

Termodinámica-Zemansky

Tomás Ricardo Basile Álvarez
316617194

May 10, 2021

Temperatura y la Ley Cero

Macroscopic Point of View

To study any branch of science it is important to start with a separation of a restricted region of space by means of a boundary. Whatever lies outside the boundary is known as the **surroundings**.

The next step is to describe the system in terms of macroscopic quantities related to the behavior of the system or interactions with the surroundings.

This quantities are called **macroscopic coordinates** and have the following properties in common:

- They involve no special assumptions concerning the structure of matter, fields or radiation.
- They are few in number needed to describe a system.
- They are fundamental.
- They can, in general, be directly measured.

In short, a macroscopic description of a system involves the specification of a few fundamental measurable properties of a system. Thermodynamics is the branch of science that deals with these properties.

Microscopic Point of View

This point of view is related to statistical mechanics. A microscopic description of a system involves the following properties:

- Assumptions are made concerning the structure of matter, fields, or radiation.

-
- many quantities must be specified to describe the system.
 - These quantities specified are not usually suggested by sensory perceptions, but rather by mathematical models.
 - They cannot be directly measured, but must be calculated.

Scope of thermodynamics

In thermodynamics, the attention is directed towards the interior of a system. A macroscopic point of view is adopted and it is the function of experiment to determine the quantities that are appropriate for a description of such an internal state. Macroscopic quantities having a bearing on the internal state of a system are called **thermodynamic coordinates**.

Thermal Equilibrium and the Zeroth law

Experiment shows that for a given composition of a gas, many different values of pressure and volume are possible. If one is kept constant, the other can vary over a wide range of values. In other words, the pressure and volume are independent coordinates.

Similarly, for a wire of constant mass, tension and length are independent quantities.

Some complicated systems may still be described with the aid of only two independent coordinates..

For the present, to simplify our discussion, we shall only deal with systems of constant mass and composition, each requiring only one pair of independent coordinates for its description. We shall use the symbols X, Y for the pair of independent coordinates. X refers to a generalized force (pressure, tension, etc) and Y to a generalized displacement (volume, length, etc).

Equilibrium State: It's a state of a system in which the coordinates X, Y have definite values that remain constant so long as the external conditions are unchanged.

Types of walls between a system and its surroundings:

- Adiabatic: A wall that perfectly seals off a system and doesn't allow exchange of mass or heat.
- Diathermic: A wall that allows exchange of heat. j0

If two systems are separated by a diathermic wall, the values of X, T and X', Y' will change spontaneously until an equilibrium state of the combined system is attained.

The two systems are then said to be in **thermal equilibrium** with each other.

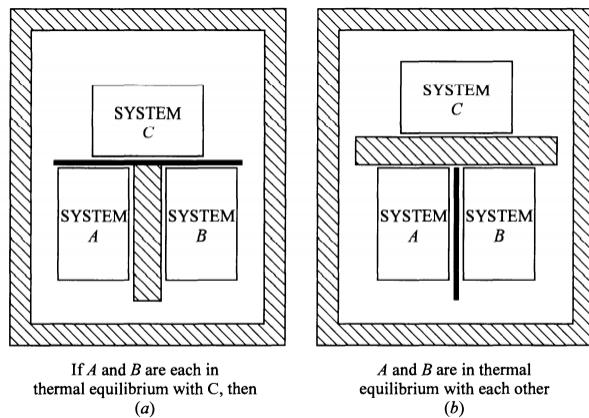
Thermal equilibrium is the state achieved by two (or more) systems, characterized by restricted values of the coordinates of the systems, after they have been in communication with each other through a diathermic wall.

Zeroth law

Imagine two systems A, B separated from each other by an adiabatic wall but each in contact simultaneously with a third system C through diathermic walls.

Experiment shows that the two systems will come to thermal equilibrium with the third system. What's more, no further change will occur if the adiabatic wall separating A and B is replaced with a diathermic one.

If, instead of allowing both systems A and B to come to equilibrium with C at the same time, we first establish equilibrium between A and C and later establish equilibrium between B and C; then, when A and B are brought into communication through a diathermic wall, they will be found to be in thermal equilibrium.



Zeroth law: Two systems in thermal equilibrium with a third are in thermal equilibrium with each other.

Concept of Temperature

Consider a system A in state X_1, Y_1 in thermal equilibrium with another system B in state X'_1, Y'_1 . If system A is removed and its state changed, we can find a second state X_2, Y_2 that is in thermal equilibrium with the original state X'_1, Y'_1 .

Experiments show that there exists a whole set of states $X_1, Y_1; X_2, Y_2; X_3, Y_3;$ at thermal equilibrium with X'_1, Y'_1 (and by the 0th law, at thermal equilibrium between each other).

We shall suppose that all such states, when plotted in a X-Y diagram, lie on a curve which we call **isotherm**.

An isotherm is the locus of points representing states at thermal equilibrium between themselves.

Similarly, we can find a whole set of states of system B at equilibrium with these states (and with themselves).

These two curves in X-Y and in X'-Y' are said to be corresponding isotherms.

We can define temperature now. The **temperature** of a system is a property that determines whether a system is in thermal equilibrium with other systems.

The temperature of all systems in thermal equilibrium can be represented by a number. The choice of scale is merely a set of rules for assigning the number that corresponds to each isotherm.

Once it is done we get the following theorem: Two systems are at equilibrium if and only if they have the same temperature.

This means that to determine if two systems are in equilibrium, there is no need to bring them together, we can do it by just measuring the temperature of each one separately using a system C (a thermometer).

Thermometer

We choose a system to work as a thermometer. In this system, we can graph all the isotherms and assign a specific number to each one (maybe a linear function of the value of the X coordinate at this isotherm). In that case:

$$\theta(X) = aX$$

Kelvin chose a single point as basis for a scale. He chose the value 273.16 K for water at its triple point. That way, the value of a can be found as:

$$a = \frac{273.16}{X_{TP}}$$

Which means that:

$$\theta(X) = 273.16K \frac{X}{X_{TP}}$$

Comparison of Thermometers

We can apply this principles to three different variables in different systems. For example, for pressure we have that the Pressure is:

$$\theta(P) = 273.16K \frac{P}{P_{TP}}$$

For a platinum wire resistor, we get:

$$\theta(R') = 273.16K \frac{R'}{R'_{TP}}$$

For a thermocouple, we get:

$$\theta(\xi) = 273.16K \frac{\xi}{\xi_{TP}}$$

We can compare these different scales.

TABLE 1.2
Comparison of thermometers

Fixed point	Copper-constantan thermometer		Platinum resistance thermometer		Constant-volume H ₂ thermometer		Constant-volume H ₂ thermometer	
	\mathcal{E} , mV	$\theta(\mathcal{E})$	R' , Ω	$\theta(R')$	P , kPa	$\theta(P)$	P , kPa	$\theta(P)$
N ₂ (NBP)	0.73	32.0	1.96	54.5	184	73	29	79
O ₂ (NBP)	0.95	41.5	2.50	69.5	216	86	33	90
CO ₂ (NSP)	3.52	154	6.65	185	486	193	73	196
H ₂ O (TP)	6.26	273	9.83	273	689	273	101	273
H ₂ O (NBP)	10.05	440	13.65	380	942	374	139	374
Sn (NMP)	17.50	762	18.56	516	1287	510	187	505

We can see that they agree at the TP of H₂O.

