Some terms that must be understood

Microscopic Variable

Macroscopic Variable

Extensive ($\propto N$)	Intensive ($\neq f(N)$)
V volume	P pressure
A area	$\mathcal{S}$ surface tension
L length	$\mathcal{F}$ tension
$\mathcal{P}$ polarization	$\mathcal{E}$ electric field
M magnetization	H magnetic field
....	....
	T temperature
U internal energy	

Adiabatic Walls

Equilibrium

Steady State

Diathermic Walls

Complete Specification:

Independent and Dependent Variables

Equation of State

$$PV = NkT$$

$$V = V_0(1 + \alpha T - \mathcal{K}_T P)$$

$$M = cH/(T - T_0) \quad T > T_0$$

In Equilibrium with Each Other

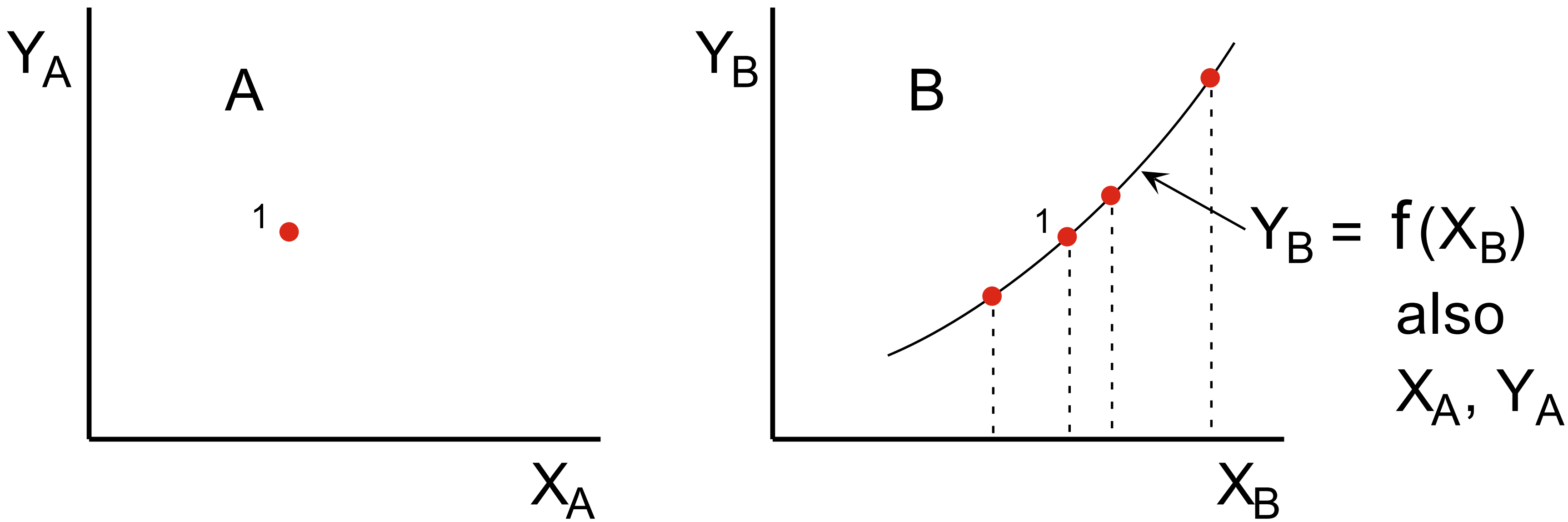
OBSERVATIONAL FACTS

"0^{th} Law"

if $A \overset{\text{equilibrium}}{\longleftrightarrow} C$ and $B \overset{\text{equilibrium}}{\longleftrightarrow} C$

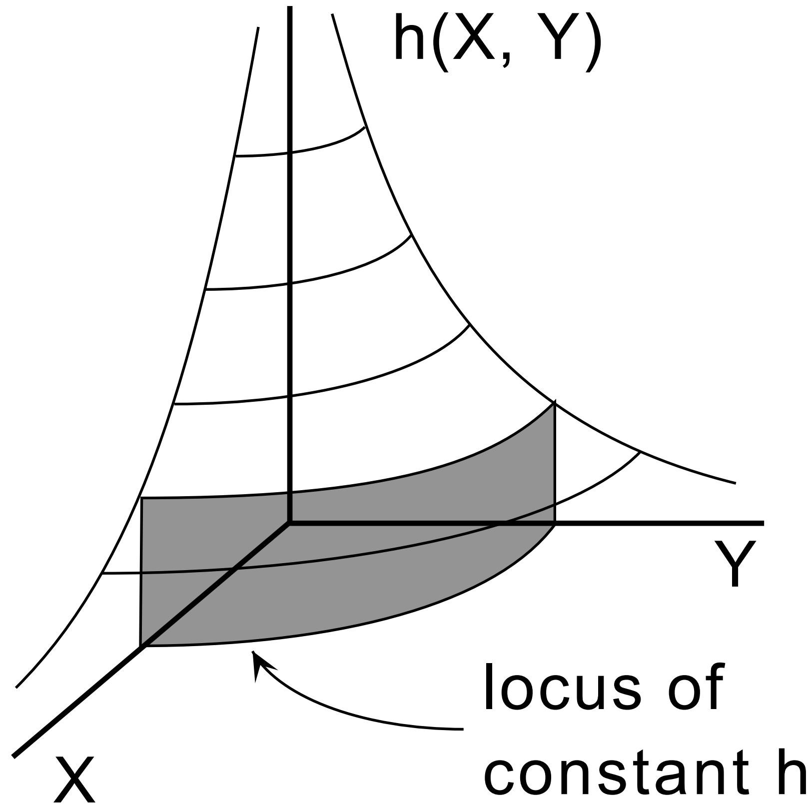
then $A \overset{\text{equilibrium}}{\longleftrightarrow} B$

