

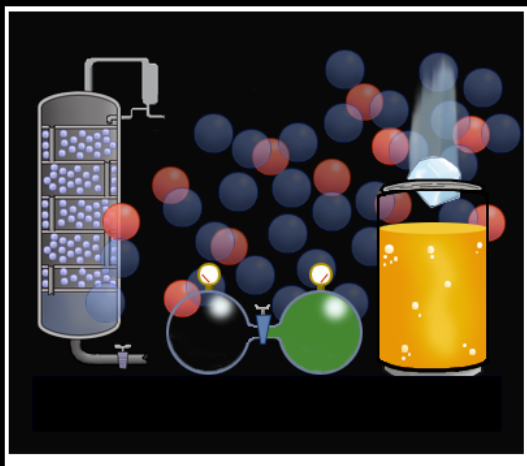
# Carnot Module

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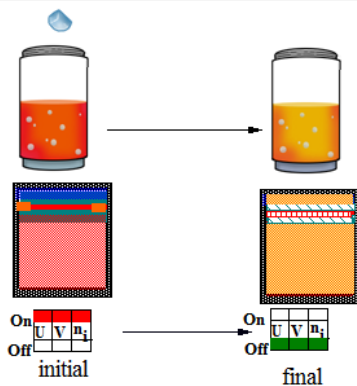
## Introduction

The goals for this module are to

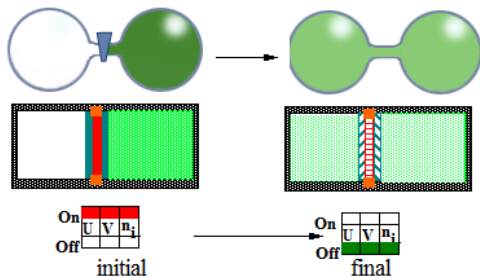
- State Carnot's law;
- Establish the link between temperature and entropy;
- Develop the equilibrium conditions resulting from the release of constraints on energy, volume and mass.
- Obtain the ideal gas equation and the equations for the heat capacity, entropy and chemical potential of an ideal gas.

Many everyday processes have a directionality we take for granted. They occur **spontaneously**.

- (1) If we mix a very small amount of **ice** with a large amount of “**hot**” water in a Dewar flask, the ice melts and we end up with **cooler** water.

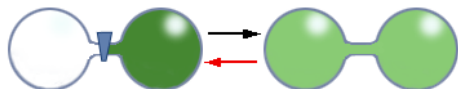
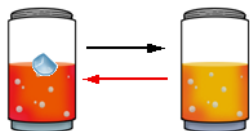


- (2) If we connect a container filled with gas to an evacuated chamber, the gas expands until its density is uniform.



After all, none of these processes violates either

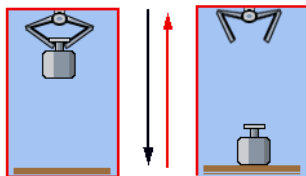
- The conservation of energy, since  $U_I^{\text{tot}} = U_{II}^{\text{tot}}$ ;
- The conservation of matter, since  $n_I^{\text{tot}} = n_{II}^{\text{tot}}$



If we release a weight, it falls, converting potential energy into kinetic energy.

In fact, molecular motion is less likely to cause an one gram weight to rise spontaneously 1 cm, than a tribe of wild monkeys punching randomly on typewriters is likely to produce 23,000,000 error-free copies of Shakespeare's complete works.

Clearly, if we wish to define equilibrium states, we need a criterion that provides a guide for the directionality of processes.



There are two ways of developing thermodynamic relationships:

- (1) The **classical approach**, which utilizes the three laws of thermodynamics, with a focus on macroscopic, not molecular, properties.
- (2) An **integrated approach**, which combines the macroscopic (thermodynamic) and microscopic (statistical mechanical) perspectives.

This approach

- Is more direct;
- Reduces abstractness;
- Clarifies some fundamental relations.

End of Section

## Carnot's Law

The goals for this section are to

- State Carnot's law;
- Establish the link between temperature and entropy;
- Develop the equilibrium conditions resulting from the release of constraints on energy, volume and mass.

