Temperature: a macroscopic property, a consequence of the microscopic behavior.

32°F can of soda

Two objects in thermal contact can exchange heat to arrive at a thermodynamic equilibrium (same temperature).

Temperature can be measured with a thermometer (mercury, gas at constant volume, electronic, etc.):

- Fahrenheit °F \( \rightarrow T_F = \frac{9}{5} T_C + 32 \)
- Celsius °C \( \rightarrow T_C = T_K - 273.16 °K \)
- Kelvin °K

Absolute zero is 0 °K.

Heat transfer (or exchange) rate: (How fast heat can be transferred) (per unit time)

\[ H = -kA \frac{dT}{dx} \]
Units: (S.I.)

\[ [H] = [k][A] \frac{[\Delta T]}{[dx]} \rightarrow \text{m} \text{m}^2 \text{m} \text{m} \text{m} \]

Energy per unit

\[ \frac{J}{s} \]

temperature: \( ^\circ \text{K} \)

\[ k \text{: thermal constant \ depends on type of materials} \]

(metal conducts heat faster, etc.)

\[ [k] = \frac{\frac{J}{s}}{m^2 \cdot ^\circ \text{K}} = \frac{\frac{W}{m \cdot ^\circ \text{K}}}{m \cdot ^\circ \text{K}} \quad (\text{SI}) \]

\[ [k] = \frac{\text{Btu}}{\text{h} \cdot \text{ft}^2 \cdot ^\circ \text{F}} \quad (\text{British system}) \]

\[ H = -kA \frac{\Delta T}{dx} \quad \rightarrow \quad H = -\frac{A \cdot \Delta T}{R} \]

R-factor: \( R = \frac{\Delta x}{k} \)

\[ \text{SI:} \quad \frac{m^2 \cdot ^\circ \text{K}}{W} \]

\[ \text{British:} \quad \frac{\text{ft}^2 \cdot ^\circ \text{F}}{\text{Btu/\text{h}}} \]

Mechanisms of heat transfer:

- conduction: (electrons, atoms, molecules)
- convection: (circulation)
- radiation
Heat exchange: \[ \Delta Q_{\text{Table}} + \Delta Q_{\text{soda}} = 0 \]

(Soda: 32°F = T_{\text{soda}}; Table: T_{\text{Table}} = 60°F; T.D. equilibrium = 59.9°F)

\[ \Delta Q = C \Delta T \]

Heat Capacity \( \left( \frac{J}{\text{kg} \cdot \text{°K}} \right) \) \rightarrow \text{mass} \rightarrow \text{mass}

\[ C = c \cdot m \]

Specific heat capacity specific to different materials (Table 16.1)

\[ C_{\text{water}} = 4184 \frac{J}{\text{kg} \cdot \text{°K}} \]

\[ C_{\text{copper}} = 386 \frac{J}{\text{kg} \cdot \text{°K}} \]

\[ C_{\text{Table}} m_{\text{Table}} (T_{D} - T_{\text{Table}}) + C_{\text{soda}} m_{\text{soda}} (T_{D} - T_{\text{soda}}) = 0 \]

Heating loss rate (per unit time) by radiation of an object of area \( A \) & temperature \( T \):

Stefan-Boltzmann Law: \[ P = e \sigma A T^4 \]

\( e \) = emissivity

Stefan-Boltzmann constant: \( \sigma = 5.67 \times 10^{-8} \text{ W/m}^2\text{°K}^4 \)
Ch 17 Thermal Behavior of Matter:

3 states of matter: gas, liquid, solid
- Low density → almost free molecule
- High density → some interaction between molecules
- More interaction

Ideal gas: completely free molecule

Manoscopic properties:
- Volume (V)
- Number of molecules (N)
- Temperature (T)
- Pressure (P)

\[ \frac{N, V, P, T}{number \ of \ molecules} \]

1. \[ PV = kN \]

Ideal Gas Law:
- \[ k = \text{Boltzmann constant} = 1.38 \times 10^{-23} \ \text{J/}^\circ \text{K} \]
- \[ N = n \times N_A; \ N_A = 6.022 \times 10^{23} \text{mol}^{-1} \]

\[ PV = k n N_A T = n \frac{kN_A T}{\overline{R}} \]
- \[ \overline{R} = 8.314 \ \text{J/}^\circ \text{K mol} \]

2. \[ \frac{2P V}{N} = kNT \]
To take into consideration some interaction between gas molecules:

\[(P + \frac{n^2 a}{V^2})(V - nb) = nRT\]

real gas law or van der Waals law

\(a\) & \(b\) are constants.