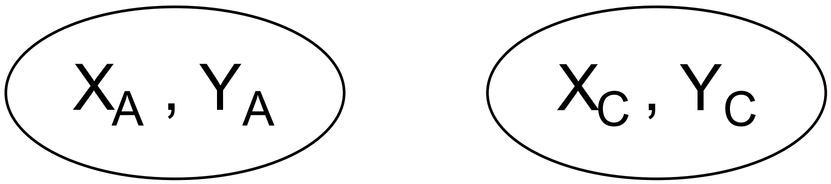
" Law 0.5 ? " Many macroscopic states of B can be in equilibrium with a given state of A



<u>THEOREM</u> A "predictor" of equilibrium h(X, Y, ...) exists

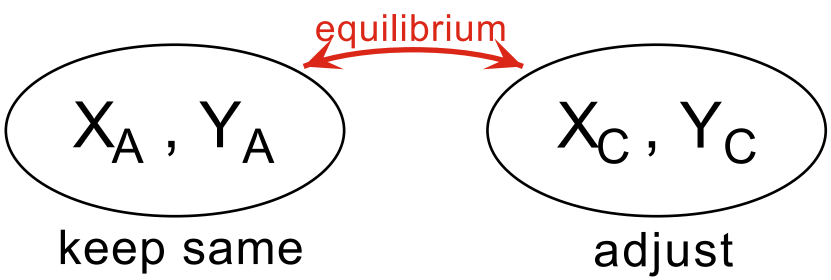
- only in equilibrium
- state variable
- many states, same h
- different systems,
  different functional forms
- value the same if
  systems in equilibrium