Gas Thermometer

We have a gas contained in the glass bulb B, which communicates with the mercury column M through a capillary. The volume of the gas is kept constant by adjusting the level of the mercury column M until the mercury level just touches the tip of a small indicial point. The pressure of the Gas equals the height h plus atmospheric pressure.

We measure this pressure twice. First when the bulb is surrounded by water at the triple point and then when the bulb is surrounded by the system whose temperature we want.

With this, the temperature is given by $\theta(P) = 273.16K \frac{P}{P_{TP}}$

Ideal Gas Temperature

In the nineteenth century, the best thermometer was the gas thermometer. The theoretical basis for this thermometer was the well understood ideal gas law:

$$PV = nRT$$

The temperature T is the the theoretical thermodynamic temperature.

θ indicates the real gas and T indicates the thermodynamic ideal-gas temperature.

The ideal gas temperature is found using a constant-volume gas thermometer.

Consider measuring the ideal-gas temperature at the normal boiling point (NBP) of water. An amount of gas is introduced into the bulb of a constant-volume gas thermometer, and one measures the P_{TP} when the bulb of the constant-volume thermometer is inserted in the triple point cell. Suppose that $P_{TP} = 120kPa$. Keeping the volume V constant, carry out the following steps :

- Surround the bulb with steam at standard atmospheric pressure, measure the gas pressure P_{NBP} , and calculate the empirical temperature θ using the equation:

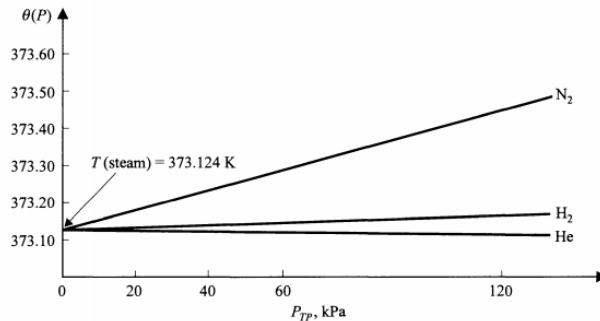
$$\theta(P_{NBP}) = 273.16K \frac{P_{NBP}}{P_{TP}} = 273.16K \frac{P_{NBP}}{120}$$

- Remove some of the gas so that P_{TP} has a smaller measured value, say 60 Kpa. Measure the new value of P_{NBP} and calculate a new value:

$$\theta(P_{NBP}) = 273.16K \frac{P_{NBP}}{60}$$

- Continue reducing the amount of gas in the bulb so that P_{TP} and P_{NBP} have smaller and smaller values, at each value of P_{TP} , calculate the corresponding $\theta(P_{NBP})$.
- Plot $\theta(P_{NBP})$ against P_{TP} and extrapolate the resulting curve to the axis where $P_{TP} = 0$. Read from the graph,

$$\lim_{P_{TP} \rightarrow 0} \theta(P_{NBP})$$



Doing this, we get the same limit regardless of the gas used. Therefore, we define the ideal - gas temperature T by the equation:

$$T = 273.16K \lim_{P_{TP} \rightarrow 0} \left(\frac{P}{P_{TP}} \right)$$

This way, the ideal-gas temperature is made to be independent of the properties of any one particular gas, though it still depends on the properties of gases in general.

Simple Thermodynamic Systems

Thermodynamic Equilibrium

Change of State: When the coordinates of a system change in any way whatsoever, whether spontaneously or by virtue of outside influence.

Thermal equilibrium: Exists when there is no spontaneous change in the coordinates of a system in mechanical and chemical equilibrium. All parts of the system are at the same temperature and so is the surroundings.

When a body is at mechanical, chemical and thermal equilibrium, it is said to be in **thermodynamic equilibrium**.

States of thermodynamic equilibrium can be described in terms of macroscopic coordinates that do not involve time.

When a system is at a nonequilibrium state, if an attempt is made to give a macroscopic description, it is found that the value of the thermodynamic coordinates (for example, pressure) varies from place to place, there is no single pressure that refers to the system as a whole.

Equation of State

Imagine a mass of gas that is a closed system.

If we know two of the variables P , V , T , the third one can be obtained directly.

This means that there is an equation relating these 3 variables, called the **equation of state**. Every system has its own equation of state. For a closed system, the equation relates temperature and two other thermodynamic variables.

The equation must be determined by experiment or by molecular theory. It is not a theoretical deduction but is usually an experimental addition to thermodynamics.

For example, for a gas at very low pressure, the equation of state of an ideal gas is:

$$PV = nRT$$

where n is the number of moles and R is a constant.

At higher pressures, the equation can be modified to produce better results, the Van der Waals equation:

$$(P + \frac{a}{v^2})(v - b) = RT$$

Clearly a system that is not at mechanical and thermal equilibrium has no equation of state, since even the thermodynamic coordinates may make no sense.

Mathamtical Theorems

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y/\partial x)_z}$$
$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Therefore, we only need two of the derivatives in order to get all 6 of them.

Hydrostatic System

Definition: An isotropic system of constant mass and constant composition that exerts on the surroundings a uniform hydrostatic pressure, in the absence of gravitational, electric and magnetic effects.

These are divided into the following categories:

- **Pure Substance:** single chemical compound
- **Homogeneous mixture:** A mixture of gases or liquids or a solution.
- **Heterogeneous mixture:** A mixture of different gases in contact with a mixture of liquids for example.

Experiments show that the state of equilibrium of a hydrostatic system of a single phase can be described in an equation of state by three coordinates PVT.

If a variable changes slightly , generally the other two will change too.

If the change of V is very small compared to V buy large enough in comparison to contain many molecules, we denote it by dV.

Similarly, if the change of P is small but bigger than the momentary variations in microscopic concentration of the particles, we denote it by dP.

In general, every infinitesimal dX in thermo must be small enough in comparison to X but large enough to warrant a macroscopic point of view.

The equation of state may be solved for a coordinate in terms of the other two (theoretically) so:

$$V = V(T, P)$$

Now, an infinitesimal change from a state of equilibrium to another involves a dV , dT and a dP , related by:

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP$$

The average coefficient of volume expansion due to temperature is defined as the change of vol. per unit vol. (relative change in volume) divided by the change in Temp.

Taking it to infinitesimal, it means we may define:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

which is called the **volume expansivity** and gives the reason between the relative change of volume and the change of temperature.

It is a nice way of quantifying the change of volume due to temperature.

In the case of an ideal gas, $PV = nRT$, we have $\beta = 1/T$

Similarly, we define:

$$k = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

And call it the **isothermal compressibility**. It gives the reason between the relative infinitesimal change of volume and the infinitesimal change in pressure.

