

# Avogadro's Number

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- *Avogadro's Number* ( $N_A$ ) is  $6.02 \times 10^{23}$  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  $n = M_{\text{sam}}/M = M_{\text{sam}}/mN_A$ , where  $M_{\text{sam}}$  is the mass of the sample.

# Ideal Gases

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- 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

$$pV = nRT \equiv Nk_B T$$

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, if 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  $pV = Nk_B T$ , where  $k_B$  is called the *Boltzmann constant*, and is equal to  $R/N_A$ .

# Temperature and Heat

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- *Heat* ( $Q$ ) is defined as the *thermal energy transferred* between two objects. We will not ever talk about a system having some amount of heat.
- Thermal (or internal) energy is associated with the motion of atoms and molecules in a system as viewed from a reference frame at rest with respect to the center of mass of the system.
- In thermodynamics, the *environment* is everything outside of the *system* under investigation.
- $Q$  is *positive* if heat is transferred *from* the environment *into* the system. This requires that the temperature of the environment ( $T_E$ ) is larger than the temperature of the system ( $T_S$ ).
- $Q$  is *negative* if heat is transferred *from* the system *to* the environment. This requires  $T_S > T_E$ .
- In general, heat is the energy *transferred* between a system and the environment because of the temperature difference between them.
- Heat is the amount of thermal energy transferred between a system and the environment, so it must have units of Joules (J).
- Other units for measuring heat are the *calorie* (1 cal = 4.186 J) and the *British Thermal Unit* (1 BTU = 1055 J).
- Note: When discussing the calories in food, the units should properly be called kilocalories, that is, 1 “food calorie” = 1 Calorie = 1,000 calories = 4186 J.

# Heat Capacity

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- Since heat is *thermal energy* flowing between the system and the environment because of a *temperature difference* between the two, we might ask how this energy flow affects the *temperature* of the system.
- If heat flows *into* an object, the *temperature* of that object will *increase* by an amount *proportional* to the amount of heat.
- This constant of proportionality between heat and change in temperature is called the *heat capacity* ( $C$ ):

$$Q = C\Delta T = C(T_f - T_i)$$

where  $Q$  is the amount of heat flowing from the environment to the object, and  $\Delta T$  is the change in temperature of the object. Heat capacity is measured in J/K.

- $Q$  can be *positive* (heat flows from the environment into the object) or *negative* (heat flows from the object to the environment). In both cases  $\Delta T = T_f - T_i$ , which can be *positive* (positive  $Q$ ) or *negative* (negative  $Q$ ).

ex. An object has a heat capacity of 100 J/K. If 500 J of heat flows *from* the object *to* the environment, what is the change in temperature of the object? -5 K.

- Objects with very *large* heat capacities will change temperature only *slightly* if a certain amount of heat  $Q$  flows into the object, but objects with small heat capacities will undergo a large change in temperature with the same amount of heat  $Q$  flowing into it.

# Specific Heat

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- Objects made of the same material need not have the same heat capacity. The heat capacity of 10 kg of water will be larger than the heat capacity of 1 kg of water.
  - ex. The heat capacity of 10 kg of water is 41900 J/K, and the heat capacity of 1 kg of water is 4190 J/K.
- The *specific heat* ( $c$ ) of a material is the heat capacity per unit mass of the material.
  - ex. The specific heat of water is 4190 J/kg·K *regardless of the amount of water*.

- We define specific heat by: 
$$Q = cm\Delta T = cm(T_f - T_i)$$

where  $c$  is measured in J/kg·K, and  $m$  is the mass of material.

- In general, the specific heat of a system will depend on the temperature. However, these variations are normally rather small, and we will neglect them for this course (with the exception of phase transitions discussed in the following).
- In our discussion of heat capacity, we have assumed that the heat flowing into or out of the object does *not change the material*.
- This need not always be the case. Adding a great deal of heat to an object can change the fundamental nature of the material. For example, by heating water we can boil the water producing steam.