X_A , Y_A , X_C , Y_C all free

$[P_A , V_A , P_C , V_C]$

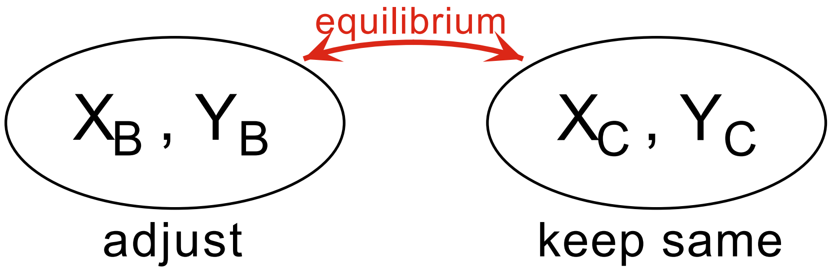


$X_C = f_1(Y_C , X_A , Y_A)$

$[P_C = P_A V_A / V_C]$

$F_1(X_C , Y_C , X_A , Y_A) = 0$

$[P_C V_C - P_A V_A = 0]$



$$X_B = g(Y_B, X_C, Y_C) \qquad [\, P_B = P_C V_C / V_B \,]$$

$$F_2(X_C, Y_C, X_B, Y_B) = 0 \qquad [\, P_C V_C - P_B V_B = 0 \,]$$

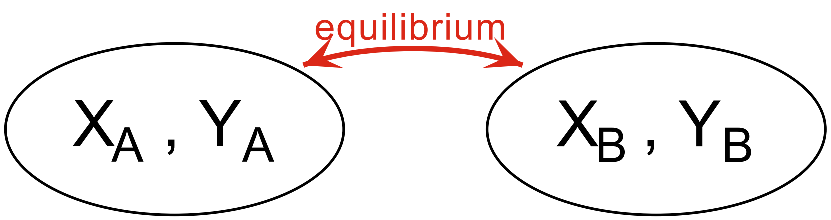
solve for X_C

$$X_C = f_2(Y_C, X_B, Y_B) \qquad [\, P_C = P_B V_B / V_C \,]$$

same value as before

$$f_1(Y_C, X_A, Y_A) = X_C = f_2(Y_C, X_B, Y_B) \quad (1)$$

$$[\, P_A V_A / V_C = P_B V_B / V_C \,]$$



due to 0^{th} law

$$\Rightarrow F_3(X_A, Y_A, X_B, Y_B) = 0 \quad (2)$$

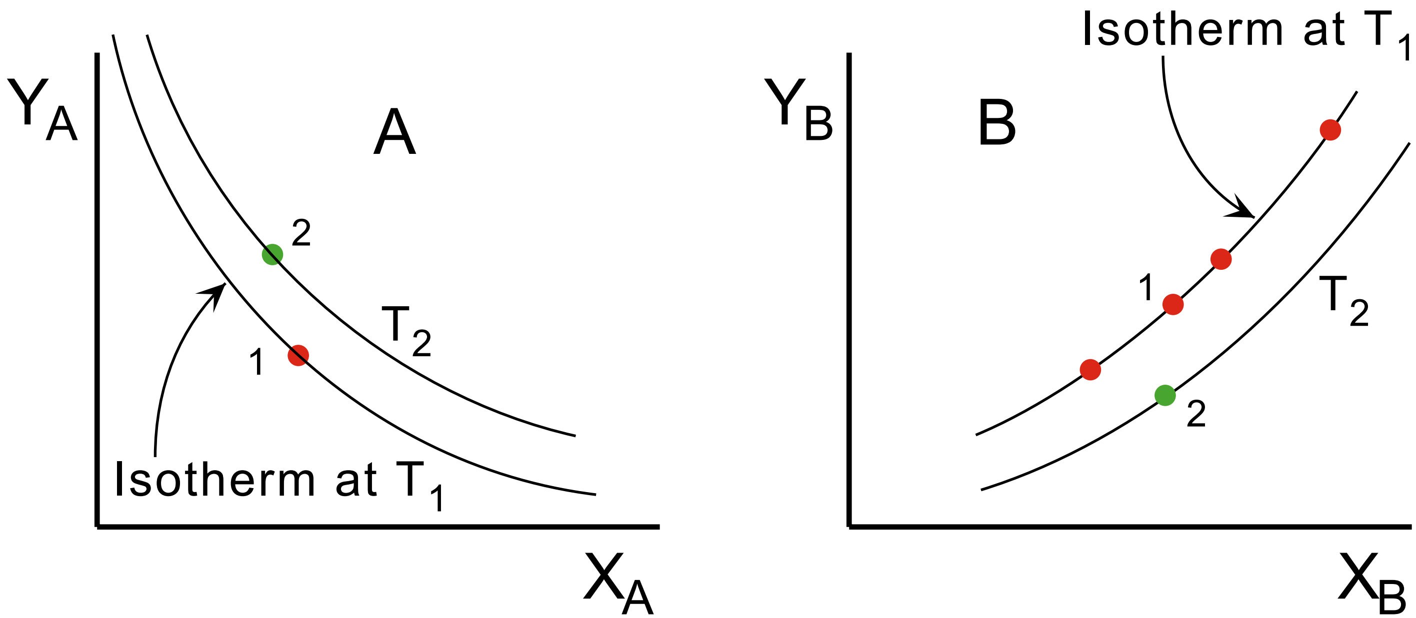
(1) + (2) $\Rightarrow$ F_3 factors

Y_C drops out

For this equilibrium condition

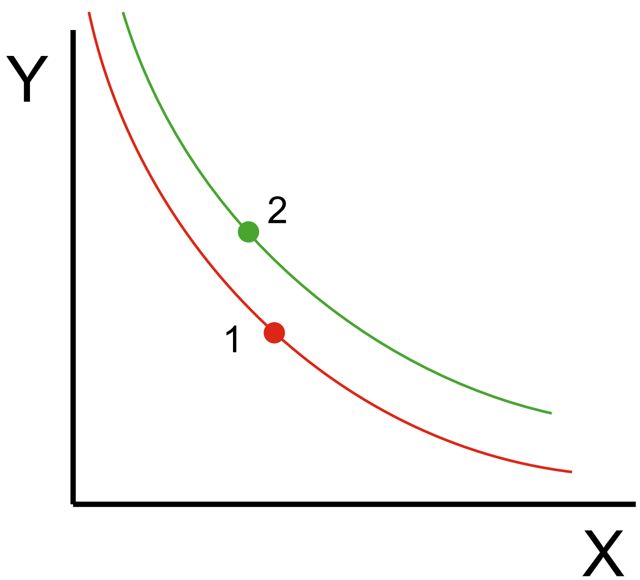
$$h(X_A, Y_A) = \text{constant} = h(X_B, Y_B)$$