In the case of an ideal gas, $PV = nRT$, we have $k = 1/P$

Alternatively, we can write P as a function of T, V :

$$\begin{aligned} P &= P(T, V) \\ \Rightarrow dP &= \left(\frac{\partial P}{\partial T} \right)_V dT + \left(\frac{\partial P}{\partial V} \right)_T dV \end{aligned}$$

Or write T as a function of P and V :

$$\begin{aligned} T &= T(P, V) \\ \Rightarrow dT &= \left(\frac{\partial T}{\partial P} \right)_V dP + \left(\frac{\partial T}{\partial V} \right)_P dV \end{aligned}$$

For example, that means that $\frac{\partial P}{\partial T} = \frac{\beta}{k}$.

Which in turn means that $dP = \frac{\partial P}{\partial T}dT + \frac{\partial P}{\partial V}dV = \frac{\beta}{k}dT - \frac{1}{kV}dV$

At constant volume, $dP = \frac{\beta}{k}dT$. So that $P_f - P_i = \int_{T_i}^{T_f} \frac{\beta}{k}dT$. And if β, k are almost constant, we can forget the integral and find a direct relation $P_f - P_i = \frac{\beta}{k}(T_f - T_i)$

Stretched wire

A sufficiently complete thermodynamical description of a wire is given by only 3 coordinates:

- The tension in the wire J measured in N
- The length L measured in m
- The abs temperature T in K

For a wire at constant temperature, we have as an approximation Hooke's law $J = -k(L - L_0)$.

We can have L as a function of the other variables as:

$$\begin{aligned}L &= L(T, J) \\ \Rightarrow dL &= \left(\frac{\partial L}{\partial T}\right)_J dT + \left(\frac{\partial L}{\partial J}\right)_T dJ\end{aligned}$$

Linear Expansivity:

$$\alpha = \frac{1}{L} \left(\frac{\partial L}{\partial T}\right)_J$$

It is the reason between the relative change of length and the infinitesimal change of temperature at constant tension. It is usually positive for metals but might be negative for rubber bands for example. Data show that it depends only slightly in J and varies mostly with T.

Young Modulus:

$$Y = \frac{L}{A} \left(\frac{\partial J}{\partial L}\right)_T$$

It is the change of tension per unit area divided by the change of length per unit length.

The equation of state of an ideal elastic substance is:

$$J = KT \left(\frac{L}{L_0} - \frac{L_0^2}{L^2} \right)$$

So that $Y = \frac{J}{A} + \frac{3KTL_0^2}{AL^2}$ and $\alpha = \alpha_0 - \frac{1}{T} \frac{L^3/L_0^3 - 1}{L^3/L_0^3 - 2}$

Surface

A surface of a liquid can be the interface of a liquid and vapor, a soap bubble, a thin film of oil on the surface of water, etc.

The **surface tension** is the force acting perpendicularly to a line of unit length in the surface.

The description requires 3 coordinates:

-
- Surface tension γ , in N/m
 - Area of the film A, in m^2
 - Abs Temperature T, in K.

Most pure liquids in equilibrium with their vapor follow the following state equation:

$$\gamma = \gamma_0 \left(1 - \frac{T}{T_c}\right)^n$$

γ_0 is the tension at a standard temperature, and T_c is the critical temperature (temperature above which no amount of pressure will condense vapor into liquid).

Dielectric Slab

Consider a capacitor consisting of two parallel conducting plates of Area A and separation l, filled with a dielectric material. If a constant voltage is established, then a uniform electric field \vec{E} exists in the dielectric between the plats. The electric field will polarize the material with polarization \vec{P} .

The electric displacement \vec{D} is given by:

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P}$$

In thermodynamics, it is not customary to use P, but we use the total polarization $\vec{\mathfrak{P}} = \vec{P}V$. So the equation becomes:

$$\vec{D} = \epsilon_0 \vec{E} + \frac{\vec{\mathfrak{P}}}{V}$$

To describe a dielectric, we need the three coordinates:

- 1 Electric field E in v/m
- 2 Total polarization $\vec{\mathfrak{P}}$ in $C \cdot m$
- 3 Abs temperature T in K

The equation of state might be in the form:

$$\frac{\vec{\mathfrak{P}}}{V} = \left(a + \frac{b}{T}\right) E$$

Paramagnetic rod

A paramagnet has no permanent magnetic field but an induced one. The effect is a **magnetization** M (per unit volume) produced by an outside field B . We can define the magnetic field strength as:

$$H = \frac{B}{\mu_0} - M$$

As in the other case, we prefer a variable $\mathcal{M} = MV$. So that:

$$H = \frac{B}{\mu_0} - \frac{\mathcal{M}}{V}$$

To describe a paramagnet, we need three coordinates:

- 1 Magnetic field H in A/m
- 2 total magnetization \mathcal{M} in $A \cdot m^2$
- 3 Temperature T in K

The equation of state is known as **curie's law** :

$$\mathcal{M} = \frac{C_c \mathcal{H}}{T}$$

With C_c called Curies constant.

TABLE 2.2
Intensive and extensive coordinates

Simple systems	Intensive coordinate	Extensive coordinate
Hydrostatic system	Pressure P	Volume V
Stretched wire	Tension \mathcal{F}	Length L
Surface	Surface tension γ	Area A
Electrochemical cell	Electromotive force (emf) \mathcal{E}	Charge Z
Dielectric slab	Electric field E	Total polarization ρ
Paramagnetic rod	Magnetic field \mathcal{H}	Total magnetization \mathcal{M}

Work

Work

If a system undergoes a displacement under the action of a force, **work** is said to be done, the amount of work equal to the product of the force and the component of displacement parallel to the force.

Internal Force: Work done by one part of the system on another.

External Force: Work done by or to the surroundings.

We don't discuss internal work. For a system to do work, it must interact with the surroundings.

On the system: When the force exerted on a mechanical system is in the same direction as the displacement of the system, the work is positive and the energy increases.

By the system: The system does work on the surroundings and loses energy.

Quasi-Static Process

A system in thermodynamic equilibrium satisfies the following:

- Mechanical equilibrium: There are no unbalanced forces or torques acting on any part of the system or no the system as a whole.
- Thermal equilibrium: There are no temperature differences between parts of the system or between the system and its surroundings.
- Chemical: There are no chemical reactions.

Once a system is in thermodynamic equilibrium and the surroundings are unchanged, no motion will take place and no work will be done.

We want to transform the system in such a way that it is always in equilibrium so that we may describe it with the thermodynamic coordinates. This is impossible because the idea of changing the system necessarily implies it is out of equilibrium.

Nevertheless, we propose an ideal process called **quasistatic** which happens infinitesimally slowly. During a quasi-static process, the system is at all times infinitesimally near a state of equilibrium, so every intermediate state can be thought of as static and described with the coordinates.

This process is ideal.

Hydrostatic System

Imagine a hydrostatic system contained in a closed cylinder with a frictionless movable piston of cross section area A and that the pressure exerted *by the system* at the piston face is P.

