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CHEM 254 COURSE NOTES

INTRODUCTION TO CHEMICAL THERMODYNAMICS

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Abstract

These notes are intended as a resource for myself; past, present, or future students of this course, and anyone interested in the material. The goal is to provide an end-to-end resource that covers all material discussed in the course displayed in an organized manner. These notes are my interpretation and transcription of the content covered in lectures. The instructor has not verified or confirmed the accuracy of these notes, and any discrepancies, misunderstandings, typos, etc. as these notes relate to course's content is not the responsibility of the instructor. If you spot any errors or would like to contribute, please contact me directly.

1 January 7, 2019

1.1 Introduction of thermodynamics

Definition 1.1 (Thermodynamics). **Thermodynamics** refers to the macroscopic scale: only bulk properties of matter (e.g. pressure, temperature, volume) are needed for a complete thermodynamic description.

Definition 1.2 (Statistical Thermodynamics). **Statistical Thermodynamics**, also known as **Statistical Mechanics**, uses atomic and molecular properties to calculate thermodynamic properties of bulk matter.

For example, heat capacity of substance is determined by available motional states of its constituent ules, such as rotational and vibrational states.

Example 1.1. Suppose initial temperature of a cup of coffee is $T_{initial} = 85^\circ\text{C}$.

The temperature would decay *exponentially* until it reaches the equilibrium temperature: the temperature of the room.

The temperature of the room would be trivially increased and thus can be treated constant.

1.2 Ideal gas law

For a gas, we need only three macroscopic variables: P (pressure), V (volume), and T (temperature).

We refer to a piston model: pressure is the force due to the mass pushing down on the piston divided by the area of the piston (force per area). Force in our piston model would simply be $F = mg$ where m is the mass of the weight and g is the gravitational constant 9.8s^{-2} .

In **equilibrium** the external pressure P_{ext} is equivalent to the pressure of the gas P .

Note that for a given particle of the gas in equilibrium, the particle with momentum with component mv_x perpendicular to the piston should be reflected and repelled, ultimately travelling with $-mv_x$ momentum. This implies that $\Delta p_{wall} = 2mv_x$ (initial momentum absorbed and additional mv_x exerted onto particle to reflect it).

From statistical mechanics we know that $\frac{3}{2}kT = \frac{1}{2}mv^2$, so the higher the velocity the higher the temperature of the gas.

The total change in pressure of the wall is $\Delta p_{total} = 2mv_x N_{coll}$ where N_{coll} the number of colliding particles. This is simply

$$N_{coll} = \frac{\# \text{ of particles}}{\text{total volume}} V_{coll} \frac{1}{2}$$

where the $\frac{1}{2}$ since half the particles are directed towards the wall and V_{coll} is the volume space for collisions. $V_{coll} = Av_x \Delta t$ where A is the area of the wall and v_x is the velocity of the particles.

We let N be the number of particles per unit volume (our fraction above).

Thus we have

$$\Delta p_{total} = mN Av_x^2 \Delta t$$

Note that force simply change in momentum over change in time or

$$F_{wall} = \frac{\Delta p_{total}}{\Delta t} = mN Av_x^2$$

Finally pressure is simply the force divided by area thus

$$P_{wall} = mv_x^2 N$$

We observe that $v^2 = v_x^2 + v_y^2 + v_z^2 = 3v_x^2$ so

$$P_{wall} = \frac{mv^2 N}{3}$$

Recall that $\frac{3}{2}kT = \frac{1}{2}mv^2$ so $mv^2 = 3kT$ therefore

$$P_{wall} = NkT = \frac{nN_A kT}{V}$$

where N_A is Avogadro's number (number of particles per mole) and n is the number of moles. If we define $N_A k = R$ to be the **ideal gas constant**, we note that this is exactly the **ideal gas law**

$$P = \frac{nRT}{V}$$

2 January 9, 2019

2.1 Definition of a system

We can define the **type of a system** in terms of how it exchanges energy and matter:

Type	Exchange of energy	Exchange of matter
isolated	no	no
open	yes	yes
closed	yes	no

NB: it is not possible to exchange matter without exchanging energy.

Some examples include

System	Type
animal	open
airtight room containing beaker with boiling water	closed
incandescent light bulb	closed
lake	open
greenhouse	closed
the earth	open

2.2 Properties of barriers

There are certain properties of barriers we care about:

moveable vs rigid allow/not allow P, V to change

adiabatic vs diathermal thermally insulating vs thermally conducting

permeable vs impermeable allow/not allow transport of matter

In order from most adiabatic to most diathermal, we have **vacuum, cork, glass, copper**.