$$[\, P_A V_A = P_B V_B \,]$$

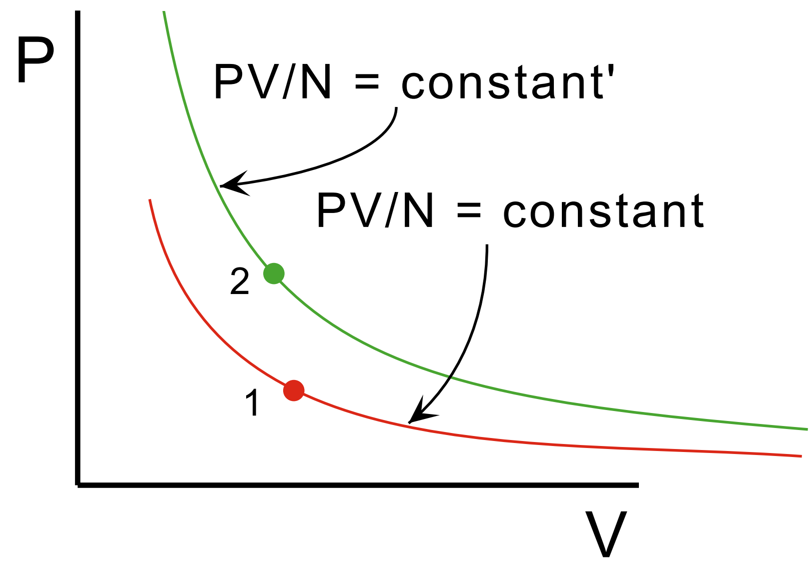


Y_A
A
2
T_2
1
Isotherm at T_1
X_A
Isotherm at T_1
Y_B
B
1
T_2
2
X_B

Empirical Temperature: t



low density gas



we could | possible alternative

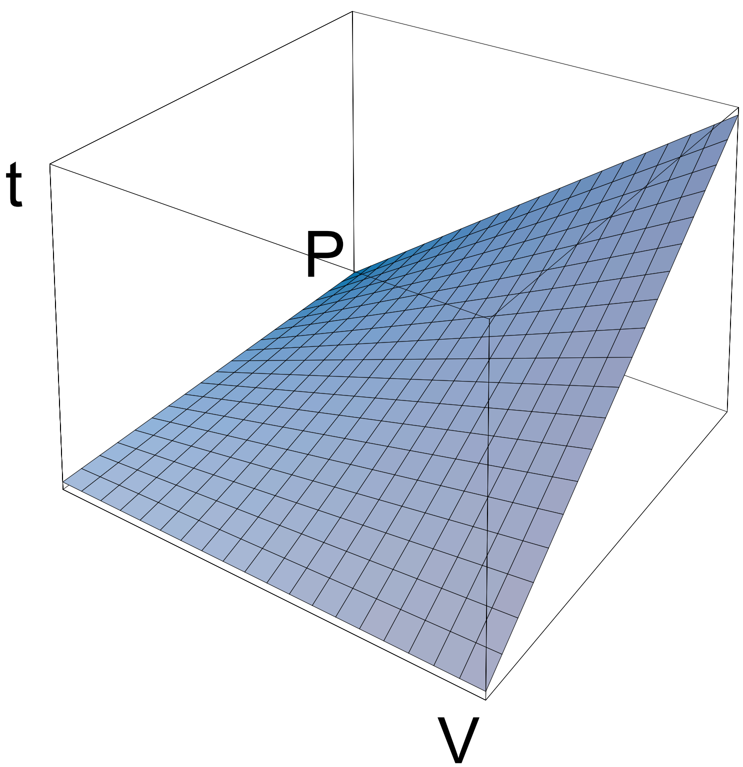
- Define $t \equiv c_g PV/N$ — $t' \equiv c_g' (PV/N)^{\alpha}$

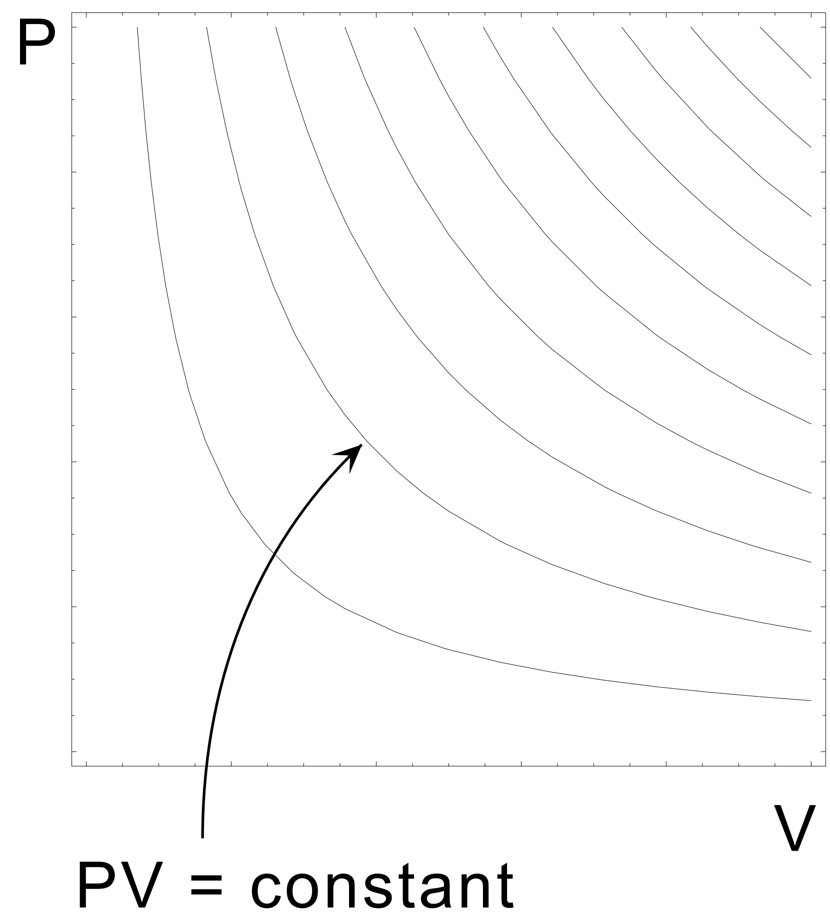
- Use to find isotherms
  in other systems