The force on the face is therefore PA .

The surroundings also exert an opposing force on the piston, which is the force the gas has to overcome to move the piston.

If under these conditions the piston moves an infinitesimal distance dx during compression, then the surroundings perform an infinitesimal amount of work $\bar{d}W$ equal to:

$$\bar{d}W = Fdx = PAdx$$

But during compression, the volume decreases, so $Adx = -dV$, so:

$$\boxed{\bar{d}W = -PdV}$$

The sign ensures that a negative dV (a compression), gives rise to positive work and conversely.

In a finite quasi static process from V_i, V_f , the work is:

$$W_{if} = - \int_{V_i}^{V_f} PdV$$

If the change in volume is quasi-static, the system pressure P is equal to the external pressure and the same in all the system. So it can be expressed as a function of T, V by means of an equation of state.

The evaluation of the integral can then be made once the function $P(V)$ is known (for which we might need the behavior of T so that P is a function of V only).

If we do the same path but now compressing, the work is done on the system (so it must be positive):

$$W_{fi} = \int_{V_f}^{V_i} PdV$$

PV Diagram

We can record all the points coordinates (P, V) during the process

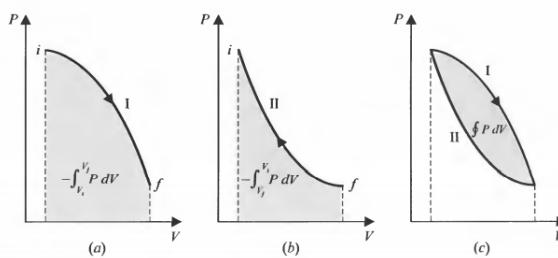
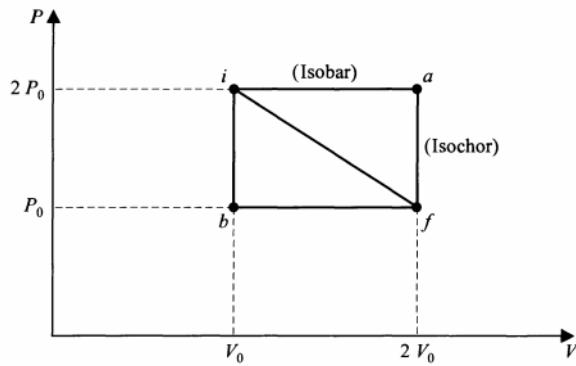


FIGURE 3-2
PV diagram of a gas with shaded area to show work done by the system or work done on the system. (a) Curve I, expansion; (b) curve II, compression; (c) curves I and II together constitute a cycle.

On I work is done by the system and on II work is done on the system. 3 is a cycle.
Clockwise cycles have a net work negative (done by the system)

Hydrostatic work depends on the path followed.

There are many ways to go from one point to another and each one might have different values of work.



Work is a path dependent integral (opposed to what happens mostly in mechanics, that's because now work depends on T).

Calculation of Work for Quasi static Processes

For an ideal gas $PV = nRT$:

- **Isothermal:** $W = - \int_{V_i}^{V_f} PdV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \log \frac{V_f}{V_i}$
- **Isobaric:** $W = -P\Delta V$
- **Isocoric:** $W = 0$
- **Adiabatic:** Let's say we move through the path $PV^\gamma = K$, then the work done is:

$$W = - \int PdV = - \int \frac{K}{V^\gamma} dV = \frac{KV_f^{1-\gamma} - KV_i^{1-\gamma}}{1-\gamma} = \frac{PV_f - P + iV_i}{\gamma - 1}$$

In a different subject.

The **Quasi static isothermal increase of pressure on a solid**. In this case, the path of integration is determined by the isothermal compressibility.

$$W = - \int PdV$$

But:

$$dV = \left(\frac{\partial V}{\partial P} \right)_T + \left(\frac{\partial V}{\partial T} \right)_P dT$$

But by definition: $k = -\frac{1}{V} \frac{\partial V}{\partial P}$.

So at constant temperature we have:

$$dV = -kVdP$$

Which results in:

$$\begin{aligned} W &= \int_{P_i}^{P_f} -kVdP \\ &\simeq \frac{kV}{2} (P_f^2 - P_i^2) \quad \text{aprox si k es cte} \\ &\simeq \frac{mk}{2\rho} (P_f^2 - P_i^2) \quad \text{porque k es mas o menos m/rho para solidos} \end{aligned}$$

Work in changing the length of a wire

Similarly to the gas, now the work is:

$$\bar{d}W = JdL$$

Where J is a function of L and T . A positive dL means stretching the wire, which is work done on the system (that's why it is positive).

So:

$$W = \int_{L_i}^{L_f} JdL$$

Work in changing area of surface film

Consider a soap film, which consists of two surfaces enclosing water stretched across a wire framework. The right side of the frame is movable and has length L .

If the surface tension is γ , then the external force F exerted on both surfaces is $2\gamma L$, so:

$$\bar{d}W = 2\gamma Ldx$$

But $2Ldx = dA$ (considering two films). Hence:

$$\begin{aligned} \bar{d}W &= \gamma dA \\ \Rightarrow W &= \int_{A_i}^{A_f} \gamma dA \end{aligned}$$

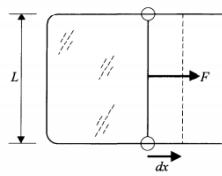


FIGURE 3-4
A soap film stretched across a rigid wire framework, known as the Maxwell frame, which has a movable wire on the right. An external force F displaces the movable wire an infinitesimal distance dx .

Work of simple systems

Simple system	Intensive coordinate (generalized force)	Extensive coordinate (generalized displacement)	Work, J
Hydrostatic system	P , in Pa	V , in m^3	$-P dV$
Wire	\mathcal{F} , in N	L , in m	$\mathcal{F} dL$
Surface film	γ , in N/m	A , in m^2	γdA
Electrochemical cell	\mathcal{E} , in V	Z , in C	$\mathcal{E} dZ$
Dielectric solid	E , in V/m	ρ , in $\text{C} \cdot \text{m}$	$E d\rho$
Paramagnetic solid	$\mu_0 \mathcal{H}$, in $\text{N/A} \cdot \text{m}$	\mathcal{M} , in $\text{A} \cdot \text{m}^2$	$\mu_0 \mathcal{H} d\mathcal{M}$

Heat and the First Law

Work and Heat

There are other means of changing the state of a system rather than only work.