2.3 Equilibriums

We define **thermal equilibrium** when two systems A, B are at the same temperature i.e. $T_A = T_B$ (e.g. two closed systems in thermal contact).

We define **thermodynamic equilibrium** when $T_A = T_B$, $P_A = P_B$ and $x_A = x_B$ where x_j is the mole fraction (concentration) (e.g. two open systems in contact).

Once equilibrium is established systems do not spontaneously “unequilibriate”.

The **Zeroth law of Thermodynamics** states that if $T_A = T_C$ and $T_B = T_C$, then $T_A = T_B$ i.e. two systems that are separately in thermal equilibrium with a third system are also in thermal equilibrium with each other.

Examples of equilibriums reached for two systems 1, 2 wherein all properties are not equivalent:

rigid, diathermal, impermeable wall $T_1 = T_2$ but $P_1 \neq P_2$ and $x_1 \neq x_2$

movable, adiabatic, impermeable wall $P_1 = P_2$ but $T_1 \neq T_2$ and $x_1 \neq x_2$

permeable, rigid, diathermal wall $T_1 = T_2$, $P_1 \neq P_2$, $x_1 \neq x_2$ (depends on which species it is permeable to)

2.4 Partial pressure

For a mixture of (ideal) gases, the total pressure is simply the sum of the partial pressures:

$$P = \sum_i P_i = \sum_i \frac{n_i RT}{V}$$

Note that since $\frac{P_i}{P} = \frac{n_i}{n} = x_i$ (mole fraction) we have $P_i = x_i P$. This assumes that the pressures of the individual gases are independent.

For real gases, the **van der Waals** equation of state tries to approximate the ideal gas law for real gases

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

where a account for the attractive interaction and b accounts for the finite molecular size (determined empirically).

3 January 11, 2019

3.1 Ideal gas law examples

Example 3.1 (Q1.14). Note the mass of a He atom is smaller than that of an Ar atom. At the same molar density, volume, and temperature, does the Ar gas exert more pressure than the He gas?

Answer. No, they exert the same pressure. We know that from statistical mechanics ($kT = mv_x^2$) for a fixed temperature the Ar atoms would have a lower velocity squared.

Therefore the pressure is solely determined by temperature not by the mass and thus the ideal gas law applies to any (ideal) gas regardless of atomic/molecular species.

Example 3.2 (Q1.3). Give an example of based on molecule-molecule interactions illustrating how the total pressure upon mixing two *real* gases could be different from the sum of partial pressures.

Answer. If molecules from two gases form **hydrogen bonds** (attractive interaction) then total pressure will be *lower* than sum of partial pressures (and vice versa for repulsive interactions).

Example 3.3 (P1.5). There is a gas mixture of ethane and butane in a sealed container having 230cm^3 capacity filled to a pressure of $97.5 \times 10^3 \text{Pa}$ at 23.1°C . If the total mass of the gas is 0.3554g what is the mole % of butane in the mixture?

Solution. Note that $n = n_1 + n_2 = \frac{PV}{RT} = 9.1 \times 10^{-3} \text{mol}$ where n_1 and n_2 are the number of moles of ethane and butane, respectively.

We also know that $n_1 M_1 + n_2 M_2 = 0.3554\text{g}$. Solving the system of two equations (two unknowns) we have

$$n_2 = \frac{9.1 \times 10^{-3} \text{mol} - \frac{0.3554\text{g}}{M_1}}{1 - \frac{M_2}{M_1}} = 2.915 \times 10^{-3} \text{mol}$$

Therefore the mol % of butane is $\frac{n_2}{n_1 + n_2} = 0.32$ or 32% .

Example 3.4 (P1.29). A balloon filled with 11.5L of Ar at 18.7°C and 1atm rises to height in the atmosphere where pressure is 207Torr and the temperature is -32.4°C . What is the final volume of the balloon? Assume pressure inside and outside are the same.

Solution. Note that

$$\begin{aligned} \frac{P_i V_i}{P_f V_f} &= \frac{n R T_i}{n R T_f} \\ \Rightarrow V_f &= \frac{P_i T_f}{P_f T_i} V_i \end{aligned}$$

where $T_i = 18.7^\circ\text{C} = 291.9\text{K}$, $T_f = -32.4^\circ\text{C} = 240.8\text{K}$, $P_i = 1\text{atm}$, $P_f = 207\text{Torr} = 0.272\text{atm}$. Solving for V_f we get 34.8L .

3.2 First law of thermodynamics

The **first law of thermodynamics** states that the internal energy U of an *isolated system* is **constant**: energy is conserved.