We need a thermodynamic variable that can identify, out of all possible values of  $U$ ,  $V$  and  $[n]$ , the subset of energies, volumes, and compositions that constitute the equilibrium state.

### **Carnot's law**

**There exists an extensive thermodynamic variable called entropy,  $S = S(U, V, [n])$ , that can be defined for all equilibrium states.**

**Entropy has the property that, when a system specified by  $U$ ,  $V$ , and  $[n]$  evolves from a constrained equilibrium state to a less constrained one**

- $\Delta S = S(\text{final}) - S(\text{initial}) > 0$ , if a new equilibrium is established;
- $\Delta S = 0$ , if the system was initially at equilibrium.

If the entropy remains constant, lifting the constraint involves no change in the respective subsystems, because they were already in equilibrium relative to one another.



Taking the first derivative of  $U = U(S, V, n_1, \dots, n_r) = U(S, V, [n])$  gives

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, [n]} dS + \left(\frac{\partial U}{\partial V}\right)_{S, [n]} dV + \sum_{i=1}^r \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_k} dn_i$$

where  $n_k$  on a partial derivative denotes all mole numbers fixed except  $n_i$ .

We identify  $-\left(\frac{\partial U}{\partial V}\right)_{S, [n]} = P$  with the mechanical pressure, and introduce the notation

$$\left(\frac{\partial U}{\partial S}\right)_{V, [n]} = T \quad \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_k} = \mu_i \quad \text{chemical potential of the } i\text{-th component}$$

$$dU = TdS - PdV + \sum_{i=1}^r \mu_i dn_i \rightarrow TdS = dU + PdV - \sum \mu_i dn_i \rightarrow dS = \frac{1}{T} dU + \frac{1}{T} PdV - \frac{1}{T} \sum \mu_i dn_i$$

Equating  $T$  to  $(\partial U / \partial S)_{V, [n]}$  suggests that we relate this partial derivative to the temperature that we read on thermometers. Indeed, that assumption will turn out to be true, but this relationship must be carefully established, not just taken for granted.

Identifying the mechanical pressure,  $P$ , with  $(\partial U / \partial V)_{S, [n]}$  also implicitly specifies the entropy term,  $TdS$ .

We can gain some insight into this relationship by considering a **closed system**,  $dn_i = 0$ , for which

$$dU = TdS - PdV \quad \text{or} \quad TdS = dU + PdV$$

where we can identify  $PdV$  as mechanical expansion work. Any change in the energy of a system at equilibrium that we cannot relate to work becomes  $TdS$ .

The equation  $dU = TdS - PdV$  is a thermodynamic statement of the conservation of energy.



$$dU = TdS - PdV + \sum_{i=1}^r \mu_i dn_i \quad dS = \frac{1}{T} dU + \frac{1}{T} PdV - \frac{1}{T} \sum \mu_i dn_i$$

The energy term  $\sum \mu_i dn_i$  has no counterpart in mechanics, so we must define it within a thermodynamic context.

We now have two questions:

- (1) What role do these thermodynamic variables,  $T$ ,  $P$ , and  $\mu$ , play as criteria for equilibrium?
- (2) What are the physical interpretations of  $T$  and  $\mu$ ?

We can state the roles that  $T$ ,  $P$ , and  $\mu$  play as criteria for equilibrium succinctly.

We begin with subsystems  $\alpha$  and  $\beta$ . Constraints prevent exchange of energy or matter and—within these subsystems—changes in their volumes. Upon releasing these constraints, the systems will achieve a new equilibrium:

#### Constraint released

- (1) Exchange of energy
- (2) Volume not fixed
- (3) Exchange of matter
- (4) Exchange of energy and matter and volume not fixed

#### Equilibrium condition

$$T^\alpha = T^\beta$$

$$P^\alpha = P^\beta$$

$$\mu^\alpha = \mu^\beta$$

$$\left[ \begin{array}{l} T^\alpha = T^\beta \\ P^\alpha = P^\beta \\ \mu^\alpha = \mu^\beta \end{array} \right]$$

