

## Thermodynamics III

### I. Heat Units

Kinetic theory tells us that temperature is a measure of the internal energy. Thus, we can raise the temperature of a system by adding energy. Heat is just the transfer of energy due to a temperature difference and is one way to raise the temperature. Another way of adding energy is by doing work on the system.

James Prescott Joule showed experimentally in the 1800's the equivalence of heat and mechanical work and is given credit for the Law of the Conservation of Energy.



Prior to this time, people had considered heat to be a fluid called caloric since they knew heat flowed and liquid also flowed.

Def. of Calorie: The energy required to raise 1 gram of water 1 degree Celsius.

1 calorie = 4.186 Joules

1 kilocalorie = 1 Dietary Calorie (C) =  $4.186 \times 10^3$  J

## II. Specific Heat

Consider a system with internal energy  $U_i$ . By kinetic theory, we know that its internal energy is related to its temperature  $T_i$  by the equation:

We now heat the gas adding  $Q$  units of heat to raise the system's internal energy to  $U_f$  and raise its temperature to  $T_f$ .

Subtracting the system's final internal energy from its initial internal energy gives us the following relationship between heat and temperature.

Thus, the change in an object's temperature is proportional to the heat added and that the heat required to raise a system's temperature is proportional to the system's number of molecules (or equivalently the number of moles or the system's mass).

This result is generally written in the following form:

**C is called the specific heat** and it is the heat required to raise one gram of the substance one degree in temperature.

One can also write the equation in terms of moles of a substance in the form:

**c is called the molar specific heat** and it is a measure of the heat required to raise one mole of the substance one degree in temperature.

Physicists at the end of the 19<sup>th</sup> and early 20<sup>th</sup> Century were extremely interested in measuring the values of specific heat for various systems as it relates to the system's internal energy and therefore is a way of studying the forces in the microscopic world.

### III. Molar Specific Heat for an Ideal Gas

We remember that from kinetic theory the internal energy of an ideal gas is related to temperature by:

If we add  $Q$  units of heat, we find the change in internal energy is given by:

Comparing this to our previous heat equation gives us a molar specific heat of

#### IV. Equipartition Theorem

The amount of internal energy stored in any mode that can be written as the square of a spatial or the square of a velocity component is given by:

An alternative way of expressing the equipartition theorem is:

Example: A mono-atomic gas

## V. Diatomic Gases

When physicists measured the molar specific heats of diatomic gases at constant volume, they found that the specific heat changed as the temperature increased by fixed amounts.



A diatomic gas can have up to seven ways to store energy.

3 Translation -

2 Rotation -

2 Vibration -

We see that not all modes are available at low temperatures. This was the one of the first indications that energy was quantized into energy levels (long before Bohr's model of the atom).

## VI. Phase Changes & Bonds

Consider two free atoms of a gas moving through space as shown below. Even when they are far apart, real gas atoms experience small interactive forces that are electrical in nature. If the atoms have sufficiently kinetic energy then they stay free, but as the temperature is decreased they eventually are moving slow enough that they may give off some of their energy and join together as a molecule.

Thus, the creation of chemical bonds (making springs) releases energy. In the same way, the breaking of a chemical bond (destroying springs) requires takes energy. This process where a substance changes bonds to go from one state to another (ex. gas to liquid) is called a phase change.

In a phase change, the temperature of the substance doesn't change even though the internal energy of the system is being changed. The change in the internal energy is accompanied by the changing of bonds which changes the degrees of freedom and consequently the specific heat of the substance rather than a change in the kinetic energy of the molecules.

**Latent Heat – L.** It is the amount of heat required by a one unit of mass of a substance to change all of its particular bonds.



**Heat of Vaporization** – The quantity of heat required to vaporize one unit mass of a liquid at constant temperature.

Water:	$L_v = 2.26 \text{ MJ/kg} = 540 \text{ cal/g}$
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**Heat of Fusion** – The quantity of heat required to melt one unit of mass of a solid at constant temperature.

Water:	$L_f = 335 \text{ kJ/kg} = 80 \text{ cal/g}$
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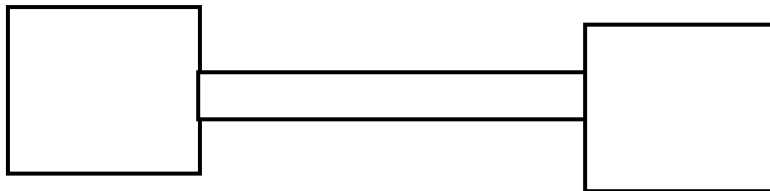
**Heat of Sublimation** – The quantity of heat required to convert one unit of mass of a substance from solid to gas at constant temperature.

## VII. Heat Transfer

Heat can transferred between systems of different temperatures in one of three ways: 1) conduction; 2) convection; and 3) radiation.

### A. Conduction

Conduction occurs when the atoms of the systems directly interact (ie the systems are in thermal contact).



The rate at which thermal energy is transferred is directly proportional to the area of contact and the temperature gradient (change in temperature divided by change in length).

$k$  is the substance's thermal conductivity.

Substance's with large  $k$ 's are said to be good thermal conductors while those with small  $k$ 's are said to be thermal insulators. For insulators, manufacturers prefer to work with R-values which is the inverse of thermal conductivity so they don't have to work with small values.

R-value =

## B. Convection

Convection is where thermal energy is transferred by mass movement as in the case of gas molecules carrying thermal energy between two surfaces.



A thermos eliminates energy loss by convection by evacuating the area between an inner metal layer that touches the liquid and an out metal layer which touches the outside air.

### C. Radiation

Atoms can give off energy in the form of electromagnetic waves which we will study later. An example of this energy is the light you see coming from an object that is heated.

The rate at which thermal energy is radiated by a heated object is given by the Stefan-Boltzmann Equation:

where  $\sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}$  is called the Stefan-Boltzmann constant.

The factor  $e$  is called the emissivity and can range from 1 (perfect absorber – black body) to 0 (perfect reflector). The best absorbers are the best emitters.

To minimize energy loss from radiation the inside of the thermos is made from shiny metal coated glass.