Thermodynamics

• *Thermodynamics* is the study of the thermal energy (or internal energy) of systems.

• If two systems are put into *thermal contact* with each other, they can exchange *thermal* (*internal*) energy with one another.

• If two systems are put into (*thermal*) *contact* but **the net** exchange of thermal energy is zero, they are said to be in *thermal equilibrium*.

• The *zeroth law of thermodynamics* states that if *both* objects A and B are in thermal equilibrium with object C, then they are *also* in thermal equilibrium with each other.

• Two objects in thermal equilibrium are said to have the same *temperature.*

Temperature

- In order to measure *temperature*, we need to define *units* to express the quantity of temperature. In the SI system, these units are called *Kelvin*, and the temperature scale is called the *Kelvin scale*.

- The *unique* temperature at which water, ice, and water vapor coexist in equilibrium (the *triple point of water*) is given a value of $T_3 = 273.16$ K.

- Under certain circumstances, the *pressure* of a gas is *proportional* to its *temperature* (this is part of the ideal gas law).

- Therefore, if we measure the pressure of a gas at T_3 as some value p_3, we can measure the temperature of an object by measuring the pressure in this gas when it is in thermal contact with this object.

- The unknown temperature of the object (T) will satisfy $pT = p_3 T_3$, where p is the measured pressure of the gas, so that:

$$T = 273.16K\left(\frac{p}{p_3}\right)$$

- This describes a *constant-volume gas thermometer*.

Celsius and Fahrenheit Scales

• There are two other commonly used temperature scales, called the Celsius scale and the Fahrenheit scale.

• The Celsius scale is similar to the Kelvin scale, in that one K equals 1^oC, but the zero of temperature is shifted so that $T_C = T - 273.15^oC$, where T_C is the Celsius temperature and T is the Kelvin temperature.

• The Fahrenheit scale is defined by $T_F = 2/5\ T_C + 32^oF$, where T_F is the Fahrenheit temperature and T_C is the Celsius temperature (expressed in ^oC)

Thermal Expansion

• Most materials *expand* when their temperature is *increased* (they are heated).

• Remembering that *temperature* is related to *internal energy*, this expansion arises because the *amplitude* of oscillation of the atoms increases as the internal energy increases.

• The *coefficient of linear expansion* (α) is a constant (depending on the type of material) relating the change in an object's temperature to its change in length, defined by:

$$\Delta L = \alpha L \Delta T$$

where ΔL is the change in length of the object, L is the initial length of the object, and ΔT is the change in temperature of the object.

• In a similar manner, we define the *coefficient of volume expansion* (β) by:

$$\Delta V = \beta V \Delta T$$

where ΔV is the change in volume, V is the initial volume of the object, and ΔT is the change in temperature.

- Because both α and β are very small (which allows us to neglect terms like α^2 and α^3), it can be shown that $\beta=3\alpha$.

- Consider a cube with sides of length L, with $V=L^3$.

- Heat the cube by some amount ΔT, so that the new length of each side is $L(1+\alpha\Delta T)$.

- The new volume is $V=L^3(1+3\alpha\Delta T+\text{terms in } \alpha^2 \text{ and } \alpha^3) \approx V(1+3\alpha\Delta T)$.

- In a similar way, the coefficient of areal thermal expansion (γ) can be approximated as $\gamma=2\alpha$, where $\Delta A = \gamma A \Delta T$.

- One other interesting point about thermal expansion is that *holes* in materials expand when the material is heated, with the same thermal expansion coefficients of the material.

Density of water on freezing

- Normally, liquids increase in volume (decrease in density) with increasing temperature.

- Between 0 ^oC and 4 ^oC, water behaves anomalously---it decreases in volume (increases in density) with increasing temperature.

- At 4 ^oC, the density of water is 1.000 g/cm^3, while at 0 ^oC the density is only 0.9999 g/cm^3.

- This may seem like a very small difference, but it is vitally important. Because water at 4 ^oC is slightly denser than water at 0 ^oC, 4 ^oC water will sink to the bottom of lakes while the top freezes over.

- This allows fish to live at the bottom of a lake where the top part is frozen.

Avogadro's Number

- *Avogadro's Number* (N_A) is 6.02×10^{23} per mole.

- This is a very large number, but is appropriate for counting the number of atoms in everyday things.

- The number of moles of a material (n) is simply N/N_A, where N is the number of molecules in the sample, and N_A is Avogadro's Number.

  ex. If a sample has $N=12 \times 10^{23}$ molecules, $n \sim 2$.

- The molar mass (M) is the mass of one mole of the sample.

  ex. Carbon-12 has a molar mass of 12 g.

- If m is the *molecular mass*, $M=mN_A$.

- Using these relations, we find that $n=M_{sam}/M=M_{sam}/mN_A$, where M_{sam} is the mass of the sample.

Ideal Gases

• An *ideal gas* is a gas in which the constituent molecules are only *weakly interacting*.

• *All* gases can be *approximated* as ideal gases at sufficiently *low densities*.

• Ideal gases satisfy the relation $pV = nRT$

where p is the *pressure* of the gas, V the *volume* of the gas, T the *temperature* of the gas, n the number of *moles* of the gas, and R is a constant given by 8.31 J/mol·K.

• It is important to note that R is a *constant* - it is the same for all gases (that can be treated as an ideal gas).

• Alternatively, it we want to express the ideal gas law in terms of the number of molecules of the gas (rather than the number of moles) we can write $pV = \mathrm{N}k_B\mathrm{T}$, where k_B is called the *Boltzmann constant*, and is equal to R/N_A.