# States of Matter

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- Matter can exist in three common states: *solid*, *liquid* and *gas*.
- These three states are called *phases* of matter, and it is possible to move from one phase to another.
- *Melting* (fusion) changes from a solid to a liquid, *freezing* changes from a liquid to a solid.
- *Vaporizing* changes from a liquid to a gas, *condensing* changes from a gas to a liquid.
- *Sublimating* changes directly from a solid to a gas or gas to a solid.

# Latent Heat

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- Changing from one phase of matter to another involves either a positive heat flow into the material (melting, vaporizing) or negative heat flow from the material (freezing, condensing).
- The amount of energy per unit mass that must be transferred as heat when a sample undergoes a phase change is called the heat of transformation (or latent heat).
- The latent heat can be positive (melting, vaporizing), or negative (freezing, condensing).
- If a sample of mass  $m$ , with latent heat  $L$  completely undergoes a phase change, the total heat energy transferred is  $Q=mL$ .
- Heat energy used to change the phase of a material will *not* also change the temperature of the matter.  
Ex. The latent heat of vaporization of a water is 2256 kJ/kg. If 2256 kJ is added to 1 kg of water at 100 °C, what is the final temperature of the steam? 100 °C, since all the heat energy is used to vaporize the water.

# Heat and Work

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- Both heat and work involve the flow of energy. It does not make sense for a system to have a certain amount of heat or a certain amount of work.
- However, we can ask about the work done by a system or the heat flowing into a system as the *state* of the system changes.
- Consider the *state* of a gas defined by the *volume* ( $V$ ), *pressure* ( $p$ ), and *temperature* ( $T$ ) of the gas.
- The procedure by which a gas changes from an initial state ( $V_i, p_i, T_i$ ) to a final state ( $V_f, p_f, T_f$ ) is called a *thermodynamic process*.
- During this process, work may be done on or by the system, and heat may be transferred to or from the system.
- Suppose that the gas is confined to a cylinder closed by a piston of fixed area  $A$ ,

Then the force exerted by the gas on the piston is  $F_{\text{gas-piston}} = pA$ , so the force exerted by the piston on the gas is  $F_{\text{piston-gas}} = -pA$

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• If the piston moves up by some small distance  $dx$ , the work done on the gas is  $dW = Fdx = -pAdx = -pdV$  (since  $dx$  is small,  $p$  is approximately constant).

• Then, the total work done on the gas can be found by integrating  $-pdV$  as:

$$W = \int dW = -\int_{V_i}^{V_f} pdV$$

• If we plot the *initial* state of the gas and *final* state of the gas on a  $p$ - $V$  diagram ( $p$  along the  $y$ -axis,  $V$  along the  $x$ -axis) the *work* done is the *area* under the curve connecting the initial and final states.

• Since there are an infinite number of curves connecting  $(p_i, V_i)$  to  $(p_f, V_f)$ , the work done by the gas depends on more than just  $(p_i, V_i)$  and  $(p_f, V_f)$ , it depends on the path taken.

• The *work* done by the gas is a *path-dependent quantity*.

• Furthermore, depending on the path taken between  $(p_i, V_i)$  and  $(p_f, V_f)$ , heat may flow into or out of the system. Therefore, *heat* is also a *path-dependent quantity*.

• A *thermodynamic cycle* is a *path* in a  $p$ - $V$  diagram which takes the system from some initial state  $(p_i, V_i)$  to some other state  $(p_f, V_f)$  and then *back to the initial state*  $(p_i, V_i)$ .

# First Law of Thermodynamics

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- We have discussed how *both*  $Q$  and  $W$  are *path dependent quantities*.
- It turns out that the quantity  $Q+W$  is not a path dependent. This quantity can be identified with the change in internal energy of the system by  $\Delta E_{\text{int}} = Q+W$ .
- The *First Law of Thermodynamics* states that the internal energy  $E_{\text{int}}$  of a system increases if *energy* is added as *heat*  $Q$  and increases if *energy* is gained as *work*  $W$  done *on* the system.
- This extends the principle of conservation of energy to systems that are not isolated. Energy can leave or enter the system as heat ( $Q$ ) and leave or enter the system as work ( $W$ ).
- NB. The work done *by* the system is the *negative* of the work done *on* the system (we discussed the work done on the system in previous chapters).