- Then in a simple paramagnet
  $t = c_m (M/H)^{-1}$ — $t' = c_m' (M/H)^{-\alpha}$

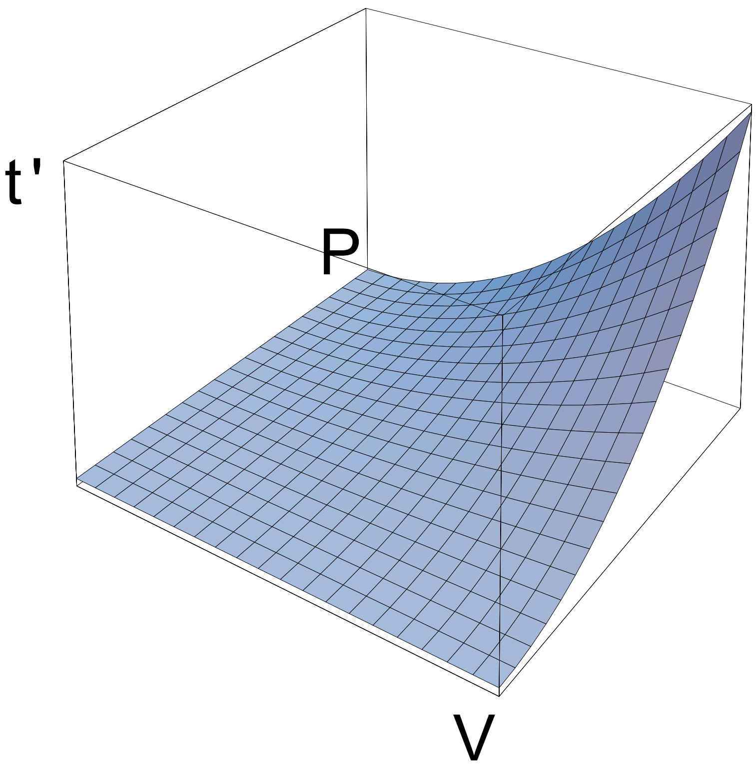
$\Longrightarrow$ Many possible choices for t