CHAPTER 4. IDEAL AND THE FIRST LAW OF THERMODYNAMICS 75

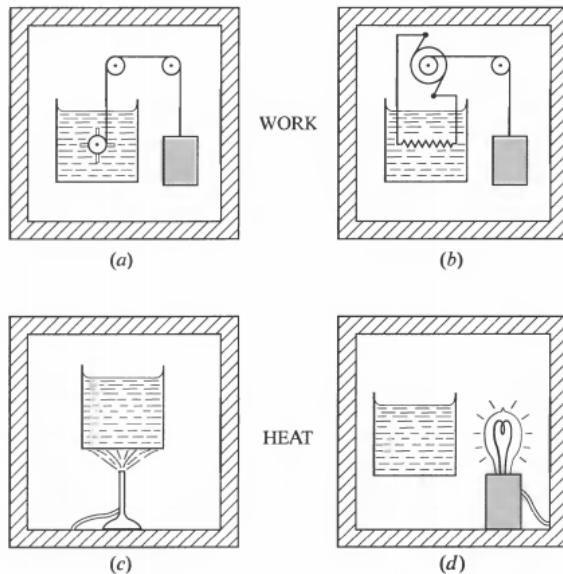


FIGURE 4-1

Distinction between work and heat: (a) and (b) show work being done on the system by means of a falling body, whereas (c) and (d) show heat entering the system from a hotter substance.

In image a) we have a falling weight that causes a paddle wheel to turn and augment the temperature of water. The weight is doing work on the system of water.

In image b) the weight does work to light up a circuit that increases the temperature of the water.

In the 2 images underneath, the effect on the water is the same but it is done in a more indirect way, this time the temperature increases because of heat.

Heat is that which is transferred between a system and its surroundings by virtue of temperature difference only. That is, without moving the walls or putting external fields.

Adiabatic Work

Adiabatic work is doing work on a system isolated by an adiabatic wall.

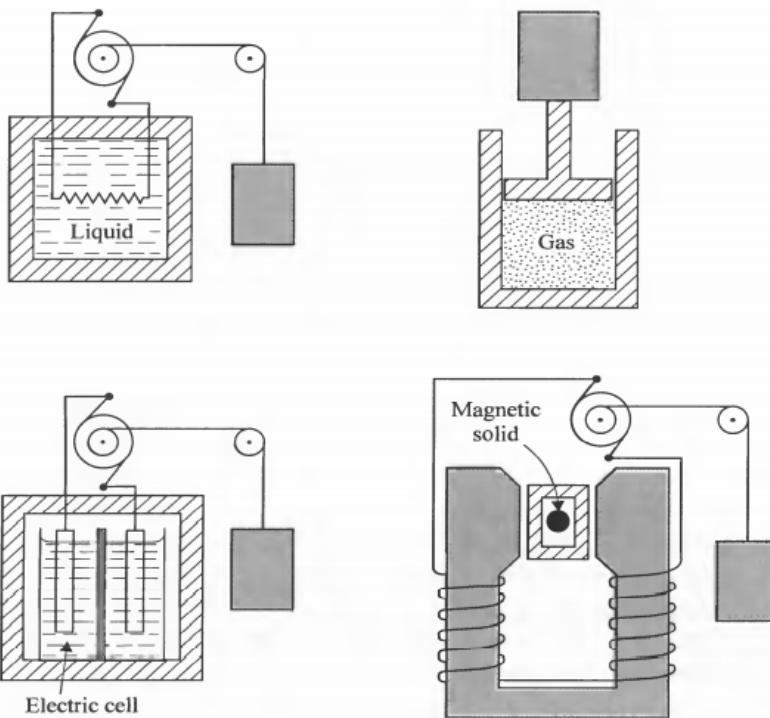


FIGURE 4-2
diabatic work for different types of systems.

Here we have different examples of adiabatic work. In which we are making sure that the only effect on the system is due to work and not heat.

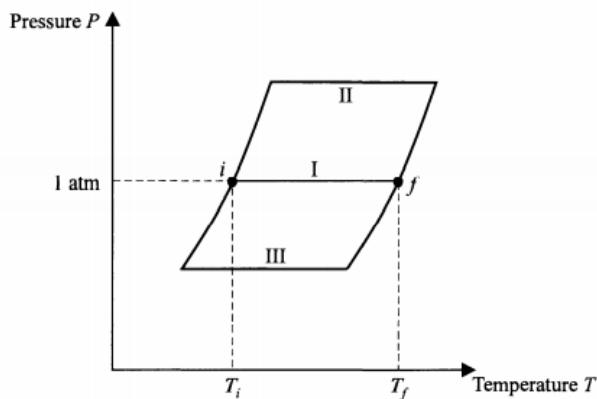


FIGURE 4-3
Changing the state of a system from the initial state i to the final state f along three different adiabatic paths.

Let's say we have a system at initial state i with $P_i = 1\text{ atm}$ and $T_i = 287.7\text{ K}$ and final state f with coordinates $P_f = 1\text{ atm}$, $T_f = 288.7\text{ K}$.

The system is a bucket of water with an electric resistor.

We want to take the system from the initial state to the final state via only adiabatic work.

Path I: We surround the water with an adiabatic wall, keep the water at atmospheric pressure and maintain a current in the resistor for a suitable interval of time.

Path II: Compress water adiabatically from i to a, then use a current in a resistor from a to b adiabatically and finally expand from b to f.

Path III: Expand, then increase temperature and then compress.

All these paths are adiabatic. And lead to the **first law of thermodynamics**:

If a closed system is caused to change from an initial state to a final state by adiabatic means only,

Then the work done on the system is the same for all adiabatic paths connecting the two states.

Because of this path independence, we can define a potential. Therefore, there must exist a function U that depends on the thermodynamic coordinates such that:

$$W_{i \rightarrow f}(\text{Adiabatic}) = U_f - U_i$$

Where U is called the **internal energy function**.

So work becomes path independent.

If positive work is done on the system, then $U_f > U_i$.

We will see later that if f cannot be reached adiabatically, then it is possible to go from f to i adiabatically.

Internal Energy function

$U_f - U_i$ is the increase in internal energy of the system. Then $W_{if} = U_f - U_i$ is the conservation of energy.

But it is more, it states that there exists an energy function, whose difference between two values is the energy change of the system.

The internal energy is a function of as many thermodynamic coordinates as necessary.

For the simple systems described earlier, we only need two coordinates because the third one is related by the equation of state.

If the coordinates characterizing the two states differ from each other infinitesimally by a difference of internal energy dU . If U is regarded as a function of T, V, then:

$$dU(T, V) = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

Or we can regard U as a function of any other pair of the coordinates.

$$dU(T, P) = \left(\frac{\partial U}{\partial T} \right)_P dT + \left(\frac{\partial U}{\partial P} \right)_T dP$$

Mathematical Formulation of the first law

In real life, not all processes are adiabatic.

Let us imagine two experiments performed on the same closed system. In one experiment, we measure the adiabatic work necessary to change the state of the system from i to f in order to obtain $U_f - U_i$.

In the other experiment, we cause the system to undergo the same change of state, so we have the same $U_f - U_i$ (because U depends only on the coordinates), but now allow the process to be diathermic, and measure the diathermic work W done.

The result is that the nonadiabatic work W is **not** equal to $U_2 - U_1$.

In order for the result to be consisting with conservation of energy, we are forced to conclude that energy has been transferred by other means aside work.

This energy transferred by the surroundings that is required to maintain the conservation of energy is called heat.

