# Lecture outline

Quiz 3: Note: midterm exam on March 3

Entropy:
- numerical magnitudes
- how entropy can be generated
  - volume change
  - add heat
  - change # particles
  - mixing: calculate via Sackur-Tetrode
    mixing identical particles doesn't change entropy
- calculating entropy from heat capacities $C_V(T)$, $C_p(T)$
- third law of thermodynamics: $S(T=0) \Rightarrow C(T) \to 0$ as $T \to 0$

Paramagnet: the last of the three models for which we
can calculate all details
system for which high-temp. behavior not explained by eq'upartitio
system can have negative temperatures
only can be understood by quantum mechanics
can use paramagnets to create low temperature refrigerators!
$T < 1K$

# Sackur-Tetrode Related to Quantum Volume

From last lecture:

for ideal monoatomic gas of N particles in volume V with constant energy U

$$\Omega(U,V,N) = \left[\left(\frac{2\pi m}{h^2}\right)^{3/2} \frac{1}{N!} \frac{1}{\left(\frac{3N}{2}\right)!}\right] V^N U^{3N/2}$$

$$\Rightarrow \quad S = k\ln\Omega \simeq Nk\left[\frac{5}{2} + \ln\left(\frac{V}{N}\left(\frac{4\pi m}{3h^2}\cdot\frac{U}{V}\right)^{3/2}\right)\right]$$

Sackur-Tetrode eq

Possible to understand complicated dependence of S on parameters?

Observing that for atomic gas $U = \frac{3}{2}NkT$ and

substituting into Sackur-Tetrode, can rewrite:

$$S = Nk\left[\frac{5}{2} + \ln\left(\frac{V/N}{\lambda_D^3}\right)\right] \qquad \lambda_D = \frac{h}{\sqrt{2\pi m kT}}$$

$\lambda = \frac{h}{p} = \frac{h}{mv}$

$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2}kT$

entropy related to volume per atom V/N compared to "quantum volume" $\lambda_D^3$ where $\lambda_D$ = thermal de Broglie wavelength

recall ideal gas occurs for $\left(\frac{V}{N}\right)^{1/3} \gg \lambda_D$

at low temperatures, small volumes, large N, $\lambda_D^3 \gtrsim V/N$

Sackur-Tetrode incorrectly gives negative entropy values

# Numerical Value of Entropy

Use Sackur-Tetrode to get numerical $S$

Consider one mole He atoms at STP

$$T \simeq 300K$$
$$V \simeq 2.5 \cdot 10^{-2} m^3 \simeq 25 l$$
$$U = \frac{3}{2} NkT = \frac{3}{2} RT = \frac{3}{2}(8.3 \cdot 300) \simeq 4 \cdot 10^3 J$$

$$S(U, V, N) \simeq 130 \frac{J}{K}$$

Note: if particles were distinguishable, $\frac{1}{N!}$ missing in $\Omega(U, V, N)$

$$S = Nk\left[\frac{5}{2} + \ln\left(V \cdot \left(\frac{4\pi m}{3h^2}\frac{N}{V}\right)^{3/2}\right)\right]$$

($1/N$ missing)

$$S_{dist} - S_{ident} = \frac{1}{2} Nk \ln N \simeq 440 \frac{J}{K}$$

(distinguishable)

So value of entropy change a lot $130 \rightsquigarrow 570 \frac{J}{K}$

Note: $S = k \ln \Omega \Longrightarrow \Omega = e^{S/k} = 10^{(\log_{10} e) S/k}$

$$\doteq 10^{S/(k \ln 10)}$$
$$\simeq 10^{4 \cdot 10^{24}}$$

$\log_{10} e = \frac{1}{\ln 10}$

$\ln 10 \simeq 2.3$ → memorize this useful #

One mole of He at STP has enormous multiplicity

# More Numerical Entropy Values

(1) Einstein solid in high-T limit

$$\Omega(N,q) \simeq \left(\frac{eq}{N}\right)^N \Longrightarrow S = Nk\ln\left[1+\ln(q/N)\right]$$

assume $N \simeq 10^{22}$, $q \simeq 10^{24}$

$S \simeq 1$ J/K, entropy of order 1

(2) shuffle deck of cards $\Omega = 52! \simeq 10^{68}$

$S = k\ln\Omega \simeq 2\cdot 10^{-21}\ \frac{J}{K}$ extremely tiny

(3) compare with entropy generated by human in one day, or order

$$\Delta S = \frac{Q}{T} \simeq \frac{2000\ \text{kcal} \times 4.2\ \frac{J}{\text{cal}}}{300\ K}$$

$\simeq 3\cdot 10^4\ \frac{J}{K}$ large amount of entropy

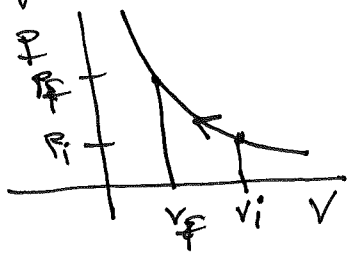
# Ways To Generate Entropy

(1) Change number $N$ of particles

$$S(U,V,N) = Nk\left[\frac{1}{2}\ln N + \frac{5}{2} + f(U,V)\right]$$

Chemical reactions change $N$, also change # degrees of freedom $f$ but we can't compute contributions of internal structure until Chapter 6

(2) Volume change. Consider constant energy $U$. so isothermal process since $U = \frac{3}{2}NkT$