Ideal gas: gas molecules: pressure exerted on the container wall by one molecule

Focus on this wall

Conservation of momentum for the molecule & wall system:

\[m v_x = -m v_x + 2m v_{x_i}\]

momentum received by the wall

by \(N\) molecules:

\[P = \frac{N}{\text{vol}} \sum_{i=1}^{N} P_i = \frac{mN}{\text{vol}} \left(\frac{\sum_{i=1}^{N} v_{xi}}{N}\right)\]

\[P = \frac{mN}{\text{vol}} \frac{v_x^2}{v_x^2}\]
\[
\frac{v_x^2}{v^2} = \frac{1}{3} \quad \text{Total velocity}
\]

\[
P = \frac{mN}{3Vv} \quad \overrightarrow{v^2}
\]

\[
PV = mN\overrightarrow{\frac{v^2}{3}}
\]

Derived from microscopic mechanics of gas molecules.

Previously: \[PV = kNT\]

\[\text{Conclusion: } \quad kT = m\overrightarrow{\frac{v^2}{3}} = \frac{2}{3} \quad \frac{1}{2}mv^2
\]

Average K.E. of a gas molecule

\[\text{The average kinetic energy of a gas molecule is } \frac{3}{2}kT\]

\[\frac{1}{2}mv^2 = \frac{3}{2}kT\]

Microscopic \quad \text{Macroscopic}

More on this in Statistical Mechanics.

\[
\text{In 3D what is the average K.E. of a gas molecule?}
\]

\[\frac{1}{2}mv_x^2 = \frac{1}{2}kT.
\]
Thermal behavior of matter:

Heat is supplied, $\Delta Q$, consequences are:

1. $\Delta T$ ($\Delta Q = cm \Delta T$)

2. Change of phase ($\Delta Q = mL$)
   - Latent heat
   - Transformation
   - $L_v$ (vap to gas)
   - $L_f$ (solid to gas)

3. Expansion $\Delta L$, $\Delta V$
   - Linear $\alpha = \frac{\Delta L}{L \Delta T}$
   - Volume $\beta = \frac{\Delta V}{V \Delta T}$

---

$25^\circ C$

$\Delta Q = cm \Delta T$

Temperature increase

Solid $\xrightarrow{\text{fusion}}$ Liquid $\xrightarrow{\text{vaporization}}$ Gas

$L_v$, $L_f$, $L_s$

Sublimation

Water starts to boil at $100^\circ C$.

After 2 min

$T = 100^\circ C$

Change of phase ($\Delta T = 0$ !)
Phase Diagram:

Normal

Solid → Liquid: we need to increase T

Water

Solid → Liquid
→ increase T
→ increase P at same T

By applying pressure on an ice cube, it melts.

\[ \text{density } P_{\text{ice}} < P_{\text{water}} \]
1st Law of Thermodynamics:

Heat absorbed by a system \( Q \)
Work done by system \( W \)
Change of internal energy: \( \Delta U \) (Conservation of energy)

\[ \Delta U = Q - W \]

\( \Delta U, T, P, V \) are state variables, (they do not depend on a particular process)
\( Q, W \) are NOT state variables, (they depend on a particular process)

In a PV diagram: the work done is the area under the curve. Work done from 1 to 2 via a isobaric + isovolumic process: \( W = A \) is less than the work done if an isothermal process is followed \( (W = B > A) \)
Why the work done is the area under the curve in a PV diagram?