Heat: When a closed system whose surroundings are at a different temperature and on which diathermic work may be done undergoes a process, then the energy transferred by non-mechanical means, equal to the difference between the change of internal energy and the diathermic work is heat. Then, we have:

$$U_f - U_i = Q + W$$

The sign convention adopted is that Q is positive when heat enters the system.

This mathematical formulation contains three ideas:

- The existans of an internal energy function (which comes from the fact that adiabatic work is path independent)
- The principle of conservation of energy
- The definition of heat as the energy needed to balance the energies in diathermic processes.

Concept of Heat

Heat is either internal energy or enthalpy in transit.

Heat is not a function of thermodinamic coordinates, it generally depends on the path taken. Therfore, we have an inexact differential $d\bar{Q}$

Within an adiabatic boundary, heat is conserved.

Differential form of the first law

In an infinitesimal process we have:

$$dU = \bar{d}Q + \bar{d}W$$

It shows that the exact differential dU is a sum of two inexact differentials, which is kind of weird.

The first law for simple systems

Simple system	First law	U is a function of any two of
Hydrostatic system	$dU = \bar{d}Q - P dV$	P, V, T
Stretched wire	$dU = \bar{d}Q + \mathcal{F} dL$	\mathcal{F}, L, T
Surface	$dU = \bar{d}Q + \gamma dA$	γ, A, T
Electrochemical cell	$dU = \bar{d}Q + \mathcal{E} dZ$	\mathcal{E}, Z, T
Dielectric slab	$dU = \bar{d}Q + E d\rho$	E, ρ, T
Paramagnetic rod	$dU = \bar{d}Q + \mu_0 \mathcal{H} dM$	$\mu_0 \mathcal{H}, M, T$

Heat Capacity

The heat capacity of a system at temperature T_i is:

$$C = \frac{\bar{d}Q}{dT}$$

Evaluated at T_i .

Here, the amount of mass may change the value of the capacity, so to transform it into a intensive value, we divide by mass.

The **specific heat capacity** is the heat capacity divided by mass $c_m = \frac{C}{m}$.

Molar heat capacity: We divide by the number of moles:

$$c = \frac{C}{n} = \frac{1}{n} \frac{\bar{d}Q}{dT}$$

Heat capacity at constant pressure

$$C_p = \left(\frac{\bar{d}Q}{dT} \right)_P$$

Heat capacity at constant volume

$$C_v = \left(\frac{\bar{d}Q}{dT} \right)_V$$

Equations for Hydrostatic system

The mathematical formulation of the first law for a hydrostatic system is

$$dQ = dU + P dV,$$

where U is a function of any two of P , V , and T . Choosing T and V , we have

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$$

Therefore, the first law becomes

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV. \quad (4.11)$$

Dividing by dT , we get

$$\frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \frac{dV}{dT}. \quad (4.12)$$

This equation is true for *any* process involving any temperature change dT and any volume change dV .

So:

$$\frac{\bar{d}Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_V + P\right] \frac{dV}{dT}$$

We can calculate it for different processes:

- If V is constant: $dV = 0$, and:

$$\left(\frac{\bar{d}Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

The term of the left is by definition C_V , so:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

- **If P is constant**

Then the equation becomes:

$$\left(\frac{\bar{d}Q}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_P$$

Then, by definition, we have:

$$C_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] V\beta$$

Then:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_V}{V\beta} - P$$

So we can obtain $\left.\frac{\partial U}{\partial V}\right|_T$ from quantities C_p, C_V, β that we can measure.

Quasi-static Flow of heat; heat reservoir

During a quasi-static process, the difference between the temperature of a system and that of its surroundings is infinitesimal. As a result, the temperature changes infinitesimally slowly.

Heat reservoir: Is a body of such large mass that it may absorb or reject an unlimited quantity of heat without experiencing an appreciable change in temperature or in any other thermodynamic coordinate.

Therefore, any quasi-static process of a system in contact with a heat reservoir is bound to be isothermal.

To describe a quasi-static flow of heat involving a change in temeprature, we conceive of the system as placed in contact with a series of reservoirs.

Thus, we imagine a series of reservoirs ranging in temperature from T_i to T_f , placed successively in contact with a system at constant pressure in such a way that the difference in temperature between the system and the reservoir with which it is in contact is infinitesimal. The flow of heat will be quasi-static and can be calculated as follows:

$$C_p = \left(\frac{\bar{d}Q}{dT} \right)_P$$

And therefore, for a quasi-static isobaric process, a path of integration is prescribed, so:

$$Q_p = \int_{T_i}^{T_f} C_p dT$$

If C_p is practically constant, then $Q_p = C_p(T_f - T_i)$.

For a quasi-static isochoric process, another path of integration is prescribed so:

$$Q_V = \int_{T_i}^{T_f} C_V dT$$

Heat conduction

heat conduction is the transport of energy between neighbor parts of a body.

A piece of material is made in the form of a slab of thickness Δx and area A . One face is at temperatur T and the other at $T + \Delta T$ Heat Q flows perpendicular to the faces for a time t . The experimental results show that:

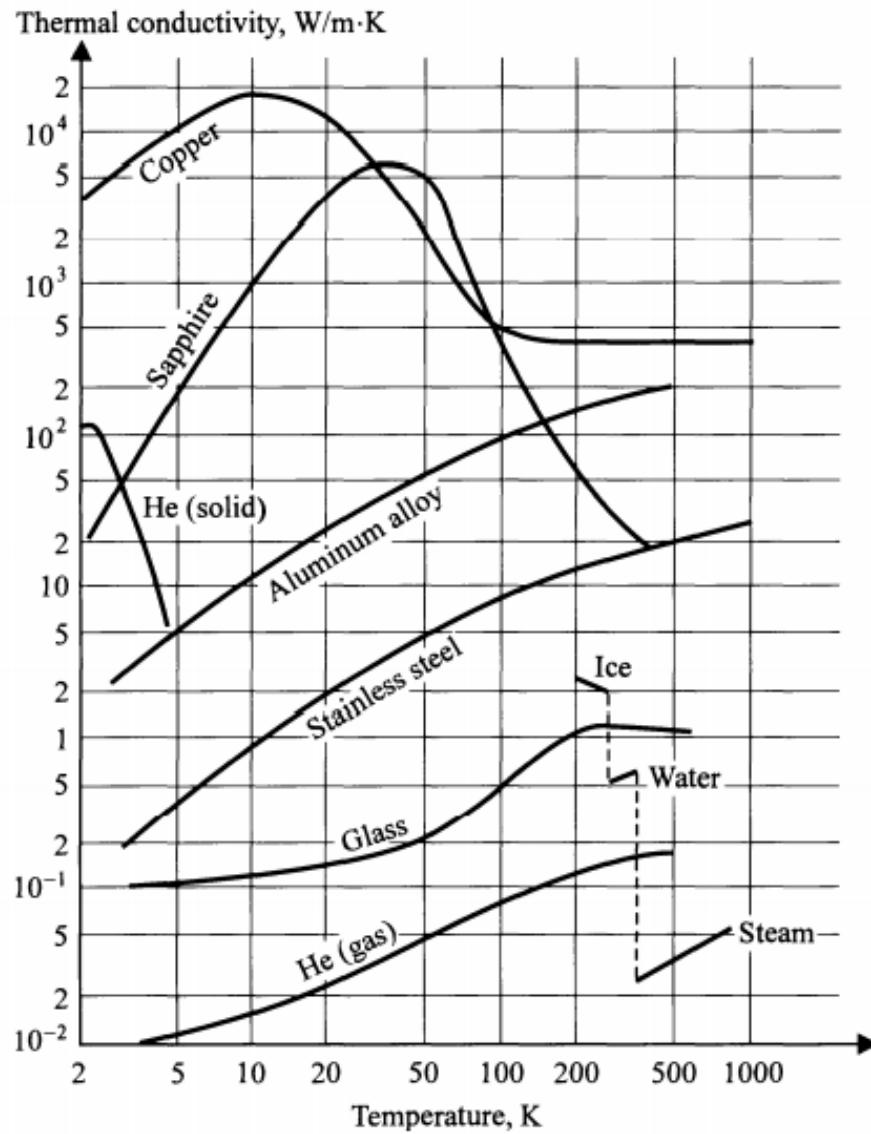
$$\frac{Q}{t} \propto A \frac{\Delta T}{\Delta x}$$

