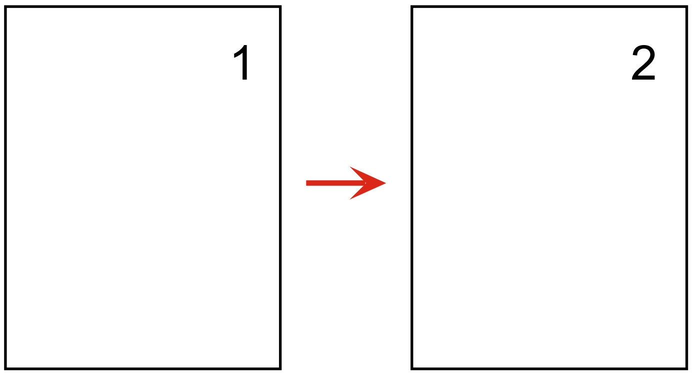
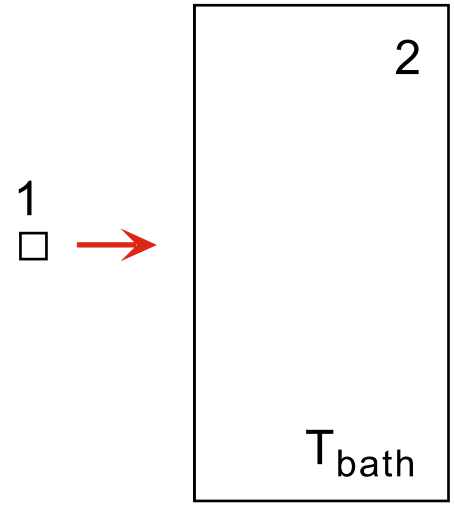
ENTROPY AND THE 2^{nd} LAW





$$dS \geq 0$$

$$dS_1 \geq \bar{d}Q_1 / T_{bath}$$

$\underline{S \text{ as a State Function}}$

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

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

Example A Hydrostatic System

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

$$= \frac{1}{T} dU + \frac{P}{T} dV \quad \text{from} \quad dU = TdS - PdV$$

$$= \left(\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right) dT + \frac{1}{T}\left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) dV$$

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) γ

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

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

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

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

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

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

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

$$dU = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{0} dV = C_V\, dT$$

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

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

CONSEQUENCES c) Ideal Gas: S

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

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

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

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{0} + \underbrace{\frac{P}{T}}_{Nk/V}.$$

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

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

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

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

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

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

Maxwell Relations

$$dE(S,V) = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV \qquad \text{expansion}$$

$$= TdS - PdV \qquad 1^{st} \text{ and } 2^{nd} \text{ laws}$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$dE(S,L) \;=\; TdS + \mathcal{F}dL \quad \Rightarrow \left(\frac{\partial T}{\partial L}\right)_S = \left(\frac{\partial \mathcal{F}}{\partial S}\right)_L$$

$$dE(S,M) \;=\; TdS + HdM \;\Rightarrow \left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial H}{\partial S}\right)_M$$

Observe:

$$d(TS) \;=\; TdS + SdT$$

$$d(PV) \;=\; PdV + VdP$$

Helmholtz Free Energy $F \equiv E - TS$

$$dF = -SdT - PdV \quad \Rightarrow \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Enthalpy $H \equiv E + PV$

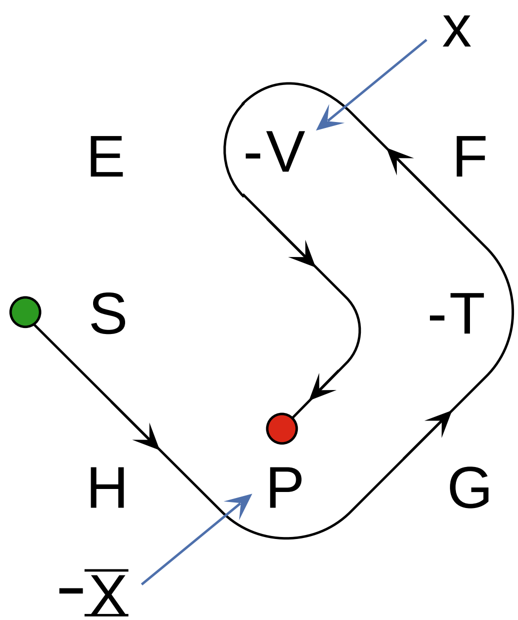
$$dH = TdS + VdP \quad \Rightarrow \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

Gibbs Free Energy $G \equiv E + PV - TS$

$$dG = -SdT + VdP \Rightarrow \qquad -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

E, F, H and G are called "thermodynamic potentials".

The Magic Square Mnemonic



$$dE = T dS + X dx$$

$$(-1)\left(\frac{\partial S}{\partial P}\right)_T = \underbrace{(-1)(-1)}_{(+1)}\left(\frac{\partial V}{\partial T}\right)_P$$

8.044 Statistical Physics I
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