Summaries of chapters for 2nd mid-term (cannot be brought to the exam) Chapter 16 (Macroscopic Description of Matter)

GENERAL PRINCIPLES

Three Phases of Matter

Solid Rigid, definite shape.

Nearly incompressible.

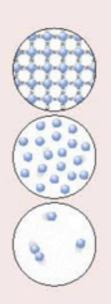
Liquid Molecules loosely held

together by molecular bonds,

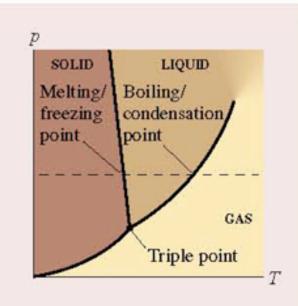
but able to move around. Nearly incompressible.

Gas Molecules move freely

through space. Compressible.



The different phases exist for different conditions of temperature *T* and pressure *p*. The boundaries separating the regions of a phase diagram are lines of phase equilibrium. Any amounts of the two phases can coexist in equilibrium. The triple point is the one value of temperature and pressure at which all three phases can coexist in equilibrium.



APPLICATIONS

Temperature scales

$$T_{\rm F} = \frac{9}{5}T_{\rm C} + 32^{\circ}$$
 $T_{\rm K} = T_{\rm C} + 273$

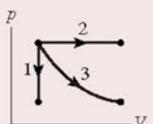
The Kelvin temperature scale is based on:

- Absolute zero at $T_0 = 0 \text{ K}$
- The triple point of water at $T_3 = 273.16 \text{ K}$

Three basic gas processes

- 1. Isochoric, or constant volume
- 2. Isobaric, or constant pressure
- 3. Isothermal, or constant temperature

pV diagram

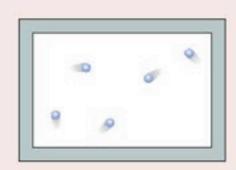


Chapter 16 (contd.)

IMPORTANT CONCEPTS

Ideal-Gas Model

 Atoms and molecules are small, hard spheres that travel freely through space except for occasional collisions with each other or the walls.



- · The molecules have a distribution of speeds.
- The model is valid when the density is low and the temperature well above the condensation point.

Ideal-Gas Law

The state variables of an ideal gas are related by the ideal-gas law

$$pV = nRT$$
 or $pV = Nk_BT$

where R = 8.31 J/mol K is the universal gas constant and $k_{\rm B} = 1.38 \times 10^{-23}$ J/K is Boltzmann's constant.

p, V, and T must be in SI units of Pa, m^3 , and K. For a gas in a sealed container, with constant n:

$$\frac{p_2 V_2}{T_2} = \frac{p_1 V_1}{T_1}$$

Counting atoms and moles

A macroscopic sample of matter consists of N atoms (or molecules), each of mass m (the atomic or molecular mass):

$$N = \frac{M}{m}$$

Alternatively, we can state that the sample consists of *n* moles

$$n = \frac{N}{N_{\rm A}}$$
 or $\frac{M({\rm in \ grams})}{M_{\rm mol}}$

Volume V

Mass M

 $N_{\rm A}=6.02\times 10^{23}\,{\rm mol}^{-1}\,{\rm is}\,{\rm Avogadro's}\,{\rm number}.$

The numerical value of the molar mass M_{mol} , in g/mol, equals the numerical value of the atomic or molecular mass m in u. The atomic or molecular mass m, in atomic mass units u, is well approximated by the atomic mass number A.

$$1 \text{ u} = 1.661 \times 10^{-27} \text{ kg}$$

The **number density** of the sample is $\frac{N}{V}$.

Chapter 17 (Work, Heat and 1st Law of Thermodynamics)

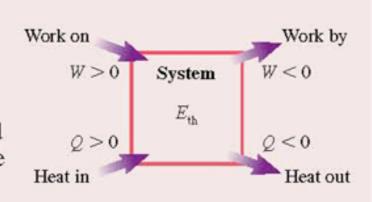
GENERAL PRINCIPLES

First Law of Thermodynamics

$$\Delta E_{\rm th} = W + Q$$

The first law is a general statement of energy conservation.

Work W and heat Q depend on the process by which the system is changed.



The change in the system depends only on the total energy exchanged W + Q, not on the process.

Energy

Thermal energy $E_{\rm th}$ Microscopic energy of moving molecules and stretched molecular bonds. $\Delta E_{\rm th}$ depends on the initial/final states but is independent of the process.

Work W Energy transferred to the system by forces in a mechanical interaction.

Heat Q Energy transferred to the system via atomiclevel collisions when there is a temperature difference. A thermal interaction.