Work done is \[ W = F \cdot \Delta x = \text{P.A.} \cdot \Delta x \]

\[ \rightarrow dW = P \, dV \rightarrow \left[ W = \int dW = \int P \, dV \right] \]

\[ \rightarrow \text{area under the curve } P(V)! \]

**Isothermal process: (const. T) b/w state 1 and state 2**

Work done in this process: \[ W = \int P \, dV \]

\[ \rightarrow \text{Need } P(V) \]

\[ \rightarrow \text{Ideal gas } \quad PV = nRT \rightarrow P = \frac{nRT}{V} \]

Work done by an ideal gas in an isothermal process:

\[ W = \int_{V_1}^{V_2} \frac{nRT}{V} \, dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \left[ \ln V_2 - \ln V_1 \right] \]

\[ = nRT \ln \left( \frac{V_2}{V_1} \right) \]

For an ideal gas, this area is \[ nRT \ln \left( \frac{V_2}{V_1} \right) \]
Ideal gas:

\[ \Delta U = \Delta K.E \]

1) All internal energy comes from kinetic energy (since we assume for an ideal gas, there is no interaction)

2) Ave. K.E per molecule: \( \frac{1}{2} m v^2 = \frac{3}{2} kT \)

3) Isothermal: \( T_1 = T_2 \) \[ \Rightarrow \Delta U = 0 \]
isochemical, ideal gas.

So then what is the heat absorbed by an ideal gas in an isothermal process?

\[ \Delta U = Q - W = 0 \quad \Rightarrow \quad Q = W = nRT \ln \frac{V_2}{V_1} \]

Suppose: \( V_1 < V_2 \) \[ \begin{cases} W > 0 \\ Q > 0 \end{cases} \]

Heat: \( Q \)
Isovolumic Process (const. Volume) b/w state 1 & state 2.

\[ W = \int_{1}^{2} PdV = 0 \]

Specific heat at constant V: 
\[ C_V = \frac{1}{n} \frac{Q}{\Delta T} = \frac{1}{n} \frac{\Delta U}{\Delta T} \]
\[ Q = nC_V \Delta T \]

Isochoric Process (const. pressure) b/w state 1 & state 2.

Specific heat at constant P: 
\[ C_P = \frac{1}{n} \frac{Q}{\Delta T} \]
\[ Q = nC_P \Delta T \]
For an ideal gas: \[ PAV = nRDT = \frac{W}{n} \]

11 Law of T.D.: \[ AU = Q - W = Q - PAV \]

\[ \downarrow \quad \downarrow \quad \downarrow \quad \text{ideal gas} \]

\[ nCVDT = nCPDT = nRDT \]

\[ mcvDT = mcpDT = mRDT \]

\[ c_v = c_p - R \quad \text{or} \quad c_p = c_v + R \]

\[ R = 8.314 \frac{J}{kmol} \]

Ideal gas: \[ c_p > c_v \]

Does this make sense? \[ \{ \text{cont. } P = Q = DU + W \} \]

\[ \{ \text{cont. } V = Q = DU + 0 \} \]

Adiabatic Process \( (Q = 0) \) b/w state 1 & state 2

\[ W = \frac{P_1V_1 - P_2V_2}{\gamma - 1} \]

11 Law of T.D.: \[ DU = -W \]

\[ P(V) \text{ is constant: } p_1V_1^\gamma = p_2V_2^\gamma \]

ideal gas \[ \gamma = \frac{c_p}{c_v} > 1 \text{ no unit (a dimensionless)} \]

\[ TV^{\gamma - 1} \text{ is constant: } T_1V_1^{\gamma - 1} = T_2V_2^{\gamma - 1} \]


→ Ideal gas: what are possible values for $\gamma$?

\[ \text{Ave. k.E per molecule: } \frac{1}{2} m v^2 = \frac{3}{2} kT \quad (3D) \]

→ Ave. kE per molecule per degree of freedom: $\frac{1}{2} kT$

→ Monatomic gases (Ne, Ar, etc.): molecules are single atomic → Ave. kE per molecule is $\frac{3}{2} kT$

