Pg 1

not a state function — States of a system {P V U}

$\Delta U = Q + W = Q - PdV$

Heat needs a Stately Partner: Entropy.

Rudolf Clausius, German, 1854, "On a different form of the second law"

Found the state function for Q!

→ Entropy (Greek for transformation)

Chose ↑ to be as similar as possible to Energy because of the close physical significance

$$Q = T\Delta S \leftarrow \text{Entropy}$$

$$\boxed{\text{Clausius} \quad \Delta U = T\Delta S - P\Delta V}$$

Ludwig Boltzmann (1844-1906) Theoretical Physicist Univ Vienna. "What is entropy"?

Answer:

$$S = \underset{\text{Boltzmann's constant}}{k} \ln \underset{\text{\# ways to realize a system.}}{\Omega}$$

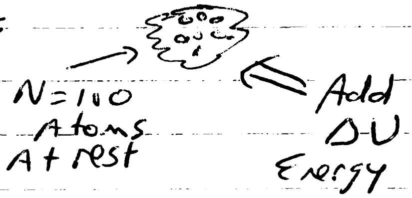
On his headstone

Example 1

Entropy of a Royal Flush low!

Entropy of a pair high!

Example 2



Ways a) Give all ΔU to 1 atom. 100 ways since 100 atoms.

b) Give $\frac{\Delta U}{2}$ to 2 atoms,

$$\frac{100 \cdot 99}{2} \text{ ways} = 4950$$

Atoms are indistinguishable →

Pg 2

Example 2 Continued:

3 atoms, $\frac{\Delta U}{3}$ each ⇒ 161,700 ways

4 atoms, $\frac{\Delta U}{4}$ each ⇒ 3,921,225 ways

5 ⇒ 75,287,520 ways

50 atoms stationary

50 $\frac{\Delta U}{50}$ ⇒ 10^{29}

!

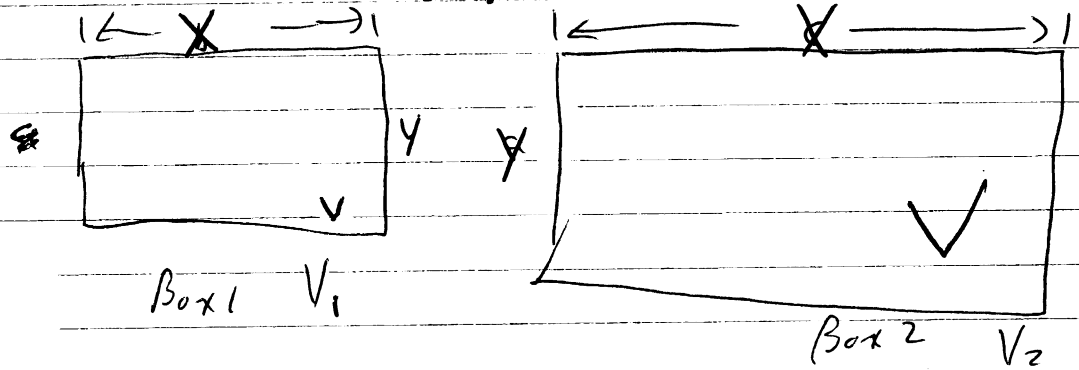
??

100 atoms, $\frac{\Delta U}{100}$ each ⇒ 1 ← highly improbable

Summary:

1) Add ΔU to system of atoms.
2) Wait.
3) ΔU is distributed among atoms to make S maximum ≡ Equilibrium.
4) Counter Example: look at the system 10^{23} times, "Never" see Only 1 atom with all ΔU and others at rest.

N atoms



$V = XY$

Quantum Particle in a box,

$$E_j = \frac{h^2}{8m}\left(\frac{n_x^2}{X^2} + \frac{n_y^2}{Y^2}\right)$$

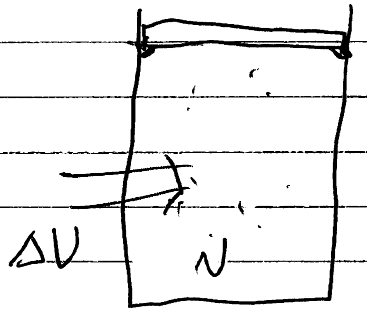
$n_x, n_y = 0, 1, 2 \ldots$

More states available to Box 2 ⇒ Larger Playground larger Entropy

Back to Thermodynamics

$$\Delta U = Q + W = T \Delta dS - P \Delta V$$

Heat capacity $C_V \equiv \left.\frac{\partial U}{\partial T}\right)_V = T \left.\frac{\partial S}{\partial T}\right)_V$ heat capacity at constant Volume



$$\Delta U = C_V \ \Delta T$$

Equipartition Theorem:

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

f = # degrees freedom.

Experiment: Apply ΔU, measure ΔT, get C_V.