Releasing a constraint on an **extensive** independent variable ( $U$ ,  $V$ , or  $[n]$ ) results in its conjugate **intensive** property ( $T$ ,  $P$ ,  $\mu$ ) becoming uniform throughout the system, when it reaches equilibrium.

$$dU = TdS - PdV + \sum_{i=1}^r \mu_i dn_i \quad dS = \frac{1}{T}dU + \frac{1}{T}PdV - \frac{1}{T}\sum \mu_i dn_i$$

Constraints  
On 

U	V	n <sub>i</sub>
Off	Off	Off

Constraints  
On 

U	V	n <sub>i</sub>
Off	On	Off

We analyze equilibrium conditions that occur when the constraints on energy, then volume and finally mass exchange are relaxed.

(1) Release of the constrain on energy ( $dV = dni = 0$ ) yeilds

$$dS = \frac{dU}{T}$$

Since  $U^{\text{tot}} = U^{\alpha} + U^{\beta}$ , exchange of energy between the subsystems requires  $dU^{\alpha} = -dU^{\beta}$

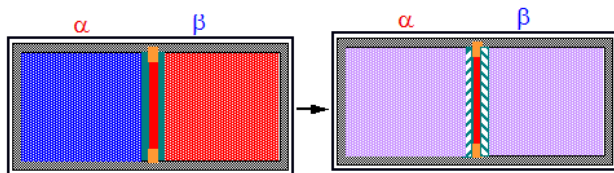
Additivity of S for the two systems gives

$$dS^{\text{tot}} = dS^{\alpha} + dS^{\beta} = \frac{dU^{\alpha}}{T^{\alpha}} + \frac{dU^{\beta}}{T^{\beta}} = dU^{\alpha} \left( \frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}} \right) = 0$$

According to Carnot's law,  $dS^{\text{tot}} = 0$  at equilibrium.

This must be true for any arbitrary value of  $dS^{\text{tot}}$ .

Therefore  $1/T^{\alpha} = 1/T^{\beta}$  or  $T^{\alpha} = T^{\beta}$



constraint on energy released

Constraint released   Equilibrium condition

Exchange of energy    $T^{\alpha} = T^{\beta}$

$$dU = TdS - PdV + \sum_{i=1}^r \mu_i dn_i \quad dS = \frac{1}{T}dU + \frac{1}{T}PdV - \frac{1}{T}\sum_{i=1}^r \mu_i dn_i$$

Constraints  
On  $\begin{matrix} U & V & n_i \\ \hline \text{Off} & & \end{matrix}$

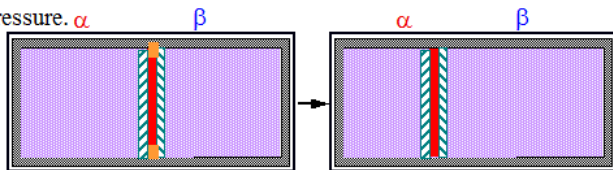
Constraints  
On  $\begin{matrix} U & V & n_i \\ \hline \text{Off} & & \end{matrix}$

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On  $\begin{matrix} U & V & n_i \\ \hline \text{Off} & & \end{matrix}$

The equilibrium condition for **pressure** follows directly

from identifying  $P$  with the mechanical pressure.  $\alpha$   $\beta$

Upon releasing the constraints on energy and volume with  $dn_i = 0$ , we can write for the two subsystems,  $\alpha$  and  $\beta$



$$U^{\text{tot}} = U^\alpha + U^\beta = \text{const} \quad V^{\text{tot}} = V^\alpha + V^\beta = \text{const}$$

**Constraints on energy and volume released**

$$dU^\alpha = -dU^\beta$$

$$dV^\alpha = -dV^\beta$$

$$dS^\alpha = \frac{1}{T^\alpha}dU^\alpha + \frac{P^\alpha}{T^\alpha}dV^\alpha \quad dS^\beta = \frac{1}{T^\beta}dU^\beta + \frac{P^\beta}{T^\beta}dV^\beta$$

$$dS^{\text{tot}} = dS^\alpha + dS^\beta = \left( \frac{1}{T^\alpha} - \frac{1}{T^\beta} \right) dU^\alpha + \left( \frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta} \right) dV^\alpha = 0$$