→ Diatomic gases (H₂, O₂, etc...): molecules are groups of 2 atoms

\[
\begin{array}{c}
\text{H} \\
3
\end{array}
\quad \begin{array}{c}
\text{H} \\
3
\end{array}
\rightarrow \text{total 6 (lose 1 if they are connected: along x: they can't move away from each other.)}
\]

→ Ave. kin. energy per molecule is $\frac{5}{2} kT$

\[
C_v = \frac{1}{n} \frac{\Delta U}{\Delta T} \left\{ \begin{array}{l}
\text{Monatomic: } \Delta U = N \frac{3}{2} kT \\
\text{Diatomic: } \Delta U = N \frac{5}{2} kT
\end{array} \right. \quad \rightarrow \quad C_v = \frac{3R}{\gamma^2}
\]

\[\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v} \left\{ \begin{array}{l}
\text{Monatomic: } \gamma = 1.67 \\
\text{Diatomic: } \gamma = 1.4
\end{array} \right. \quad \text{ideal gas.} \]
\( \Delta U = Q - W \rightarrow \Delta U_{A B C A} = 0 \)

\( Q_{A B C A} = W_{A B C A} = 13 \text{ J} \)

\( Q_{A B} + Q_{B C A} = 13 \text{ J} \)

\( Q_{B C A} = 13 \text{ J} - Q_{A B} = 13 - 35 = -22 \text{ J} \)

\( \text{(From B to C to A gas delivers 22 J)} \)
\[ V_i = 25 \text{ L} \quad \gamma = 1.67 \quad T_i = 250 \text{ \degree K} \quad P_i = 50 \text{ kPa} \]

\[ \text{adiabatic} \]

\[ \text{in thermal} \quad 250 \text{ \degree K} \]

\[ \text{c} \]

\[ \text{1} \]

\[ P_1 \]

\[ V_1 \]

\[ V \]

\[ \text{a)} \quad \text{Work done on gas?} \]

We can find work done by the gas \( W_{1231} \)

\[ W_{1231} = W_{12} + 0 + W_{31} \]

\[ W_{31} = nRT \ln \frac{V_i}{V_3} = nRT \ln \frac{V_i}{V_2} \rightarrow \text{need} \]

\[ \text{b)} \quad \text{From 1 via adiabatic:} \quad P_i \gamma V_i = P_2 V_2^\gamma \]

\[ V_i^\gamma = 3 V_2^\gamma \]

\[ V_2 = \left( \frac{V_i}{V_2} \right)^\gamma = 3 \quad \Rightarrow \quad \frac{V_i}{V_2} = \frac{3}{8} \]

\[ \text{Also:} \quad P_i V_i = nRT \]

\[ \frac{V_i^\gamma}{V_2^\gamma} = 3 \quad \Rightarrow \quad \frac{V_i}{V_2} = \frac{P_i V_i}{V_2} \ln 3 \]

\[ W_{31} = P_i V_i \ln \frac{V_i}{V_2} = P_i V_i \ln 3 = \frac{P_i V_i}{\gamma} \ln 3 \]

\[ = \frac{50 \times 10^3 \times 25 \times 10^{-3}}{1.67} \ln 3 \quad J = 822 \ J \]
\[ W_{12} = \frac{p_1 V_1 - p_2 V_2}{\gamma - 1} = \frac{p_1 V_1 - 3p_1 V_1}{\gamma - 1} \left(1 - \frac{1}{\gamma} \right) \]
\[ = p_1 V_1 \frac{1 - 3}{\gamma - 1} \left(\frac{0.61}{1.67}\right) \]
\[ = 50 \text{ m}^3 \times 25 \text{ kg/m}^3 \times 1 - 3 \times \frac{0.61}{1.67} \]
\[ = -1033 \text{ J} \]

\[ W_{1231} = -1033 + 822 = -211 \text{ J} \]

\[ \rightarrow \text{ Work done on gas is } -211 \text{ J} \]

(17.46)

Refrigerator extracts energy from its inside at \( \frac{85 \text{ J}}{s} \).