K is called the **thermal conductivity**. A substance with a large thermal conductivity is a conductor and a small thermal conductivity is called an insulator.

To measure it, we can use:

$$K = \frac{L}{A(T_1 - T_2)} \frac{\bar{d}Q}{dt}$$

Thermal conductivity depends on temperature.



7

ves showing temperature dependence of thermal conductivity.

Heat Convection

$$\frac{\bar{Q}}{dt} = hA\Delta T$$

Black Body

A substance may be stimulated to emit electromagnetic radiation in a number of ways:

-
- Electrons oscillating
 - Thermal radiation emitted by a hot solid or liquid
 - A gas experiencing an electric discharge may emit radiation
 - A radioactive substance.

We shall concentrate only on thermal radiation.

When thermal radiation is dispersed by a prism, one obtains a continuous spectrum of light. We are interested in the energy distribution in this spectrum.

The loss of energy due to emission may be compensated by immersing the body in radiation such that the entering radiation is equal to the emitting.

absorptivity: The fraction of the total incident radiant power that is absorbed.

In equilibrium for a black body, the processes of absorption and emission of radiant power are equal and opposite.

Total emissivity ϵ : Is the fraction of power provided to a real body that is emitted through the material surface as thermal radiation.

Radiant exitance R : Total radiant power emitted per unit area.

Total emissivity ϵ : Fraction of the total radiant power that is emitted as thermal radiation.

The **blackbody** is an ideal substance capable of absorbing all energy and emitting all energy provided to it in the form of thermal radiation.

$$\epsilon_{bb} = 1$$

bb = black body.

A very good experimental approximation to a blackbody is provided by a cavity enclosed by high temperature opaque walls. The interior walls maintained at uniform temperature, permit thermal radiation to pass through a small hole.

The radiation emitted by the interior walls is similarly absorbed or diffusely reflected a large number of times, so that the cavity is filled with isotropic blackbody radiation.

irradiance: radiant power per unit area incident upon a surface within the cavity we denote it by H:

$$\text{Radiant power absorbed per unit area} = \epsilon_{bb}H = H$$

$$\text{Radiant power emitted per unit area} = R_{bb}$$

For a black body, since the temperature is constant, then:

$$H = R_{bb}$$

or the irradiance within a cavity whose walls are at temperature T is equal to the radiant exitance of a blackbody at the same temperature. For this reason, the radiation enclosed within a cavity is called blackbody radiation.

Since H is independent of the materials of which the interior walls are composed, it follows that the radiant exitance of a blackbody is a function of the temperature only.

Kirchhoffs Law

The radiant exitance of a non blackbody depends as much on the nature of the surface as on the temperature. Suppose that a non blackbody at the temperature T, with radiant exitance R and emissivity ϵ , is introduced into a cavity whose interior walls are at the same temperature and where the irradiance is H. Then:

$$\begin{aligned} \text{Radiant power absorbed per unit area} &= \epsilon H \\ \text{Radiant power emitted per unit area} &= R \end{aligned}$$

Since the non-blackbody is in equilibrium,

$$\begin{aligned} R &= \epsilon H \\ &= \epsilon R_{bb} \end{aligned}$$

Because of $H = R_{bb}$ for a bb.

So the radiant exitance of any body at any temperature is equal to a fraction of the radiant exitance of a blackbody at that temperature, this fraction being the emissivity at the temperature.

This equation is Kirchhoff's law

Imagine a cavity whose interior walls are at T_W . And a non blackbody is placed at temperature T inside it.

Let H be the irradiance within the cavity and R the radiant exitance and ϵ the emissivity of the body. Then:

$$\begin{aligned} \text{Radiant power absorbed per unit area: } &\epsilon H \\ \text{Radiant power emitted per unit area} &= R \end{aligned}$$

But now these two powers are not equal. The difference between them is the heat transferred by radiation per second per unit area. If dQ is the heat transferred in time dt to the non bb of area A, then:

$$\frac{dQ}{dt} = A(\epsilon H - R)$$

By kirchhoff's law, as they are functions of T, we have:

$$R = \epsilon(T)R_{bb}(T)$$
$$H = R_{bb}(T_W)$$

Hence:

$$\frac{dQ}{dt} = A\epsilon(T)[R_{bb}(T_W) - R_{bb}(T)]$$

Stefan Boltzmann law

For a black body:

$$R_{bb}(T) = \sigma T^4$$

as can be proven in quantum.

Where $\sigma = 5.67051 \times 10^{-8} W/m^2 \cdot K^4$

Then, as we found from the last subsection:

$$\frac{dQ}{dt} = A\epsilon\sigma(T_W^4 - T^4)$$

First Law (B)

Joule did some experiments to measure the amount of work needed to give water a rise in temperature of 1C (a calorie)

He realized that the amount of work is the same for any type of work done (paddles, friction, resistance)

Adiabatic wall: We can only change the state of the system by doing work (no heat).

Inspiration for 1st law

- **Joule observation:** If a system goes from a state i) to a state f) adiabatically with different types of work, the amount of work needed is always the same.
This type of work is called **adiabatic work**

Therefore, there exists a state variable such that $\Delta U = U_f - U_i = W_{ad}$

So its value only depends on the endpoints (if W is adiabatic). This is **internal energy**.

- Now, we take the system from i) to f) in an arbitrary way.
Experimentally, we find that work now is not the same as before $W \neq W_{ad}$.
Therefore, to be sure that U is still a state function, we **define heat** as:

$$Q = \Delta U - W$$

- Therefore, we get the **first law for closed systems**

$$\Delta U = Q + W$$

Work is in some sense an ordered transition of energy, while heat is more of a disordered one.