Constraint released    Equilibrium condition

Exchange of energy     $T^\alpha = T^\beta$

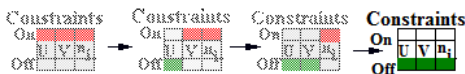
Exchange of energy  
and volume     $T^\alpha = T^\beta$   
 $P^\alpha = P^\beta$

At equilibrium,  $dS^{\text{tot}} = 0$ , and since  $U$  and  $V$  are independent variables

$$\left( \frac{1}{T^\alpha} - \frac{1}{T^\beta} \right) = 0 \quad \left( \frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta} \right) = 0$$

$$T^\alpha = T^\beta \quad \text{and} \quad P^\alpha = P^\beta$$

$$dU = TdS - PdV + \sum_{i=1}^r \mu_i dn_i \quad dS = \frac{1}{T}dU + \frac{1}{T}PdV - \frac{1}{T}\sum \mu_i dn_i$$



We can obtain the equilibrium condition for the **chemical potential,  $\mu_i$** , from the following analysis

Conservation of energy, volume and mass requires

$$dU^\alpha = -dU^\beta, \quad dV^\alpha = -dV^\beta, \quad dn_i^\alpha = -dn_i^\beta$$

Releasing the constraints on exchange of energy, volume and mass results in  $T^\alpha = T^\beta$  and  $P^\alpha = P^\beta$  and

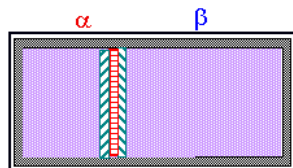
$$dS^{\text{tot}} = -\frac{1}{T} \sum (\mu_i^\alpha - \mu_i^\beta) dn_i^\alpha$$

The **condition for equilibrium** occurs when  $dS^{\text{tot}} = 0$ , which is satisfied when  $\mu_i^\alpha = \mu_i^\beta$  for all  $i$ .

For  $\mu_i^\beta > \mu_i^\alpha$ ,  $dS^{\text{tot}} > 0$  and  $T > 0$ ,  $dn_i^\alpha > 0$  and component  $i$  moves from  $\beta$  to  $\alpha$ .

Thus a component moves from a high to a low chemical potential/

Note:  $n_i^\alpha$  can vary independently of  $n_j^\alpha$ .



**Constraints on energy, volume and mass released**

Constraint released    Equilibrium condition

Exchange of energy     $T^\alpha = T^\beta$

Exchange of energy and volume     $T^\alpha = T^\beta$   
 $P^\alpha = P^\beta$

Exchange of energy, volume and mass     $T^\alpha = T^\beta$   
 $P^\alpha = P^\beta$   
 $\mu_i^\alpha = \mu_i^\beta$

A few further comments on temperature. Upon release of the constrain on energy

$$dS^{\text{tot}} = dU^{\alpha} \left( \frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}} \right)$$

If initially  $dS^{\text{tot}} = 0$ , then

$$1/T^{\alpha} - 1/T^{\beta} = 0 \quad \rightarrow \quad T^{\alpha} = T^{\beta}$$

(system initially in equilibrium)

If  $dS^{\text{tot}} > 0$ , and initially

$$1/T^{\alpha} > 1/T^{\beta} \quad \rightarrow \quad T^{\beta} > T^{\alpha} \quad \text{then} \quad dU^{\beta} > 0$$

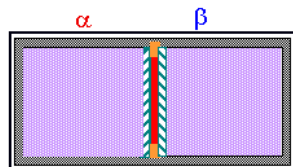
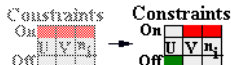
(energy goes from  $\beta$  to  $\alpha$ )

or initially

$$1/T^{\beta} > 1/T^{\alpha} \quad \rightarrow \quad T^{\alpha} > T^{\beta} \quad \text{then} \quad dU^{\alpha} > 0$$

(energy goes from  $\alpha$  to  $\beta$ )

This analysis shows that Carnot's law is consistent with our experience that heat goes from the warmer to the colder body.