SUMMARY OF BASIC GAS PROCESSES

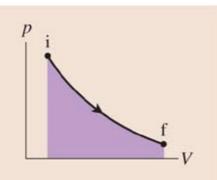
Process	Definition	Stays constant	Work	Heat
Isochoric	$\Delta V = 0$	V and p/T	W = 0	$Q = nC_{V}\Delta T$
Isobaric	$\Delta p = 0$	p and V/T	$W = -p\Delta V$	$Q = nC_{\rm P}\Delta T$
Isothermal	$\Delta T = 0$	T and pV	$W = -nRT \ln (V_{\rm f}/V_{\rm i})$	$\Delta E_{ m th}=0$
Adiabatic	Q = 0	pV^{γ}	$W=\Delta E_{ m th}$	Q = 0
All gas processes		Ideal-gas law First law	$pV = nRT$ $\Delta E_{ m th} = W + Q = nC_{ m V}\Delta T$	

Chapter 17 (contd.)

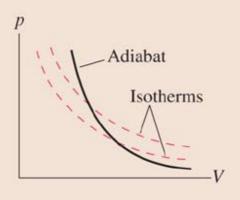
Important Concepts

The work done on a gas is

$$W = -\int_{V_i}^{V_f} p \, dV$$
$$= -(\text{area under the } pV \text{ curve})$$



An adiabatic process is one for which Q = 0. Gases move along an adiabat for which $pV^{\gamma} = \text{constant}$, where $\gamma = C_P/C_V$ is the specific heat ratio. An adiabatic process changes the temperature of the gas without heating it.



Calorimetry When two or more systems interact thermally, they come to a common final temperature determined by

$$Q_{\text{net}} = Q_1 + Q_2 + \cdots = 0$$

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The heat of transformation *L* is the energy needed to cause 1 kg of substance to undergo a phase change

$$Q = \pm ML$$

The specific heat c of a substance is the energy needed to raise the temperature of 1 kg by 1 K:

$$Q = Mc\Delta T$$

The molar specific heat C is the energy needed to raise the temperature of 1 mol by 1 K:

$$Q = nC\Delta T$$

The molar specific heat of gases depends on the *process* by which the temperature is changed:

 $C_{\rm V} = {\rm molar}$ specific heat at **constant volume** $C_{\rm P} = C_{\rm V} + R = {\rm molar}$ specific heat at **constant pressure**

Heat is transferred by conduction, convection, radiation, and evaporation.

Conduction: $Q/\Delta t = (kA/L)\Delta T$

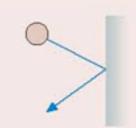
Radiation: $Q/\Delta t = e\sigma A T^4$

Chapter 18 (The Micro/Macro Connection)

IMPORTANT CONCEPTS

Pressure is due to the force of the molecules colliding with the walls.

$$p = \frac{1}{3} \frac{N}{V} m v_{\rm rms}^2 = \frac{2}{3} \frac{N}{V} \epsilon_{\rm avg}$$

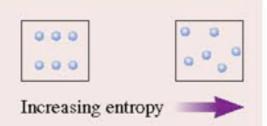


The average translational kinetic energy of a molecule is

$$\epsilon_{
m avg}=rac{3}{2}k_{
m B}T$$
. The temperature of the gas $T=rac{2}{3k_{
m B}}\epsilon_{
m avg}$

measures the average translational kinetic energy.

Entropy measures the probability that a macroscopic state will occur or, equivalently, the amount of disorder in a system.



The thermal energy of a system is

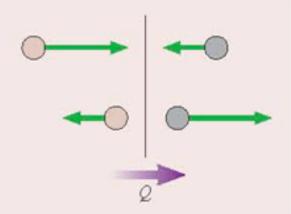
 E_{th} = translational kinetic energy + rotational kinetic energy + vibrational energy

• Monatomic gas
$$E_{\rm th} = \frac{3}{2}Nk_{\rm B}T = \frac{3}{2}nRT$$

• Diatomic gas
$$E_{\text{th}} = \frac{5}{2}Nk_{\text{B}}T = \frac{5}{2}nRT$$

• Elemental solid
$$E_{th} = 3Nk_BT = 3nRT$$

Heat is energy transferred via collisions from more-energetic molecules on one side to less-energetic molecules on the other. Equilibrium is reached when $(\epsilon_1)_{\text{avg}} = (\epsilon_2)_{\text{avg}}$, which implies $T_{1\text{f}} = T_{2\text{f}}$.



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Chapter 18 (contd.)

GENERAL PRINCIPLES

Kinetic theory, the micro/macro connection, relates the macroscopic properties of a system to the motion and collisions of its atoms and molecules.

The Equipartition Theorem

Tells us how collisions distribute the energy in the system. The energy stored in each mode of the system (each **degree** of **freedom**) is $\frac{1}{2}Nk_BT$ or, in terms of moles, $\frac{1}{2}nRT$.

The Second Law of Thermodynamics

Tells us how collisions move a system toward equilibrium. The entropy of an isolated system can only increase or, in equilibrium, stay the same.

- Order turns into disorder and randomness.
- · Systems run down.
- Heat energy is transferred spontaneously from the hotter to the colder system, never from colder to hotter.