How long to freeze \( m_w = 0.75 \text{ kg} \) at \( T_w = 0 \text{°C} \)?

\[ Q = \text{how much heat we need to extract from the water to freeze it?} \rightarrow \text{Heat of transformation:} \]

\[ Q = m_w L_f = 0.75 \text{ kg} \times 334 \text{ kJ/kg} = 250.5 \text{ kJ} \]

\[ \text{Table 17.1: } 334 \text{ kJ/kg} \]

\[ t = \frac{Q}{95.5} = \frac{250500 \text{ J}}{95.5 \text{ J/s}} = \frac{1400 \text{ min}}{60 \text{ s}} = 43.35 \text{ min} \]
The pressure of a gas can be expressed as

\[ P_{\text{gas}} = \frac{d_h}{d} \]

The pressure gauge reading is

\[ P_L = 80 \text{ mm HG} \]

and the pressure in the reservoir is

\[ P_H = 125 \text{ mm HG} \]

The volume is constant, hence

\[ P_L V_L = P_H V_H \]

Using the equation for the radius of a sphere,

\[ \frac{4}{3} \pi \left( \frac{d^3}{2} \right) = \frac{4}{3} \pi \left( \frac{d_{\text{H}}}{2} \right)^3 \]

\[ P_L \frac{4}{3} \pi \left( \frac{d_L^3}{2} \right) = P_H \frac{4}{3} \pi \left( \frac{d_{\text{H}}}{2} \right)^3 \]

\[ P_L d_L^3 = P_H d_{\text{H}}^3 \]

\[ d_{\text{H}} = \left( \frac{P_L}{P_H} \right) d_L \]

\[ = \left( \frac{80 + 760}{125 + 760} \right)^{1/2} = \frac{1.52}{1.49} \text{ mm} \]

We can use mm HG instead of Pa in this problem because conversion factors will cancel up & down.

What is 1 atm in mm HG?

\[ \frac{1 \text{ atm}}{101300 \text{ Pa}} = \frac{133.3 \text{ Pa}}{1 \text{ mm HG}} = \frac{133.3 \text{ atm}}{101300 \text{ mm HG}} = \frac{1 \text{ atm}}{133.3} \]

\[ 1 \text{ atm} = \frac{760 \text{ mm HG}}{1} \]
1) Work done by heart?

Work done by gas = isothermal process (const. temp at
the body temp.)

\[ W_{LH} = nRT \ln \left( \frac{V_H}{V_L} \right) = P_L V_L \ln \left( \frac{d_H}{d_L} \right) = 3P_L V_L \ln \left( \frac{d_H}{d_L} \right) \]

\[ = 3(80 + 760) \cdot \frac{133.3}{1} \cdot \frac{4\pi (0.76 \times 10^{-3})^3}{8} \ln \left( \frac{1.49}{1.52} \right) \]

\[ = 617675 \times 10^{-9} \ln \left( \frac{1.49}{1.52} \right) = -12312 \times 10^{-9} J \]

\[ = -12 \times 10^{-6} J = -12 \mu J \]

18.57

\[ \text{Ar} \ (\text{monatomic}) \quad \& \quad \text{O}_2 \ (\text{diatomic}) \]

\[ P_1 \quad \text{click. expansion} \quad \frac{P_1}{3} \quad 2V_1 \rightarrow \text{get } Y_1 \]

What fraction of molecules are Ar?
Heat reservoir: source of heat, at constant temperature

Repeating
"cycles:

Heating Engine

Putting an ideal gas in contact with a heat reservoir: it absorbs heat $\rightarrow$ expands (doing work)

Next, putting gas in contact with a cold reservoir at $T_c$: it loses heat $\rightarrow$ compresses (receiving work)

$T_h$ $\rightarrow Q_h$ $\rightarrow W$ $\rightarrow Q_c$ $\rightarrow T_c$
\[ \Delta U_{\text{engine}} = Q_{\text{net}} - W = Q_h - Q_c - W \]

1st law of T.D.

ideal, isothermal process = 0

\[ Q_h - Q_c = W \]

Efficiency of an ideal gas heat engine:

\[ \eta = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} \]

\[ = 1 - \frac{|Q_c|}{|Q_h|} < 1 \]

2nd law of T.D.: it is impossible to build a heat engine operating in cycles that extract heat from a hot reservoir and returning some of it to a cold reservoir that can deliver a 100% of work.

