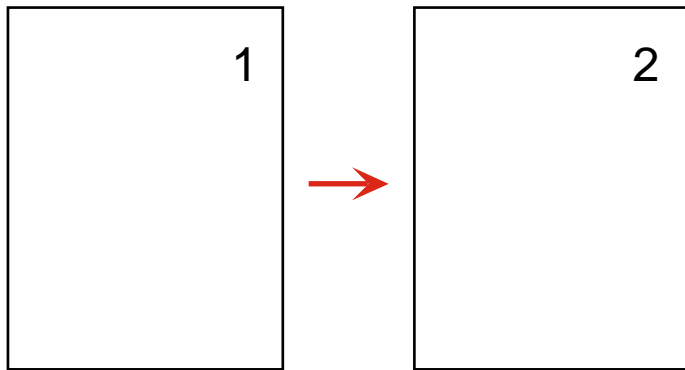
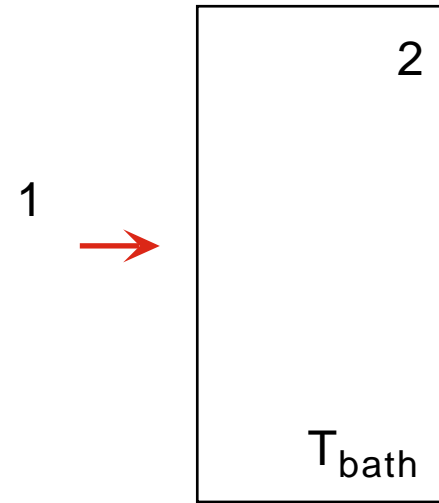


# ENTROPY AND THE 2<sup>nd</sup> LAW



$$dS \geq 0$$



$$dS_1 \geq dQ_1 / T_{\text{bath}}$$

## $S$ as a State Function

Note: adiabatic ( $\equiv dQ = 0$ )  $\Rightarrow$  constant  $S$  if the change is quasistatic. This is the origin of the subscript  $S$  on the adiabatic compressibility.

$$\kappa_T \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad \kappa_S \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S$$

## Example A Hydrostatic System

$$\begin{aligned}dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad \text{by expansion} \\ &= \frac{1}{T} dU + \frac{P}{T} dV \quad \text{from } dU = TdS - PdV \\ &= \left(\frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V\right) dT + \frac{1}{T} \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) dV\end{aligned}$$

by expansion of  $U$

But the cross derivatives of  $S$  must be equal.

$$\frac{\partial}{\partial V} \left[ \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V \right]_T = \frac{1}{T} \frac{\partial^2 U}{\partial V \partial T}$$

$$\frac{\partial}{\partial T} \left[ \frac{1}{T} \left( \left( \frac{\partial U}{\partial V} \right)_T + P \right) \right]_V = -\frac{1}{T^2} \left( \left( \frac{\partial U}{\partial V} \right)_T + P \right) + \frac{1}{T} \frac{\partial^2 U}{\partial V \partial T} + \frac{1}{T} \left( \frac{\partial P}{\partial T} \right)_V$$

Equating these two expressions gives

$$\left( \frac{\partial U}{\partial V} \right)_T + P = T \left( \frac{\partial P}{\partial T} \right)_V$$

$$\underline{\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P}$$

New Information! Does not contain  $S$ !

## CONSEQUENCES a) $\gamma$

$$dQ = dU + PdV = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \underbrace{\left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)}_{T\left(\frac{\partial P}{\partial T}\right)_V} dV$$

$$\left.\frac{dQ}{dT}\right|_P \equiv C_P = C_V + T \left(\frac{\partial P}{\partial T}\right)_V \underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{\alpha V}$$

Use  $\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$  and  $\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$ .

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T} = \frac{(-1) \left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\alpha}{\kappa_T}$$

$$C_P - C_V = T \left(\frac{\alpha}{\kappa_T}\right) \alpha V = \frac{T\alpha^2 V}{\kappa_T} \rightarrow \underline{\underline{\gamma - 1 = \frac{T\alpha^2 V}{\kappa_T C_V}}}$$

For an ideal gas  $PV = NkT \Rightarrow \alpha = 1/T$  and  $\kappa_T = 1/P$ .

Thus

$$C_P - C_V = \frac{V/T}{1/P} = Nk$$

This holds for polyatomic as well as monatomic gases.

CONSEQUENCES b) Ideal Gas:  $C_V$

$$P = \frac{NkT}{V} \quad \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{Nk}{V}\right) - P = P - P = \underline{0}$$

$$dU = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_0 dV = C_V dT$$

$$U = \int_0^T C_V(T', V) dT' + \text{constant}$$

$(\partial U/\partial V)_T = 0$  for all  $T \Rightarrow C_V$  is not  $f(V)$ ;  $C_V = C_V(T)$ .

## CONSEQUENCES c) Ideal Gas: $S$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$dQ = TdS \quad \left.\frac{dQ}{dT}\right|_V \equiv C_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

$$dU = TdS - PdV \Rightarrow dS = \frac{dU}{T} + \frac{P}{T}dV$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_0 + \underbrace{\frac{P}{T}}_{Nk/V}.$$

$$dS = \frac{C_V(T)}{T} dT + \frac{Nk}{V} dV$$

$$S(T, V) = \int_{T_0}^T \frac{C_V(T')}{T'} dT' + Nk \ln\left(\frac{V}{V_0}\right) + S(T_0, V_0)$$

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For a monatomic gas  $C_V = (3/2)Nk$ .

$$S(T, V) - S(T_0, V_0) = (3/2)Nk \ln\left(\frac{T}{T_0}\right) + Nk \ln\left(\frac{V}{V_0}\right)$$

$$= Nk \ln \left[ \frac{V}{V_0} \left( \frac{T}{T_0} \right)^{3/2} \right]$$

$$\text{isentropic (adiabatic)} \Rightarrow \left. \begin{array}{l} VT^{3/2} \\ V^{2/3}T \\ V^{5/3}P \end{array} \right\} \text{ are constant}$$