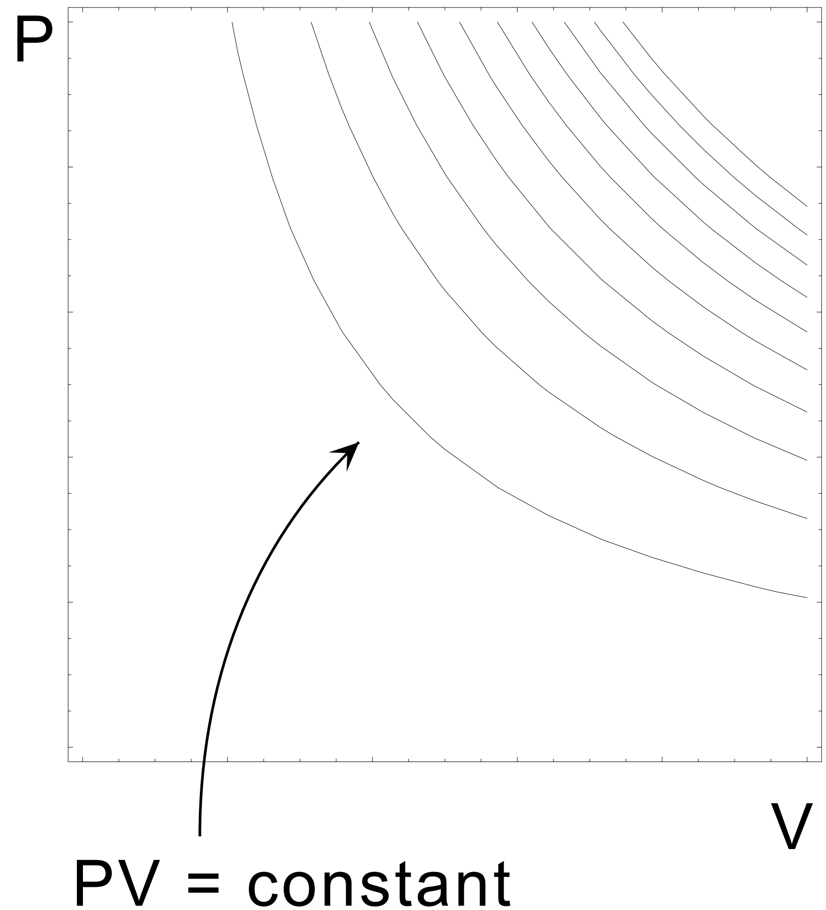
$$PV = Nkt \rightarrow t = PV/Nk$$



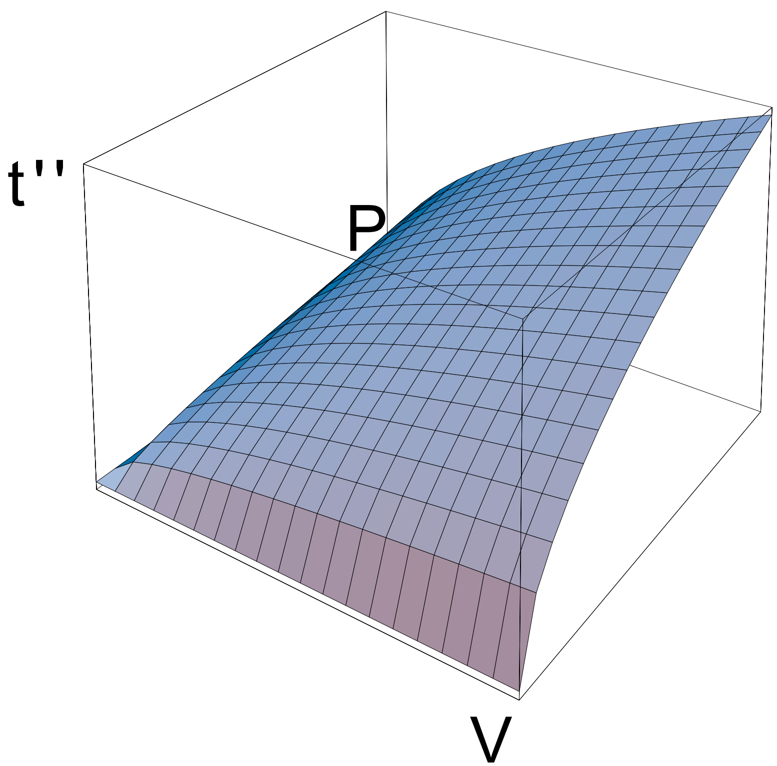


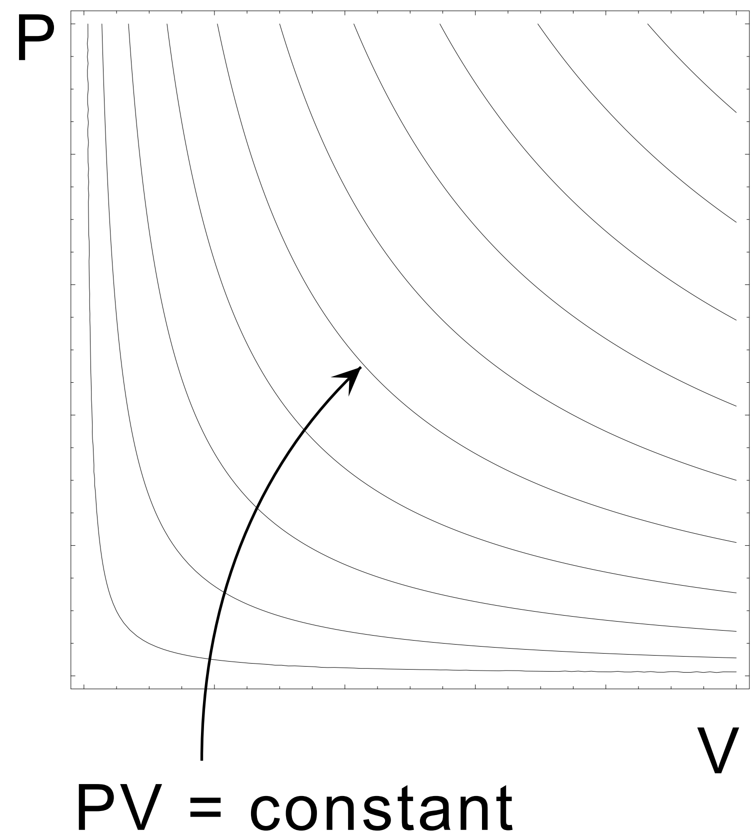
$$t' = (PV/Nk)^2$$





$$t'' = \sqrt{PV/Nk}$$





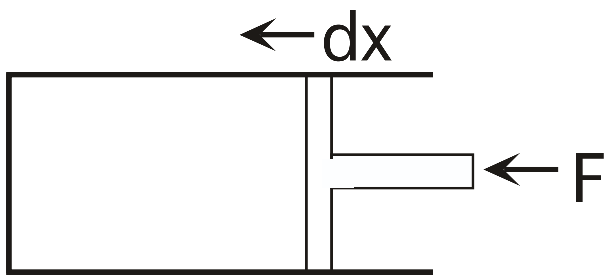
<u>Work</u>

$\text{đ}W \equiv$ differential of work done <u>on</u> the system

$= -$ (work done <u>by</u> the system)