$PV = NkT = \text{const}$

$$S = Nk\left[\ln(V) + f(N,U)\right]$$

$f$ doesn't depend on $V$

$$\boxed{\Delta S = Nk\ln V_f - Nk\ln V_i = Nk\ln\left(\frac{V_f}{V_i}\right)}$$

isothermal process

But $\Delta U = 0 = Q + W \Rightarrow Q = -W = \int_{V_i}^{V_f} P(V)\,dV$

$$= \int_{V_i}^{V_f} \frac{NkT}{V}\,dV = NkT\ln\left(\frac{V_f}{V_i}\right)$$

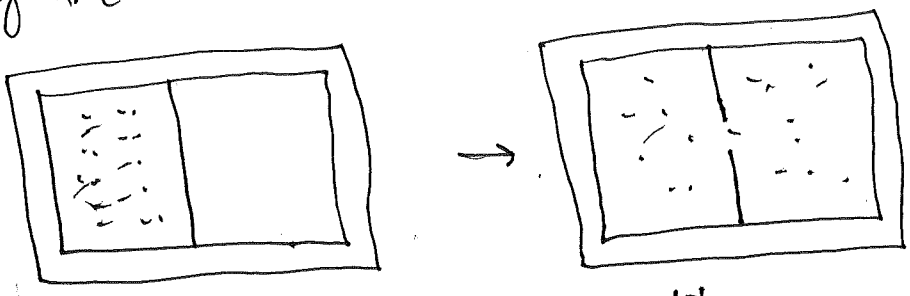
$$= T\Delta S$$

understand $\Delta S$ for isothermal as heat added to gas

$$\boxed{\Delta S = \frac{Q}{T}}$$

isothermal process

# Entropy Change Does Not Require Heat or Work: Free Expansion



open hole in partition

$\Delta U = 0$ no change in temperature

$W = 0$ no work done, no force applied over distance

$Q = 0$ isolated, $Q = \Delta U - W$

But $\Delta S = Nk \ln\left(\frac{V_f}{V_i}\right)$ just like isothermal process

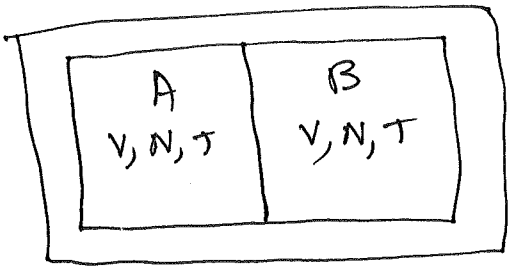
since $V_f > V_i$, $\Delta S > 0$

process is spontaneous and <u>irreversible</u>

definition: physical process is irreversible if <u>total</u> entropy change of system plus environment is positive, $\Delta S_{total} = \Delta S_{system} + \Delta S_{envi} > 0$

most processes are strongly irreversible

# Entropy Change By Mixing




monoatomic gases like He, Ar

initial entropy:

$$S_A^i = Nk\left[\ln V + f_A(U,N)\right]$$
$$S_B^i = Nk\left[\ln V + f_B(U,N)\right]$$

} depends on $m_A$, $m_B$, $U_A$, $U_B$

final entropy:

$$S_A^f = Nk\left[\ln(2V) + f_B(U,N)\right]$$
$$S_B^f = Nk\left[\ln(2V) + f_B(U,N)\right]$$

$$\Delta S = \left(S_A^f + S_B^f\right) - \left(S_A^i + S_B^i\right) = \boxed{2Nk\ln 2}$$

so-called "entropy of mixing"

irreversible process

## No entropy change for mixing identical gases

$$S^i = 2 \times Nk\left[\frac{5}{2} + \ln\left(\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{3/2}\right)\right]$$

$$S^f = (2N)k\left[\frac{5}{2} + \ln\left(\frac{2V}{2N}\left(\frac{4\pi m}{3h^2}\frac{2U}{2N}\right)^{3/2}\right)\right]$$

"mixed" gases have $2N$ atoms in volume $2V$ with total energy $2U$

so $\Delta S = S^f - S^i = 0$

This makes sense but only works if particles are exactly identical. For distinguishable atoms

$$S = Nk\left[\frac{5}{2} + \ln\left(V\left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{3/2}\right)\right]$$

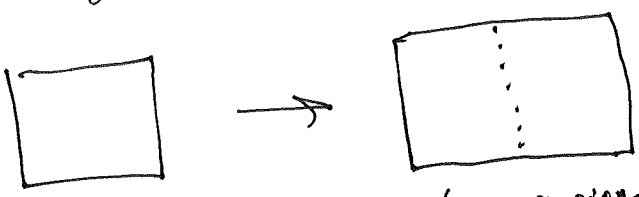
$N$ factor missing for distinguishable particles, comes from $1/N!$

and mixing identical gases would ~~be~~ generate entropy, violate additivity

Josiah Gibbs, great pioneer and developer of thermal physics, put $1/N!$ in by hand to fix this "Gibbs paradox".

# Intensive vs Extensive Thermodynamic Variables

Gibbs paradox depends on important property of thermodynamic variables, how they change if you "replicate" system



two versions of same system merged

$N, V, U, S$: extensive, additive

$P, T, \frac{N}{V}, \mu$: intensive variables, independent of size of system provided system remains homogeneous

$$S = S(U, V, N) = N \cdot f\left(\frac{U}{N}, \frac{V}{N}\right)$$

in order to be extensive, additive

could not write $S = f\left(\frac{U}{N}, \frac{V}{N}\right)$, wrong behavior

note: extensive + extensive is extensive

extensive × intensive is extensive

$\frac{\text{extensive}}{\text{extensive}}$ intensive e.g. $\frac{1}{T} = \frac{\partial S}{\partial U}$