Ex Water: $C = \frac{1 \text{ cal}}{\text{g K}} * 4.18 \frac{\text{J}}{\text{cal}} * \frac{1000 \text{ g}}{\text{kg}}$

Specific heat capacity = $\frac{\text{Heat capacity}}{\text{mass}}$

$$C = 4180 \frac{\text{J}}{\text{kg K}}$$

Per molecule, $c = C * \frac{\overset{M_w}{18 \text{ Kg}}}{1000 \text{ moles}} * \frac{1 \text{ mole}}{\underset{N_a}{\cancel{6 \times 10^{23} \text{ molecules}}}}$

Ignorantly set $c = C_V = \frac{f}{2} k$

$$\therefore f = \frac{2 \cdot C \cdot m_w}{\underbrace{N_a k}_{R_0}} = \frac{2 * 4180 \frac{\text{J}}{\text{kgK}} * \frac{18 \times 10^{-3} \text{kg}}{\text{mole}}}{8.3143 \text{ J/mole K}}$$

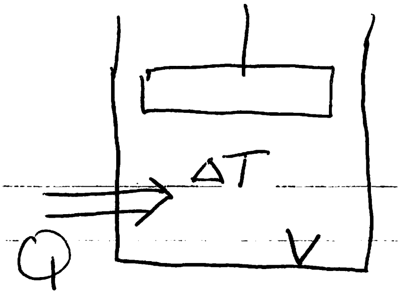
$$f \sim 18 \text{ for liquid water}$$

1) Equipartition theorem does not hold (non quadratic energy terms)

2) Many "Pathways" for dumping energy into water.

Pg 4

Example : C_P



moveable Piston
Pressure Constant
Work can be done

$$C_P \equiv \left.\frac{Q}{\Delta T}\right)_P = T\left.\frac{\partial S}{\partial T}\right)_P$$

$$C_P = \frac{\Delta U + P\Delta V}{\Delta T}$$

Ideal Gas

Constant Volume	Constant Pressure
$C_V = \frac{\Delta U}{\Delta T}$	$C_P = \frac{\Delta U + P\Delta V}{\Delta T}$

For ideal gas $\Delta U = f/_2\, Nk\Delta T$ (function only of T)

So $C_P > C_V$

?

$$C_P = C_V + P\left.\frac{\Delta V}{\Delta T}\right)_P = C_V + P\left.\frac{\partial V}{\partial T}\right)_P$$

$$V = \frac{NkT}{P}, \quad \left.\frac{\partial V}{\partial T}\right)_P = \frac{Nk}{P}$$

So
$$C_P = C_V + Nk = \frac{f}{2}Nk + Nk$$

$$C_P = \frac{f+2}{2}Nk$$

Then

$$\gamma \equiv \frac{C_P}{C_V} = \frac{f+2}{f}$$

e.g. $PV^\gamma = \text{constant}$ for adiabat.

More Generally,

$$C_V = T\frac{\partial S}{\partial T}\Big)_V \qquad C_P = T\frac{\partial S}{\partial T}\Big)_P .$$

For a gas or liquid, what is the relationship of C_V and C_P?

To solve: Consider $S = S(\overbrace{T, P}^{\text{independent variables}})$

$$dS = \frac{\partial S}{\partial T}\Big)_P dT + \frac{\partial S}{\partial P}\Big)_T dP \qquad \text{so}$$

$$\frac{\partial S}{\partial T}\Big)_V = \frac{\partial S}{\partial T}\Big)_P + \frac{\partial S}{\partial P}\Big)_T \frac{\partial P}{\partial T}\Big)_V$$

$$\frac{C_V}{T} = \frac{C_P}{T} + \underbrace{-\frac{\partial V}{\partial T}\Big)_P}_{\text{Maxwell Relation}} \; \underbrace{\frac{-\frac{\partial V}{\partial T}\Big)_P}{\frac{\partial V}{\partial P}\Big)_T}}_{\text{Chain Rule}}$$

Define: Isothermal compressibility

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial P}\Big)_T \quad > 0 \text{ generally}$$

Volume coefficient of expansion

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\Big)_P \quad > 0$$

So

$$\boxed{C_P - C_V = VT\frac{\alpha^2}{\kappa}} = Nk \text{ for ideal gas.}$$

Pg6

$\frac{C_p - C_v}{Nk} = 1$ I.G.