In thermodynamics, we define **temperature** by

$$(dU / dS)_{V, [n]} = T$$

and as we shall see, for all equilibrium systems, as  $U \rightarrow 0$ ,  $T \rightarrow 0$ .  
This unambiguously defines one point on a temperature scale.

Choosing a second reference point and assigning a value to it defines a temperature scale. An international convention assigns a value of 273.16 K (K = kelvin) to the **triple point of water**, where ice, liquid water and vapor coexist ( $T = 273.16$  K,  $P = 4.585$  torr).

Other older temperature scales that remain in common use were formulated in terms of more accessible, but less well defined reference states.

- Fahrenheit used ice + salt (NaCl) to fix zero and the temperature of blood to fix 100°.
- Celsius on the other hands used melting ice and boiling water at 1 atm to fix zero and 100°.
- Rankine used the same scale as Fahrenheit but fixed zero at absolute zero.

Temperatures expressed in the different systems are related by

$$\text{Celsius} \quad t^{\circ}\text{C} = T(\text{K}) - 273.15$$

$$\text{Rankine and Fahrenheit} \quad t^{\circ}\text{F} = T^{\circ}\text{R} - 495.67 = (9/5)t^{\circ}\text{C} + 32$$

End of Section

## Ideal Gases

The goals for this section are to

- Obtain the ideal gas equation and relate it to the kinetic theory of gases;
- Obtain the equations for the heat capacity, entropy and chemical potential of an ideal gas.



We are now in a position to obtain the thermodynamic expression for an ideal gas by combining results from the kinetic theory of gasses

$$U = \frac{2}{3}PV \quad \left[ \frac{\partial(U/n)}{\partial V} \right]_{KE} = 0$$

with the thermodynamic equation for a closed single-component system

Identifying the temperature with the increase in kinetic energy of an ideal gas implies  $U/n$  is solely a function of temperature.

$$\frac{3}{2}U = PV = \sum \frac{1}{2}m \langle v^2 \rangle = nf(T) = n \text{ constant } T = nRT$$

To be consistent with  $dU = + TdS$ ,  $f(T) = \text{constant } T$ .

If we set the constant equal to  $R$  (8.31 J/mol K) we obtain the ideal gas equation,  $pV = nRT$ , the best-known equation of state in thermodynamics.

$$\frac{2}{3}U = PV = nRT$$

$$\frac{2}{3}U = PV = nRT$$

(1) It is often useful to express  $U$  in terms of molecules rather than moles.

$$\frac{2}{3}U = nN_V \cdot \frac{RT}{N_V} = NkT \quad k = R/N_A \text{ is the Boltzmann constant}$$

(2) Now we can relate the root mean square velocity from kinetic theory to the temperature.

$$\frac{1}{2}Nm \langle v^2 \rangle = U = \frac{3}{2}NkT \longrightarrow \langle v^2 \rangle = 3\frac{kT}{m}$$

kinetic theory                  thermodynamics

For translation in only one dimension  $\langle v_x^2 \rangle = \frac{RT}{M}$

(3) The change in  $U$  with respect to  $T$ , where  $V$  is constant, plays an important role in thermodynamics, and it is called the **heat capacity at constant volume** :

$$C_V \doteq \left( \frac{\partial U}{\partial T} \right)_{V, [n]} = \left( \frac{\partial (3/2)nRT}{\partial T} \right)_{V, [n]} = \frac{3}{2}nR$$

For an ideal gas  $C_V = n\frac{3}{2}R$  and  $\Delta U = U_{II} - U_I = \frac{3}{2}nR(T_{II} - T_I)$

This equation for  $C_V$  includes translational motion for a monatomic ideal gas. For a polynuclear molecule, additional motions contribute to  $C_V$ .

$$\frac{2}{3}U = PV = nRT \quad C_V = \frac{3}{2}R \quad \Delta U = U_{II} - U_I = \frac{3}{2}nR(T_{II} - T_I)$$

