

## Physical constants

Avagadro's number	$N_A$	$6.022 \times 10^{23} / \text{mol}$
Boltzmann constant	$k_B$	$1.38 \times 10^{-23} \text{ J/K}$ $8.617 \times 10^{-5} \text{ eV/K}$
Ideal gas constant	$R$	$8.314 \text{ J/mol K}$ $8.206 \times 10^{-2} \text{ l atm / mol K}$ $k_B N_A$
Gravity at sea level	$g$	$9.8 \text{ m/s}^2$
One atmosphere		$1.013 \times 10^5 \text{ Pa (J/m}^3\text{)}$
speed of light	$c$	$2.998 \times 10^8 \text{ m/s}$
Planck constant	$h$	$6.626 \times 10^{-34} \text{ J s}$ $4.135 \times 10^{-15} \text{ eV s}$
	$\hbar$	$1.054 \times 10^{-34} \text{ J s}$ $0.658 \times 10^{-15} \text{ eV s}$
electron volt	eV	$1.602 \times 10^{-19} \text{ J}$
electron charge	$e$	$1.602 \times 10^{-19} \text{ C}$
electron mass	$m_e$	$9.109 \times 10^{-31} \text{ kg}$
electron magnetic moment	$\mu_e$	$9.2848 \times 10^{-24} \text{ J/T}$
proton mass	$m_p$	$1.673 \times 10^{-27} \text{ kg}$
proton magnetic moment	$\mu_p$	$1.4106 \times 10^{-26} \text{ J/T}$
neutron mass	$m_n$	$1.675 \times 10^{-27} \text{ kg}$ $939.6 \text{ MeV}/c^2$

### Molecular masses

Particle	g/mol
$\text{N}_2$	28
$\text{O}_2$	32
He	4
Ar	40
$\text{CO}_2$	44
$\text{H}_2$	2
Si	28
Ge	73
Cu	64
Al	27

# Mathematical identities and combinatorics

$N$  distinguishable particles with  $M$  possible states each  
 $N$  indistinguishable particles with  $M$  possible states each  
Choose  $q$  from  $N$  options without replacement

$$\begin{aligned} M^N \\ M^N/N! \\ \binom{N}{q} = \frac{N!}{q!(N-q)!} \end{aligned}$$

$$\begin{aligned} \ln(A) - \ln(B) &= \ln(A/B) \\ e^{A+B} &= e^A e^B \end{aligned}$$

# Derivatives and differentials

Thermodynamic derivative notation.

$$\left(\frac{dS}{dU}\right)_{V,N} \equiv \frac{\partial S(U, V, N)}{\partial U}$$

Integration to find changes

$$\Delta x = \int dx$$

Chain rule

$$\frac{dz}{dx} = \frac{dz}{dy} \frac{dy}{dx}$$

# Definitions of thermodynamic quantities

Symbol	meaning
$T$	Temperature
$U$	Internal energy
$S$	Entropy
$\Omega$	Number of equally probable states
$C_V$	Heat capacity at constant volume
$C_p$	Heat capacity at constant pressure
$V$	Volume
$p$	Pressure
$\mu$	Chemical potential
$N$	Number of particles
$n$	Number of moles of particles ( $n = N/N_A$ )
$dW_{on}$	Work on $-pdV$
$dW_{by}$	Work by $pdV$
$H$	Enthalpy $U + pV$

$$S = k_B \ln \Omega$$

$$\frac{1}{T} \equiv \left( \frac{dS}{dU} \right)_{V,N}$$

$$\frac{p}{T} \equiv \left( \frac{dS}{dV} \right)_{U,N}$$

$$\frac{\mu}{T} \equiv - \left( \frac{dS}{dN} \right)_{U,V}$$

Heat capacity

Always true

$$C \equiv \frac{dQ}{dT}$$

Constant volume

$$C_V = \frac{dU}{dT}$$

Constant pressure

$$C_p = \frac{dU}{dT} + p \frac{dV}{dT}$$

## Ideal gas

Equation of state

$$pV = NkT$$

Isothermal processes

$$p = \frac{NkT}{V}$$

Adiabatic processes

$$p = \frac{C}{V^\gamma},$$

$C$  constant,  $\gamma = \frac{2}{N_{DOF}} + 1$

Kinetic ideal gas assumption:

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT$$

## Equipartition

$$U = \frac{N_{DOF}}{2} NkT + \text{constant}$$

Translational and rotational motion counts as 1 degree of freedom each, vibrational counts as 2 degrees of freedom each.

## Thermodynamic processes

First law of thermodynamics (division into work and heat)

$$dU = dQ - pdV$$

Second law of thermodynamics

$$\int_{S_i}^{S_f} dS \geq 0$$

Fundamental relation of thermodynamics

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

At constant number,

$$dS = \frac{dQ}{T} = \frac{C}{T}dT$$

Typical processes:

Isothermal	$T$ constant	reversible
Isobaric	$p$ constant	irreversible
Isochoric	$V$ constant	irreversible
Adiabatic	$Q = 0$	reversible