Refrigerators: reversed heat engines

Coefficient of Performance: C.O.P. = \[ \frac{Q_c}{W} \]

2nd law of T.D.: it is impossible to transfer heat from a cold reservoir to a hot reservoir without requiring any work.
Entropy: 

\[ \Delta S = \int_{1}^{2} \frac{dQ}{T} \]

3rd Law of T.D: entropy of a closed system cannot decrease \( \Delta S \geq 0 \)

(entropy is related to order)

(A)

\[ T_1 = 700^\circ K, \quad T_2 = 300^\circ K \]

\[ N_1 = 1000, \quad N_2 = 1000 \]

\[ V_1 = V_2 \]

\( p_2 > p_1 \), why?

\( PV = nRT \) (macroscopic)

\( \sqrt{\frac{3kT}{m}} \) (microscopic): higher thermal speed, higher pressure on the wall

\( \rightarrow \)

(A) \( \rightarrow \) (B) spontaneously mixed together: order has decreased. \( (\Delta S \) increased).

\( \rightarrow \) Natural process is always increasing entropy.
Cannot Engine

4 reversible process

\[ \begin{align*}
&2 \text{ isothermal} \\
&2 \text{ adiabatic}
\end{align*} \]

\[ \rightarrow \text{ideal gas, max. achievable efficiency: } \eta_{\text{max}} \]

\[
\eta_{\text{max}} = ? \\
\eta = 1 - \frac{|Q_c|}{|Q_h|}
\]

\[ Q_h = \text{heat absorbed from hot reservoir during isothermal exp. A} \rightarrow \beta \]

\[ Q_c = \text{(isothermal } C \rightarrow D) = nRT_c \ln \frac{V_D}{V_C} \]

There is a connection b/w the volume:

\[ B \rightarrow C \text{ adiabatic: } T_B V_B^{\gamma-1} = T_C V_C^{\gamma-1} \]

\[
\frac{V_B}{V_C} = \frac{V_D}{V_A} \text{ then:
}
\]

\[ \rightarrow \left( \frac{V_B}{V_C} \right)^{\gamma-1} = \frac{T_C}{T_B} = \frac{T_{\text{cold}}}{T_h} = \frac{T_c}{T_h} \]

\[ D \rightarrow A \text{ adiabatic: } T_D V_D^{\gamma-1} = T_A V_A^{\gamma-1} \]

\[ \left( \frac{V_D}{V_A} \right)^{\gamma-1} = \frac{T_A}{T_D} = \frac{T_h}{T_c} \]
\[ e = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{|nRT_c \ln \frac{V_B}{V_c}|}{|nRT_h \ln \frac{V_B}{V_A}|} = 1 - \frac{nRT_c \ln \frac{V_c}{V_B}}{nRT_h \ln \frac{V_B}{V_A}} \]

\[ e_{\text{max}} = 1 - \frac{T_c}{T_h} < 1 \]

**Otto Cycle Engine**: 4 reversible processes

\[ \begin{array}{c}
\text{2 adiabatic} \\
\text{2 isochoric} \\
\end{array} \]

\[ \begin{align*}
\Delta S &= \int_1^2 \frac{dQ}{T} \\
&= \int_1^2 ncv \frac{dT}{T} = ncv \int_1^2 \frac{dT}{T} = ncv[\ln T]_1^2 \\
\text{isothermal:} &\quad \Delta S = \frac{1}{T} \int_1^2 dQ = \frac{Q_2 - Q_1}{T} = \frac{\Delta Q}{T}
\end{align*} \]