(4) We can derive the entropy of an ideal gas using

$$dS = \frac{1}{T}dU + \frac{P}{T}dV \quad dS = \frac{3}{2} \frac{nR}{T}dT + \frac{nR}{V}dV$$

$$U = \frac{3}{2}nRT$$

$$dU = \frac{3}{2}nRdT \quad \frac{P}{T} = \frac{nR}{V}$$

This equation for  $dS$  can be integrated with respect to one variable at a time since  $3nR/2T$  is independent of  $V$  and  $nR/V$  independent of  $T$ :

$$\Delta S = S(T_{II}, V_{II}, [n_r]) - S(T_I, V_I, [n_r]) = -\frac{3}{2}nR \ln \frac{T_{II}}{T_I} + nR \ln \frac{V_{II}}{V_I}$$

$$\Delta S = S(T_{II}, V_{II}, [n_r]) - S(T_I, V_I, [n_r]) = -n \underset{\downarrow}{C_V} \ln \frac{T_{II}}{T_I} + nR \ln \frac{V_{II}}{V_I}$$

For example, at constant  $T$

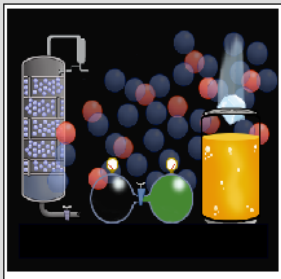
$$\Delta S = S(T, V^\beta, [n]) - S(T, V^\alpha, [n]) = nR \ln \frac{V^\beta}{V^\alpha}$$

We can also express  $\Delta S$  in terms of pressure changes,

using  $V = nRT/P$ ,

$$\Delta S = S(T, V^\beta, [n]) - S(T, V^\alpha, [n]) = -nR \ln \frac{P^\beta}{P^\alpha}$$

We will discuss the chemical potential of an ideal gas in the module on Transformations



**You have reached the end of this module.**

**You may review any section within this module.**

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Having introduced the notion of constraints, we are in a position to provide a more precise formulation of the “second law of thermodynamics,” which has been stated in many ways.

Carnot was primarily inspired by the advent of steam engines. Consequently, in his original publication (1825), he formulated this law in terms of work, heat and temperature in a heat engine. Chemical processes and heat engines do not appear to have much in common, but in fact the concept of equilibrium is applicable to both.

Formulation of the second law should be based on a statement of the properties of the equilibrium state that is as general as possible. Many formulations of this law ignore the fact that entropy is only defined for equilibrium states. Thus, it is necessary in one way or another—directly or indirectly—to introduce the concept of a constrained equilibrium when associating an entropy increase with an approach towards equilibrium.

Because Carnot was the first to formulate a coherent statement of this law, it is named after him.



We can define the mathematical form of the entropy with the following stipulation:

The entropy of a composite system,  $S = S(U, V, n)$ , is

- (1) Additive over the constituent subsystems;
- (2) Continuous and differentiable;
- (3) A monotonically increasing function of the energy.

From Carnot's law and this stipulation, we can derive a number of mathematical statements:

- (1) Additivity:

$$S = \Sigma S^\alpha$$

- (2) Entropy of a subsystem is a function solely of the extensive properties of that subsystem.

$$S^\alpha = S(U^\alpha, V^\alpha, n_1^\alpha, \dots, n_r^\alpha)$$

- (3) Additivity of S for subsystems requires that S is an extensive variable so that

$$S(\lambda U, \lambda V, \lambda n_1, \dots, \lambda n_r) = \lambda S(U, V, n_1, \dots, n_r)$$

- (4) The monotonic dependence of U on S implies

$$\left( \frac{\partial S}{\partial U} \right)_{V, n} = 0$$

- (5) Provided that U is a single-valued, continuous and differential function of S, V,  $n_1, \dots, n_r$ , we can solve  $S = S(U, V, [n])$  to obtain

$$U = U(S, V, n_1, \dots, n_r)$$

To develop either  $S(U, V, n_1, \dots, n_r)$  or  $U(S, V, n_1, \dots, n_r)$  further, we simply assert (and demonstrate later) that maximizing S is equivalent to minimizing U.