Maximum Carnot efficiency between two reservoirs at  $T_H, T_C$

$$\frac{W}{Q_H} \leq 1 - \frac{T_C}{T_H}$$

Coefficient of performance

- Refrigeration:  $Q_C/W$
- Heat pump:  $Q_H/W$

## Boltzmann factors and quantum systems

Boltzmann factor for state  $i$

$$f_i = e^{-E_i/kT}$$

Probability of state  $i$

$$P(i) = \frac{f_i}{\sum_j f_j}$$

Average internal energy

$$U = \sum_i P_i E_i$$

Heat capacity of a collection of harmonic oscillators with energy separation  $hf$

$$C_V = 3Nk \frac{x^2 e^x}{(e^x - 1)^2}, x = \frac{hf}{kT}$$

Number of ways to distribute  $q$  quanta in  $N$  oscillators

$$\binom{N+q-1}{q}$$

## Helmholtz free energy (T,V,N)

$$F = U - T_{env}S$$

- Equilibrium occurs at minimum  $F$
- $W_{max} = -\Delta F$

Chemical potential

$$\mu = \left( \frac{dF}{dN} \right)_{T,V}$$

Solutions

$$\frac{N_{solute}}{N_{solvent}} = C e^{-\Delta/kT}$$

Semiconductors

$$\frac{N_{conductors}}{N_{atoms}} = C e^{-\Delta/2kT}$$

Conductivity is proportional to the number of conductors.

## Gibbs free energy (T,p,N)

$$G = U - TS + pV = \mu(p, T)N$$

- Equilibrium occurs at minimum  $G$
- $W_{max} = -\Delta G$

## Phases and phase transitions

Only exist at fixed pressure and temperature (otherwise coexistence of phases). Lowest  $\mu \rightarrow$  equilibrium phase.

Latent heat:

$$L = \Delta H = T \Delta S$$

Variation of the chemical potential of phase  $X$  as a function of pressure and temperature:

$$d\mu_X = \frac{V_X}{N_X} dp - \frac{S_X}{N_X} dT$$

- Number Density:  $N_X/V_X$
- Entropy per particle:  $S_X/N_X$

# Physics 213 Formula Sheet

**First law:**  $dU = dQ + dW_{on}$

**Second law:**  $dS \geq 0$

**Entropy:**

- $S \equiv k \ln \Omega$
- $S_{total} = S_1 + S_2$

**Temperature, pressure, and chemical potential:**

- $T^{-1} \equiv \left(\frac{dS}{dU}\right)_{V,N}$
- $p \equiv T \left(\frac{dS}{dV}\right)_{U,N}$
- $-\mu \equiv T \left(\frac{dS}{dN}\right)_{U,V}$   
 $= -\left(\frac{dF}{dN}\right)_{T,V}$

**Fundamental relation:**

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN$$

**Ideal Gas Law:**

$$pV = NkT$$

**Thermodynamic potentials:**

- $F \equiv U - TS$
- $G \equiv U - TS + pV$

**Work:**

$$dW_{on} = -dW_{by} = -pdV$$

**First Law:**

$$dU = dQ - pdV$$

**Equipartition:**

$U = \left(\frac{1}{2}\right) k_B T$  per quadratic degree of freedom

**Heat Capacity:**

- $C \equiv \frac{dQ}{dT}$
- Constant volume:  $C_V = \frac{dU}{dT}$
- Constant pressure:  
 $C_p = \frac{dU}{dT} + p \frac{dV}{dT}$

**Thermodynamic Processes:**

- Isothermal:  $T = \text{const.}$
- Isobaric:  $p = \text{const.}$
- Isochoric:  $V = \text{const.}$
- Adiabatic:  $Q = 0$

**Boltzmann Factor:**

- $P(E_i) = Z^{-1} e^{-\frac{E_i}{k_B T}}$ ,
- $Z = \sum_i e^{-E_i/k_B T}$

**Thermal Radiation**

- $J = \sigma_B T^4$

**Counting particles**

- Distinguishable:  $\Omega = M^N$
- Indistinguishable:  $\Omega = \frac{M^N}{N!}$
- $q$  quanta in  $N$  oscillators:  
 $\binom{N-1+q}{q} = \frac{(N-1+q)!}{q!(N-1)!}$

## Constants, Data, Definitions

- Temperature:  $0 \text{ K} = -273.15^\circ\text{C} = -459.67^\circ\text{F}$
- Avogadro's number:  $N_A = 6.022 \times 10^{23} / \text{mole}$
- Boltzmann constant:  $k = 1.38 \times 10^{-23} \frac{\text{J}}{\text{K}} = 8.617 \times 10^{-5} \frac{\text{eV}}{\text{K}}$  [note: also written as  $k_B$ ]
- Universal gas constant:  $R = k N_A = 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} = 8.206 \times 10^{-2} \frac{\text{J}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$  (Universal gas const.)
- Planck's constant:  $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s} = 4.136 \times 10^{-15} \text{ eV}\cdot\text{s}$ ,  $\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34} \text{ J}\cdot\text{s}$ ,
- Magnetic moments: electron:  $\mu_e = 9.2848 \times 10^{-24} \frac{\text{J}}{\text{T}}$ , proton:  $\mu_p = 1.4106 \times 10^{-26} \frac{\text{J}}{\text{T}}$
- Mass: electron:  $m_e = 9.109 \times 10^{-31} \text{ kg}$ , proton:  $m_p = 1836 m_e = 1.673 \times 10^{-27} \text{ kg}$
- STP:  $T = 0^\circ\text{C}$ ,  $p = 100 \text{ kPa}$
- Stefan-Boltzmann constant:  $\sigma_B = 5.670 \times \frac{10^{-8} \text{ W}}{\text{m}^2\text{K}^4}$
- $c = 2.998 \times 10^8 \frac{\text{m}}{\text{s}}$ ,  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ ,  $g = 9.8 \frac{\text{m}}{\text{s}^2}$ ,  $1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$ ,  $1 \text{ liter} = 10^{-3} \text{ m}^3$

particle	g/mol
N <sub>2</sub>	28
O <sub>2</sub>	32
He	4
Ar	40
CO <sub>2</sub>	44
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