(\frac{\partial u}{\partial T} \right)_V$$

matter for non-ideal

Again

$$U = \frac{f}{2} N k T$$

$$\textcircled{*} \rightarrow \left(\frac{\partial u}{\partial T} \right) = \frac{f}{2} N k \quad \leftarrow \text{does not depend on pressure or volume}$$

$$\left(\frac{\partial V}{\partial T} \right)_P \xrightarrow{\leftarrow \text{const}}$$

$$P V = N k T$$

$$P \Delta V = N k \Delta T$$

$$P \left(\frac{\Delta V}{\Delta T} \right)_P = N k$$

$$\rightarrow C_P|_{\text{IDEAL}} = \left(\frac{\partial u}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

$$= \frac{f}{2} N k + N k$$

$$= \left(\frac{f}{2} + 1 \right) N k$$

$$C_P|_{\text{IDEAL}} = \left(\frac{f}{2} + 1\right) Nk$$

$$C_V|_{\text{IDEAL}} = \frac{f}{2} Nk$$

$$C_P > C_V \quad \text{TRUE IDEAL GAS}$$

ACTUALLY TRUE - THERMODYNAMICALLY
STABLE SYSTEM.

$C_P \rightarrow$ More heat to raise temp
 $\rightarrow$ Some energy goes into expanding
 system.

$$C_P = \left(\frac{\partial u}{\partial T}\right)_P + P \left(\frac{\partial v}{\partial T}\right)_P$$

$$C_V = \left(\frac{\partial u}{\partial T}\right)_V$$

IS THIS BECAUSE $\left(\frac{\partial v}{\partial T}\right) > 0$.

NOT Always true.

(12)

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\text{Change of } V}{\text{Change of } T} > 0 ?$$

Normally heating $\rightarrow$ expansion.

For water $0^\circ\text{C} \rightarrow 4^\circ\text{C}$ contracts as

it is heated, expands as it cools.
 $\rightarrow$ just before freezing.

Ice FLOATS $\rightarrow$ takes up more
volume than
water

$$\text{So } \left(\frac{\partial V}{\partial T}\right)_P < 0.$$

Water $0^{\circ}\text{C} \rightarrow 4^{\circ}\text{C}$ $\frac{\Delta V}{\Delta T} < 0$

$$C_p = \left(\frac{\partial u}{\partial T}\right)_p + p \left(\frac{\partial v}{\partial T}\right)_p$$

$\nwarrow < 0$

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v$$

Is $C_p < C_v$ for water? — NO

$$\left(\frac{\partial u}{\partial T}\right)_p \neq \left(\frac{\partial u}{\partial T}\right)_v$$

NOT an ideal substance

can show that

$$C_p = C_v - T \left(\frac{\partial p}{\partial v}\right)_T \left[\left(\frac{\partial v}{\partial T}\right)_p\right]^2$$

ANY THERMODYN
STABLE

Really shows

$$C_p > C_v$$

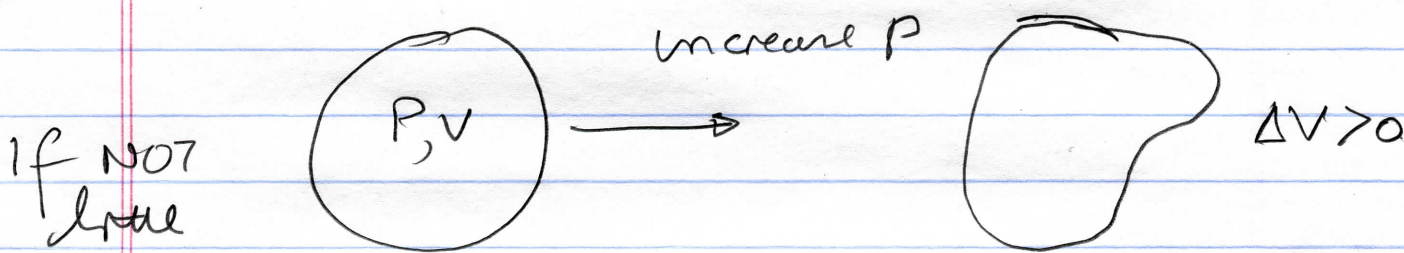
THERMODYNAMICALLY STABLE

$$C_p - C_v = -T \left(\frac{\partial P}{\partial V} \right)_T \left[\left(\frac{\partial V}{\partial T} \right)_P \right]^2$$

κ always > 0

< 0 for STABLE SYSTEM

$\left(\frac{\partial P}{\partial V} \right)_T$ = pressure change for volume increase



$$\Delta P \uparrow \rightarrow \Delta V \uparrow \rightarrow \Delta P \uparrow \rightarrow \Delta V \uparrow$$

UNSTABLE

$$\text{if } \Delta V > 0 \rightarrow \Delta P < 0 \text{ STABLE EQUILIB}$$