Fundamentals of Thermodynamics
Lecture 4

References: *An Introduction to Atmospheric Thermodynamics*, Tsonis
Introduction to Theoretical Meteorology, Hess
Physical Chemistry (4th edition), Levine
Thermodynamics and an Introduction to Thermostatistics, Callen

IDEAL GASES

- An *ideal gas* is a gas with the following properties:
  - There are no intermolecular forces, except during collisions.
  - All collisions are elastic.
  - The individual gas molecules have no volume (they behave like point masses).
- The equation of state for ideal gasses is known as the *ideal gas law*.
- The ideal gas law was discovered empirically, but can also be derived theoretically. The form we are most familiar with,

$$pV = nRT \qquad Ideal\ Gas\ Law \qquad (1)$$

  R = 8.3145 J mol^{-1} K^{-1}, and n is the number of moles
- A true ideal gas would be monatomic, meaning each molecule is comprised of a single atom.
- Real gasses in the atmosphere, such as O2 and N2, are diatomic, and some gasses such as CO2 and O3 are triatomic.
  - Real atmospheric gasses have rotational and vibrational kinetic energy, in addition to translational kinetic energy.
- Even though the gasses that make up the atmosphere aren't monatomic, they still closely obey the ideal gas law at the pressures and temperatures encountered in the atmosphere, so we can still use the ideal gas law.

FORM OF IDEAL GAS LAW MOST USED BY METEOROLOGISTS

- In meteorology we use a modified form of the ideal gas law. We first divide (1) by volume to get

$$p = \frac{n}{V}RT$$

we then multiply the RHS top and bottom by the molecular weight of the gas, *M*, to get

$$p = \frac{Mn}{V}\frac{R}{M}T$$

Mn/V is just the density of the gas. By defining *R/M* to be the specific gas constant, $\acute{R}$, we get the following form of the ideal gas law

$$p = \rho\acute{R}T \qquad (2)$$

- The specific gas constant is different for each gas! It is found by dividing the universal gas constant by the molecular weight of the gas.
- Dry air has a molecular weight of 28.964 g/mol. The specific gas constant for dry air is then 287.1 J kg^{-1} K^{-1}, and is given the symbol R_d. The ideal gas law for dry air is then

$$p = \rho R_d T \qquad (3)$$

or equivalently, in terms of specific volume,

$$p\alpha = R_d T \qquad (4)$$

USEFUL RELATIONS FOR COMPARING TWO STATES OF AN IDEAL GAS

- One very useful consequence of the ideal gas law that it can be rewritten [from Eq. 4 for an arbitrary gas] as

$$\frac{p\alpha}{T} = \acute{R} \qquad (5)$$

This allows us to compare variables for two different states of the same gas by writing

$$\frac{p_1\,\alpha_1}{T_1} = \frac{p_2\,\alpha_2}{T_2} \qquad (6)$$

As an example, imagine if a gas expands to twice its original volume while maintaining a constant pressure. From Eq. (6) we can immediately figure out the ratio of its final and initial temperatures by writing

$$\frac{T_2}{T_1} = \frac{p_2}{p_1}\frac{\alpha_2}{\alpha_1} = \frac{\alpha_2}{\alpha_1} = \frac{2}{1}$$

which shows that the gas's temperature would also double.

- As another example, imagine if a gas's pressure increases to four times its original value while keeping a constant temperature. Manipulating Eq. (6) shows that its volume would decrease to one-fourth its original size,

$$\frac{\alpha_2}{\alpha_1} = \frac{T_2}{T_1}\frac{p_1}{p_2} = \frac{p_1}{p_2} = \frac{1}{4}$$

- As a final example, imagine if a gas's pressure increases to six times its original value while the volume decreases to one-fourth its original size. Manipulating Eq. (6) shows that the temperature increase by 150%,

$$\frac{T_2}{T_1} = \frac{p_2}{p_1}\frac{\alpha_2}{\alpha_1} = \frac{6}{1}\cdot\frac{1}{4} = \frac{3}{2}$$

INTERNAL ENERGY OF AN IDEAL GAS

- Since there are no intermolecular forces in an ideal gas, there is no internal potential energy. The internal energy of a monatomic gas is therefore due solely to the translational kinetic energy of the molecules.
- If the molecules have more than one atom, then there is also kinetic energy due to rotation and vibration.
  - Though technically not an ideal gas, at normal temperatures and pressures the main atmospheric gasses closely follow the ideal gas law, so we can still speak of air as an ideal gas.
- The translational kinetic energy has a value of

$$u_{trans} = \frac{1}{2}\overline{v^2} = \frac{1}{2}\frac{m}{m}\overline{v^2} = \frac{3}{2}\frac{kT}{m} = \frac{3}{2}\frac{N_A k}{N_A m}T = \frac{3}{2}\acute{R}T$$

  - The rotational kinetic energy depends on whether the molecule is monatomic or multi-atomic, and whether it is linear or bent. It is

$$u_{rot} = 0\,; \qquad monamatic\ molecule$$

$$u_{rot} = \acute{R}\,T; \qquad linear\ molecule$$

$$u_{rot} = \frac{3}{2}\acute{R}T\,; \qquad bent\ molecule$$

  The vibrational kinetic energy is a complicated function of temperature. For light diatomic molecules (such as N_2 and O_2) it can be considered a constant except at extremely high temperatures.

- Thus, the internal energies for most monatomic and diatomic molecules are

$$\boxed{\begin{aligned} u &= u_{trans} = \frac{3}{2}\acute{R}T + const. \quad ; \qquad monatomic\ gas \\ u &= u_{trans} + u_{rot} + u_{vib} = \frac{5}{2}\acute{R}T + const.\,; \qquad diatomic\ gas \end{aligned}}$$

Internal Energy

  - Note that when temperature is 0K, there is still some kinetic energy. Motion does not cease at absolute zero.

- An important point to notice is that, <u>for an ideal gas, the internal energy is a function of temperature only.</u>

EXERCISES

1. From the ideal gas law $pV = nRT$, calculate how many molecules are contained in a cubic centimeter (cm^3) of air at a pressure of 1013.25 mb and a temperature of 15 ^oC? (R = 8.3145 J mol^{-1} K^{-1}; $N_A = 6.022 \times 10^{23}$ molecules/mol)

2. How many oxygen molecules are there in a cm3 of air at a pressure of 1013.25 mb and a temperature of 15 oC?

3. The table below gives the molecular weights and volume percentages for the standard atmosphere. Use them to show that the molecular weight of air is 28.964 g/mol.

Gas	**M (g/mol)**	**% by volume**
N_2	28.0134	78.084
O_2	31.9988	20.9476
Ar	39.9480	0.934
CO_2	44.00995	0.0314

4. Show that the specific gas constant for dry air (R_d) is equal to 287.1 J kg^{-1} K^{-1}.

5. Levels of CO_2 in the atmosphere have been increasing since the industrial revolution. Is the specific gas constant for dry air larger or smaller now than it was in 1800?

6. Explain why moist air is lighter than dry air (at the same pressure and temperature).