That is isolated system = system of interest + surroundings where

$$\begin{aligned} \Delta U_{\text{total}} &= \Delta U_{\text{system}} + \Delta U_{\text{surroundings}} = 0 \\ \Rightarrow \Delta U_{\text{system}} &= -\Delta U_{\text{surroundings}} \end{aligned}$$

3.3 Energy and heat

Note **energy** can be thought of as capacity of one physical system to do **work** on another physical system. Work is defined as

$$w = \int_{y_i}^{y_f} \vec{F} \cdot d\vec{y}$$

one can always model work as raising a mass m up or down in Earth's gravitational field by height Δh or $mg\Delta h$. For example, a gas expanding and moving a piston of mass m of area A up (which exerts $P_{\text{external}} = \frac{mg}{A}$) does work

$$w = \int_{y_i}^{y_f} \vec{F} \cdot d\vec{y} = - \int_{y_i}^{y_f} P_{\text{external}} A dy = - \int_{y_i}^{y_f} P_{\text{external}} dV = -mg\Delta y$$

Where did the energy come from to do the work? This may be from a heat source that heated up the gas to cause it to expand.

Heat is defined as the energy that flows across the system/surrounding boundary because of a *temperature difference* between the system and surroundings.

Note that both **heat** and **work** are **transitory**: in equilibrium states one cannot quantify heat or work but only the energy.

Restating the first law, we have

$$\Delta U = \Delta U_{system} = q + w = -\Delta U_{surroundings}$$

where q is the heat and w is the work associated with a process.

Note that $q > 0$ is when the system temperature is **raised** and $w > 0$ denotes work done **on the system**.

4 January 14, 2019

4.1 Calculating work (at constant P, V, T) example

Note the following terms are used for describing constant properties:

isochoric constant volume

isothermal constant temperature

isobaric constant pressure

Example 4.1. A 1.5 mole sample of ideal gas at 28.5C expands isothermally from an initial volume of 22.5dm³ to a final volume of 75.5dm³. Calculate w for this process for expansion against an external pressure of $0.498 \times 10^5 Pa$

Solution. Note that $P_{external}$ is constant to integrating over the change in volume we have

$$w = -P_{external}(V_f - V_i) = -0.498 \times 10^5 Pa(75.5 - 22.5) \times 10^{-3} m^3 = -2.64 \times 10^3 J$$

(NB: $dm = 10^{-1}m$ so $(dm)^3 = 10^{-3}m^3$).

4.2 Heat capacity

How much does a certain heat flow change affect the temperature of a system? We define

$$C = \lim_{\Delta T \rightarrow 0} \frac{q}{T_f - T_i} \\ = \frac{dq}{dT}$$

C is an **extensive** property (depends on molar amount), so usually the *molar heat capacity* C_m (units $JK^{-1}mol^{-1}$) (**intensive**) is used in calculations. Note that $C = C(T)$ in general depends on *temperature*.

C depends on the material and on the conditions which it is measured. We define

$C_{V,m}$ molar heat capacity at constant volume

$C_{P,m}$ molar heat capacity at constant pressure

We can calculate heat flow into/out of a system at constant volumes or pressures e.g.

$$q_P = \int_{T_i}^{T_f} C_P(T) dT$$

$$q_V = \int_{T_i}^{T_f} C_V(T) dT$$

Let us look at the **microscopic origin** of heat capacity. A small molecule have a number of ways to store energy/heat:

1. Putting electrons into higher energy levels (quantum mechanical excited states)
2. Vibration (CO (carbon monoxide) has one vibrational degrees of freedom (DOF), stretch along bond axis)
3. Rotation (CO has two rotation DOFs: rotation axes perpendicular to bond axis)
4. Translate (3 DOFs)

Energy can be stored into each DOF. Each DOF of translate and rotation contributes $\approx R/2$ heat capacity (R is the ideal gas constant). For vibration, if $\frac{\Delta E}{kT} < 0.1$ (low excitation) then it contributes $\approx R$; if $\frac{\Delta E}{kT} > 10$ then it contributes ≈ 0 heat capacity (high energy excitation).

For energy states, we know that the relative probability of being in state i and j is

$$\frac{Pr(E_i)}{Pr(E_j)} = e^{-\frac{E_i - E_j}{kT}}$$

notice that if $E_i \approx E_j$ then $Pr(E_i) \approx Pr(E_j)$.