Hydrostatic system

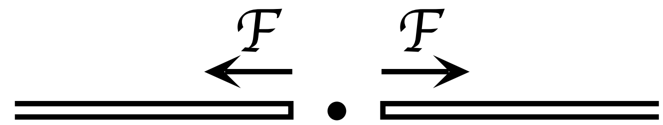
$\text{đ}W = -PdV$



$\text{đ}W = Fdx = (PA)(-dV/A) = -PdV$

Wire

$đW = \mathcal{F}dL$

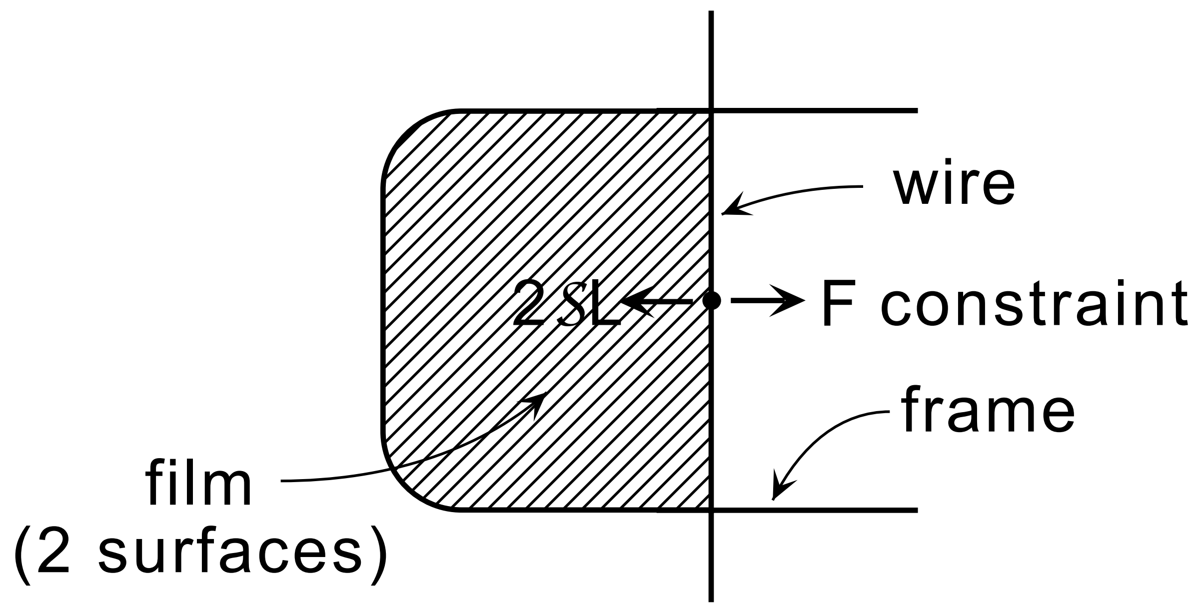


P pushes, $\mathcal{F}$ pulls

$đW = Fdx = (\mathcal{F})(dL) = \mathcal{F}dL$

Surface

$đW = \mathcal{S}dA$



$đW = Fdx = (\mathcal{S}L)(dA/L) = \mathcal{S}dA$

Chemical Cell (battery)

$$đW = \mathcal{E}_{EMF}\, d\mathcal{Z}_{CHARGE}$$

Electric charges

$$đW = \mathcal{E} d\mathcal{P}$$

Magnetic systems

$$đW = H dM$$

Field in absence of matter as set up by external sources. Does not include energy stored in the field itself in the absence of the matter.