Evaluate $\frac{C_p - C_v}{Nk}$ for water

ρ_w (kg/m3)	T (C)	α $(MK)^{-1}$	κ $(GPa)^{-1}$	$\frac{C_p-C_v}{Nk}$
999.8	0	-68	0.51	5.4×10^{-3}
999.7	10	88	0.48	9.9×10^{-3}
998.2	20	207	0.46	5.9×10^{-2}
998.0	50	458	0.44	0.33
958.4	100	750	0.49	0.97

increases strongly

$$\frac{C_p - C_v}{Nk} = 1 \quad \text{for ideal gas}$$

$$\boxed{C_p - C_v = VT\frac{\alpha^2}{\kappa}}$$

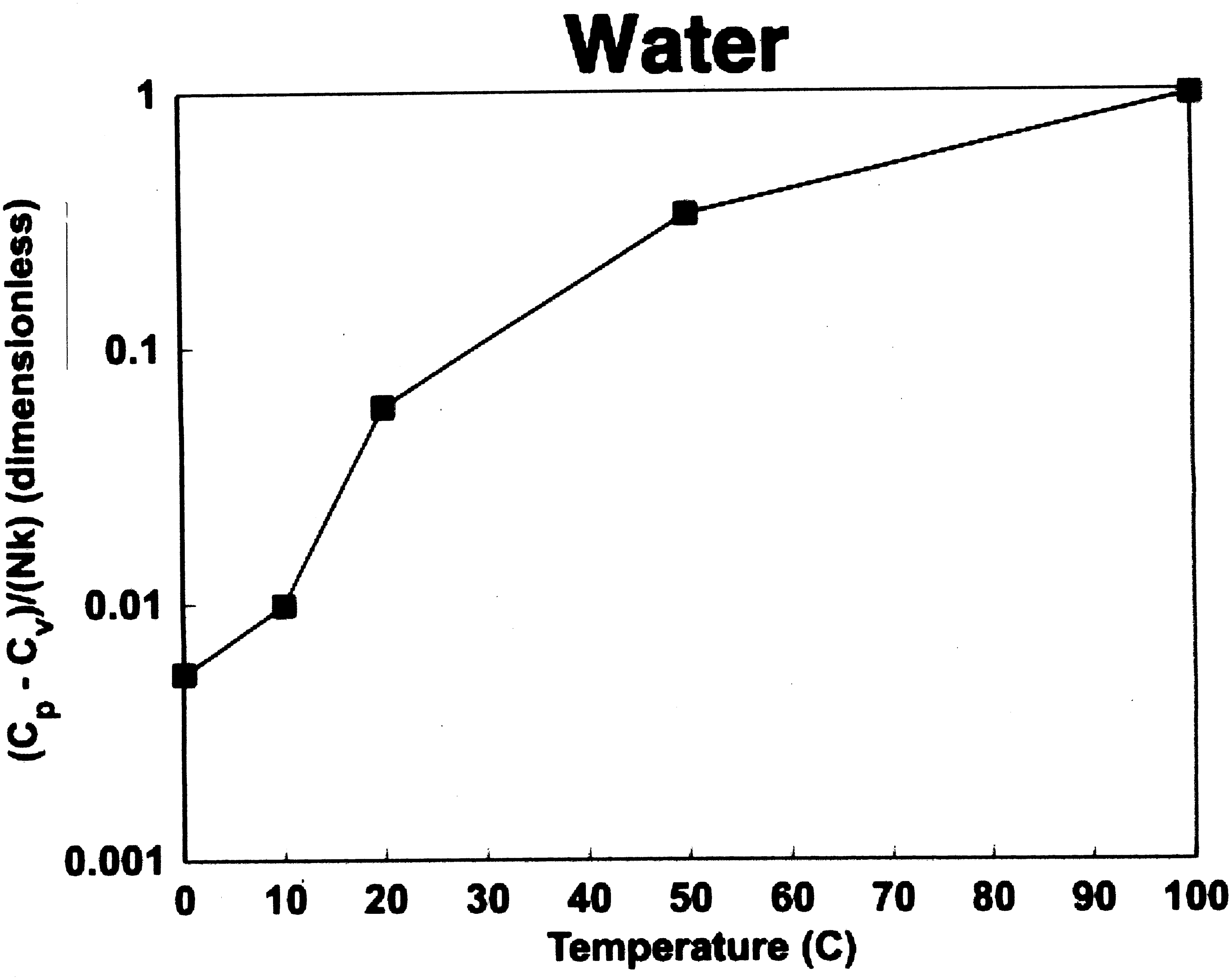
$$V = \frac{N_{molecules}}{\rho_{water}} \times \frac{M_w}{N_a}$$

$$\frac{C_p - C_v}{Nk} = \frac{M_w T}{\rho_w \cdot N_a k} \, \underset{\substack{\uparrow \\ \text{Units in table}}}{\frac{\alpha^2}{\kappa}} \, \frac{1}{(MK)^2} \, \frac{MK^2}{10^{12}K^2} \, \frac{GPA \times 10^9 PA}{GPA}$$

I.G. $\alpha = \frac{1}{T}$ @ 373K, $\alpha = \frac{2.7\times10^{-3}}{K}$

Compare,

Water $\alpha = \frac{7.5\times10^{-4}}{K}$ @ 373K


Water
1
0.1
0.01
0.001
(C_p - C_v)/(Nk) (dimensionless)
0
10
20
30
40
50
60
70
80
90
100
Temperature (C)