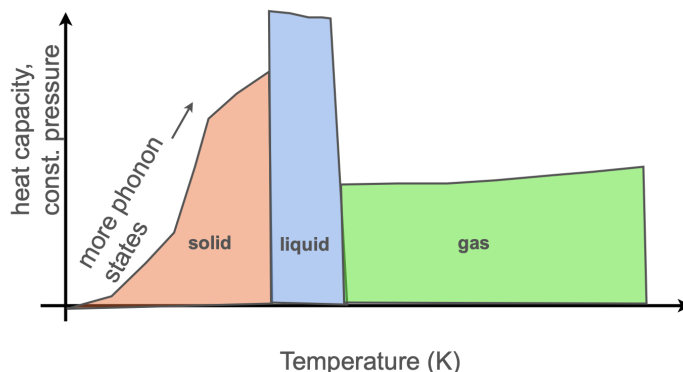
Molecules exchange energy by **collisions** where a colliding molecule gain or loses $\approx kT$ energy.

4.3 Heat capacity vs temperature and phase

For solids, it is much easier to measure $C_{P,m}$. Note that in the solid-state energy can be taken up in **lattice vibrations (phonons)**. As temperature increases the number of phonon states *increases*.

Liquids have even a greater heat capacity: in addition to local vibrational modes it also has additional *low energy modes* and more degrees of freedom.

$C_{P,m}$ drops for gas since a lattice no longer exists (no phonons).



4.4 Difference in C_P and C_V for a gas

At *constant pressure*, work is done on the surrounds where $\Delta U = q + w$ (piston can move). On the contrary at *constant volume*, no work is done so $\Delta U = q$, so the energy is transferred into heat that is stored in the molecules. In other words for a given heat flow dq we have $dT_P < dT_V$ (change in temperature when pressure is constant is less than change in temperature when volume is constant).

We must conclude that $C_P > C_V$ (we will prove that $C_{P,m} - C_{V,m} = R$ for an ideal gas).

4.5 Heat capacity example

Example 4.2. An electric motor connected to drilling machinery can heat 11.6kg of ice water ($T = 273\text{K}$) to $T = 355\text{K}$ in 2.5 hours. Assuming the same rate of work how high could the same motor raise a 225kg weight in 2.5 minutes? Assume the heat specific heat capacity of water is $4.18\text{JK}^{-1}\text{g}^{-1}$.

Solution. We first calculate the rate of energy from the motor

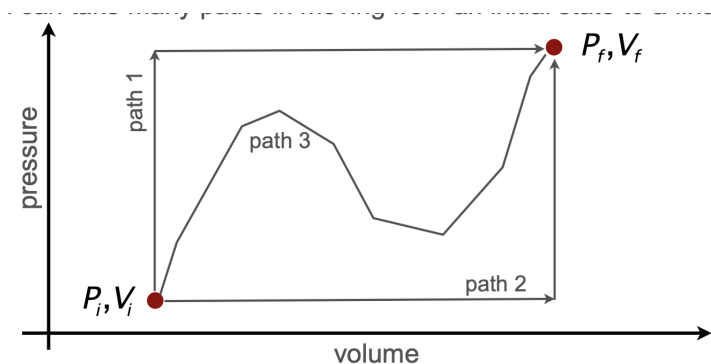
$$\text{rate}(\text{energy}/s) = \text{power} = \frac{C_P m_{H_2O} \Delta T}{2.5 \text{ hours}} = 442 \text{Js}^{-1}$$

now relating the work done in 2.5 minutes to the potential of gravity

$$mgh = 442 \text{Js}^{-1} \cdot 150\text{s} \Rightarrow h = 30\text{m}$$

4.6 State functions vs Path functions

A system can take many paths in moving from an initial state to a final state



A **state function** only depends on the initial and final states, *not* on the path taken. For example, **internal energy** U is a **state function** where $U = U(P, V)$ and

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV$$

If the second partial derivatives are symmetric

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial U}{\partial V}\right)_P\right)_V = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial P}\right)_V\right)_P$$

it can be proven that dU is an exact *differential* where

$$\int_{U_i}^{U_f} dU = U_f - U_i = \Delta U$$

thus U would be a **state function** (Note that U is not easily measureable whereas ΔU is).

Note that work w is a **path function** since we integrate over the change in volume of time ($w = -\int P_{ext} dV$). Since w is not a state function, then $\Delta U = q + w$ is not a state function. Also $q = \Delta U - w$ is not a state function either.

In other words, the change in internal energy is not a state function but the actual internal energy is a state function.

5 January 16, 2019

5.1 Review of calculus

Coverage: integration, partial derivatives, and the **total differential**, defined as

$$df = \left(\frac{\partial f}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y}\right) dy$$

As previously stated if the second partial derivatives are symmetric i.e. $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$ then f is a **state function**.