# Examples of Thermodynamic Processes

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## *Adiabatic Processes*

An adiabatic process is one for which there is no transfer of energy as heat, so that  $\Delta E_{\text{int}} = W$ .

## *Constant-volume Processes*

A process in which the volume of the system does not change (isovolumetric = isochoric). This means that no work is done by the system, so  $\Delta E_{\text{int}} = Q$ .

## *Cyclical Processes*

Processes for which  $(p_i, V_i) = (p_f, V_f)$ . No internal state of the system can change, so  $\Delta E_{\text{int}} = 0$  and  $Q = W$ .

## *Free Expansion*

Adiabatic process in which no transfer of heat occurs between the system and environment, and the system does no work so  $Q = W = 0$  and  $\Delta E_{\text{int}} = 0$ .

## *Isothermal Process*

For an ideal gas,  $E_{\text{int}}$  depends only on temperature, so  $Q = -W$  as  $\Delta E_{\text{int}} = 0$ .

# Mechanisms for Heat Transfer

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- Heat is the flow of thermal energy from a system to its environment. How can this happen?

## *Conduction*

- Heat can flow between two systems that are in contact by conduction. Basically, conduction involves the motion of the atoms and electrons in one system affecting the motion of the atoms and electrons in the other system.

- Consider two reservoirs (hot and cold) that are connected by a slab of material having surface area  $A$  in contact with the reservoirs, and a thickness  $L$ .

- Then the conduction rate (the rate of heat flow) is given by:

$$P_{cond} = \frac{Q}{t} = \kappa A \frac{T_H - T_C}{L}$$

- Where  $T_H$  is the temperature of the hot reservoir,  $T_C$  is the temperature of the cold reservoir, and the constant  $\kappa$  is the thermal conductivity of the material.

- Materials with *large* values of  $\kappa$  (such as metals) are *good* thermal conductors, materials with *small* values of  $\kappa$  (such as wood) are *bad* thermal conductors.

## Convection

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- Thermal energy can also be transported by convection in a fluid.
- Convection occurs when the fluid in contact with the high temperature reservoir heats up (normally by thermal conduction) and then moves to another location.
  - ex. As water is heated in a pot, the water on the bottom (closest to the heating element) heats very quickly. It becomes less dense than the other water, and moves to the top of the pot.
- Often, convection transports thermal energy much more rapidly than conduction.

## Radiation

- All objects at a temperature above  $T=0$  K will emit *thermal radiation* (a form of electromagnetic waves).
- The rate at which an object emits thermal radiation (which carries energy) is proportional to the fourth power of its temperature

$$P_{rad} = \sigma \epsilon A T^4$$

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•The quantity  $\sigma$  is called the Stefan-Boltzmann constant,  $\varepsilon$  is the emissivity of the objects surface (a number between 0 and 1), and the temperature  $T$  is measured in Kelvin.

•Objects also absorb thermal energy from the environment at temperature  $T_{env}$  at a rate

$$P_{abs} = \sigma\varepsilon AT_{env}^4$$

where  $\sigma$  and  $\varepsilon$  are exactly the same as for the emitted thermal radiation equation.

•Therefore, an object at temperature  $T$  sitting in an environment at a temperature  $T_{env}$  will have a net heat flow rate of

$$P_{net} = P_{abs} - P_{rad} = \sigma\varepsilon A(T_{env}^4 - T^4)$$

•This will be positive if heat is flowing into the object, and negative if heat is flowing out of the object.

•A perfect radiator with  $\varepsilon=1$  is called a *black body*.