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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**

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