APPLICATIONS

The root-mean-square speed $v_{\rm rms}$ is the square root of the average of the squares of the molecular speeds:

$$v_{\rm rms} = \sqrt{(v^2)_{\rm avg}}$$

For molecules of mass m at temperature T,

$$v_{\rm rms} = \sqrt{\frac{3k_{\rm B}T}{m}}$$

Molar specific heats can be predicted from the thermal energy because $\Delta E_{\text{th}} = nC\Delta T$.

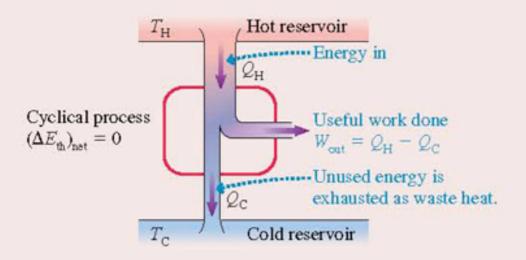
- Monatomic gas $C_V = \frac{3}{2}R$
- Diatomic gas $C_V = \frac{5}{2}R$
- Elemental solid C = 3R

Chapter 19 (Heat Engines and Refrigerators)

GENERAL PRINCIPLES

Heat Engines

Devices which transform heat into work. They require two energy reservoirs at different temperatures.



Thermal efficiency

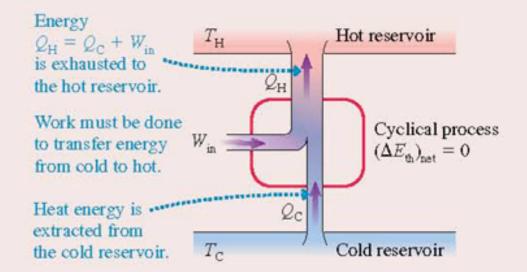
$$\eta = rac{W_{
m out}}{Q_{
m H}} = rac{{
m what \ you \ get}}{{
m what \ you \ pay}}$$

Second law limit:

$$\eta \le 1 - \frac{T_{\rm C}}{T_{\rm H}}$$

Refrigerators

Devices which use work to transfer heat from a colder object to a hotter object.



Coefficient of performance

$$K = \frac{Q_{\rm C}}{W_{\rm in}} = \frac{\text{what you get}}{\text{what you pay}}$$

Second law limit:

$$K \le \frac{T_{\rm C}}{T_{\rm H} - T_{\rm C}}$$

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Chapter 19 (contd.)

IMPORTANT CONCEPTS

A perfectly reversible engine (a Carnot engine) can be operated as either a heat engine or a refrigerator between the same two energy reservoirs by reversing the cycle and with no other changes.

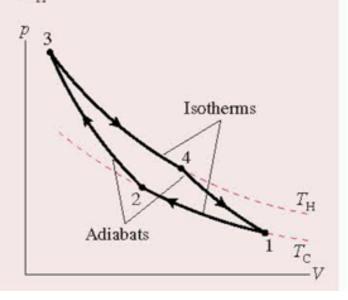
 A Carnot heat engine has the maximum possible thermal efficiency of any heat engine operating between T_H and T_C.

$$\eta_{ ext{Carnot}} = 1 - rac{T_{ ext{C}}}{T_{ ext{H}}}$$

 A Carnot refrigerator has the maximum possible coefficient of performance of any refrigerator operating between T_H and T_C.

$$K_{
m Carnot} = rac{T_{
m C}}{T_{
m H}\,-\,T_{
m C}}$$

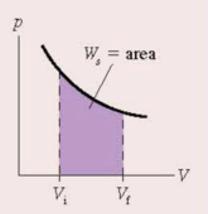
The Carnot cycle for a gas engine consists of two isothermal processes and two adiabatic processes.



An energy reservoir is a part of the environment so large in comparison to the system that its temperature doesn't change as the system extracts heat energy from or exhausts heat energy to the reservoir. All heat engines and refrigerators operate between two energy reservoirs at different temperatures $T_{\rm H}$ and $T_{\rm C}$.

The work W_s done by the system has the opposite sign to the work done on the system.

 $W_s = \text{area under } pV \text{ curve}$



APPLICATIONS

To analyze a heat engine or refrigerator:

MODEL Identify each process in the cycle.

VISUALIZE Draw the pV diagram of the cycle.

SOLVE There are several steps:

- Determine p, V, and T at the beginning and end of each process.
- Calculate $\Delta E_{\rm th}$, $W_{\rm s}$, and Q for each process.
- Determine $W_{\rm in}$ or $W_{\rm out}$, $Q_{\rm H}$, and $Q_{\rm C}$.
- Calculate $\eta = W_{\text{out}}/Q_{\text{H}}$ or $K = Q_{\text{C}}/W_{\text{in}}$.

ASSESS Verify $(\Delta E_{\text{th}})_{\text{net}} = 0$. Check signs.