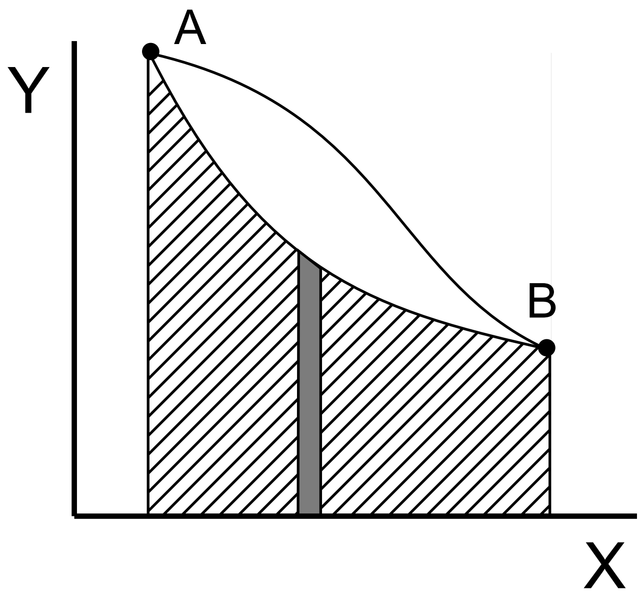
- All differentials are extensive

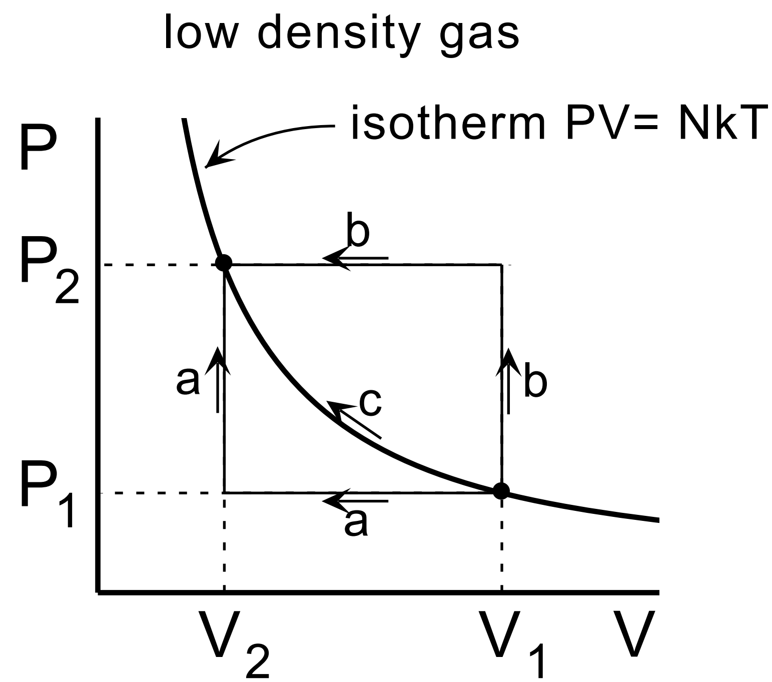
- Only -PdV has a negative sign

- Good only for <u>quasistatic processes</u>

- $\Delta W = \int_a^b đW$ depends on the path

  $\Longrightarrow$ W is not a state function





$đW = YdX$

depends on Y(X)

(a) $W_{1\to 2} = -P_1(V_2 - V_1) = P_1(V_1 - V_2)$

(b) $W_{1\to 2} = -P_2(V_2 - V_1) = P_2(V_1 - V_2)$

(c) $W_{1\to 2} = -\int_1^2 P(V)\, dV = -\int_1^2 \frac{NkT}{V}\, dV = -NkT \int_1^2 \frac{dV}{V}$

$$= -NkT \ln \frac{V_2}{V_1} = NkT \ln \frac{V_1}{V_2} = P_1 V_1 \ln \frac{V_1}{V_2}$$

MATH

I) 3 variables, only 2 are independent

$$F(x, y, z) = 0$$

$$\Rightarrow x = x(y, z), \quad y = y(x, z), \quad z = z(x, y)$$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}, \quad \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Given some $W = W(x, y, z)$ where only 2 of the 3 variables in the argument are independent,

then along a path where W is constrained to be constant

$$\left(\frac{\partial x}{\partial y}\right)_W \left(\frac{\partial y}{\partial z}\right)_W \left(\frac{\partial z}{\partial x}\right)_W = 1$$

then it follows that $\left(\frac{\partial x}{\partial y}\right)_w = \frac{\left(\frac{\partial x}{\partial z}\right)_w}{\left(\frac{\partial y}{\partial z}\right)_w}$

II) State function of 2 independent variables

$$S = S(x, y)$$

$$dS = \underbrace{\left(\frac{\partial S}{\partial x}\right)_y}_{A(x,y)} dx + \underbrace{\left(\frac{\partial S}{\partial y}\right)_x}_{B(x,y)} dy$$

An <u>exact differential</u>

$$\left(\frac{\partial A}{\partial y}\right)_x = \frac{\partial^2 S}{\partial y \partial x} = \frac{\partial^2 S}{\partial x \partial y} = \left(\frac{\partial B}{\partial x}\right)_y$$

$\Rightarrow$ necessary condition, but it is also sufficient

Exact differential if and only if $\left(\frac{\partial A}{\partial y}\right)_x = \left(\frac{\partial B}{\partial x}\right)_y$

Then $\int_1^2 dS = S(x_2, y_2) - S(x_1, y_1)$ is independent of the path.

III) Integrating an exact differential

$$dS = A(x,y)\,dx + B(x,y)\,dy$$

1. Integrate a coefficient with respect to one variable

$$\left(\frac{\partial S}{\partial x}\right)_y = A(x,y)$$

$$S(x,y) = \underbrace{\int A(x,y)\,dx}_{y\ \text{fixed}} + f(y)$$

2. Differentiate result with respect to other variable

$$\left(\frac{\partial S}{\partial y}\right)_x = \frac{\partial}{\partial y}\left[\int A(x,y)\,dx\right] + \frac{d\,f(y)}{dy} = B(x,y)$$

3. Integrate again to find $f(y)$

$$\frac{d\,f(y)}{dy} = \left\{B(x,y) - \frac{\partial}{\partial y}\int A(x,y)\,dx\right\}$$

$$f(y) = \int \{\cdots\}\,dy$$

done