Reversible Process: A process is reversible when its evolution direction can be reverted by doing infinitesimal changes in the state variables.

It means that we can reverse by only doing infinitesimal changes.

A reversible process must be **quasistatic**

For example, suppose we have a gas in a piston.

We apply an external force to it, if F_{ext} is differentially higher than the pressure, we can compress the gas.

However, if we augment the pressure by only dP , the gas now exerts a bigger force than F_{ext} and expands, we have changed the direction of the process by only changing differentially the variables.

We see that if there was some friction in the piston, augmenting P by dP wouldn't reverse the compression, because we now need to overcome the finite friction force.

We see that reversible processes allow for the possibility of reversing the system and leaving all the universe unchanged. Irreversible processes necessarily change the universe if we bring them back to their initial state.

Heat Capacities

They are defined as:

$$C_x := \left(\frac{\partial Q}{\partial T} \right)_x$$

In some processes, Q coincides with a state function which makes this definition better:

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_T = \left(\frac{\partial U}{\partial T} \right)_V$$

And

$$C_p := \left(\frac{\partial Q}{\partial T} \right)_P \left(\frac{\partial H}{\partial T} \right)_P$$

Where $H = U + PV$

We can also find the following formula:

$$C_p - C_V = \frac{\beta^2 VT}{k_T}$$

Where $\beta = \frac{1}{V} \frac{\partial V}{\partial T}$ and $k = -\frac{1}{V} \frac{\partial V}{\partial P}$
in the specific case of an **ideal gas**, $C_p - C_V = nR$

Two Experiments

If we know $C_V = \frac{\partial U}{\partial T})_V$, we only need the derivative $\frac{\partial U}{\partial V})_T$ to be able to determine U as a function of P, V, T (or whichever two we choose).

Similarly, if we know $C_P = \frac{\partial H}{\partial V})_P$, we have to find $\frac{\partial H}{\partial P})_T$ to determine H

Joule Free expansion

We have two connected recipients (adiabatically insulated) connected by a valve.

One of the recipients is full of a gas and the other one is empty.

The experiment consists in letting the valve open and the gas expand.

In this experiment, we must have that $U = cte$ (because it is adiabatically insulated and the gas is expanding against nothing, so it is not doing work).

With this experiment we might be able to measure $\left(\frac{\partial T}{\partial U}\right)_V : \mu_J$

Therefore, using the cyclical identity, we can find what we really want:

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U \left(\frac{\partial T}{\partial U}\right)_V &= -1 \\ \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T \frac{1}{\mu_J} \frac{1}{C_V} &= -1 \end{aligned}$$

So we conclude:

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = -\mu_J C_V}$$

Where μ_J can be measured in this experiment.

Then, we have enough information to determine $U(V, T)$

There is an alternative to determine $\partial U / \partial V)_T$ using the ETE (derived way later)

$$\mu_J = (\partial U / \partial V)_T = -P + \frac{T\beta}{k} = -P + T\partial p / \partial T)_V$$

For an **ideal gas**, we get $\mu_J = 0$, so U doesn't depend on V (which makes sense).

Therefore, we get $dU = (\partial U / \partial T)_V dT + (\partial U / \partial V)_T dV = C_V dT$

Therefore, $U = \int C_V dT$

Joule Thomson Experiment

We have a gas that enters a tube that has in the middle a porous sponge of some type.

We let gas enter the tube from one side and it leaves from the other, we look for a stationary state in which gas enters the tube and goes out the other side in a stationary way.

There is a pressure P_1 and temperature T_1 in the left and P_2, T_2 in the right. This process is of constant enthalpy, so we can calculate:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H$$

Using this and the cyclic relation, we can find that:

$$\left(\frac{\partial H}{\partial p} \right)_T = -\mu_{JT} C_p$$

$\mu_{JT} = 0$ for an ideal gas.

For a general gas, there is a region where $\mu_{JT} > 0$, which means that a diminishing of pressure diminishes temperature (at constant enthalpy) and this can be used for cooling gases. There is also a region where $\mu_{JT} < 0$ obviously.

It is important to note that both processes are irreversible. The first one is easy to see its irreversibility and in the second one it is due to the finite difference of pressures, that doesn't allow a change in direction due to only an infinitesimal change of variables.

Ideal Gas

Equation of State of a Gas

Experiments show that for a gas, we can find the following relation:

$$Pv = A(1 + BP + CP^2 + \dots)$$

Where $v = V/n$ (n is the number of mol).

It can be found that for low pressure, we have $\lim(PV) = nRT$, so we have:

$$\frac{Pv}{RT} = 1 + BP + CP^2 + DP^3 + \dots$$

Internal energy of ideal gas

Imagine a thermally insulated vessel with rigid walls, divided in two compartments by a partition. There is gas in one compartment and vacuum in the other. If the partition is removed, the gas will undergo a **free expansion**.

From the first law, since Q, W are zero in this expansion, the internal energy remains unchanged during a free expansion.

We are interested in measuring if there is a change of temperature in a free expansion, that is, the coefficient $(\partial T / \partial V)_U$.

In general, the internal energy of a gas is a function of P, V, T . The differential of U as a function of T, V is:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

If there was no temperature change ($dT = 0$) during the free expansion ($dU = 0$), then it follows that:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

So U does not depend on V .

On the other hand, if we consider U to be a function of T, P , we have:

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

If there is no temperature change ($dT = 0$) in a free expansion ($dU = 0$), then it follows that:

$$\left(\frac{\partial U}{\partial P}\right)_T = 0$$

So U does not depend on P .

Then it is evident that if no temperature change takes place in a free expansion, then U is independent of V, P and therefore U is a **function** of T only.

Thus, to determine if U is a function of temperature, one must perform an experiment where the temperature is constant and measure whether $(\partial U / \partial V)_T$ or $(\partial U / \partial P)_T$ is zero.

This can be done in experiments.

Experiments led to the conclusion that U is a function of T, P .

But for an ideal gas, we propose $\partial U / \partial P)_T = 0$

Ideal Gas

An ideal gas satisfies by definition:

$$PV = nRT$$

$$\left(\frac{\partial U}{\partial P} \right)_T = 0$$

The requirement $(\partial U / \partial P)_T = 0$ may be written in other ways. Thus:

$$\left(\frac{\partial U}{\partial V} \right)_T = \left(\frac{\partial U}{\partial P} \right)_T \left(\frac{\partial P}{\partial V} \right)_T$$

And since $(\partial P / \partial V)_T = -nRT/V^2 = -P/V$, and is not zero, but $(\partial U / \partial P)_T$, then:

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

Then finally we conclude that:

$$U = f(T) \quad \text{only}$$

For an infinitesimal quasi-static process of a hydrostatic system, the first law is:

$$\bar{d}Q = dU + PdV$$

and heat capacity at constant volume is:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

In an ideal gas U is a function of T only. Therefore, the partial derivative is the same as the full complete:

$$C_V = \frac{dU}{dT}$$

And then:

$$\bar{d}Q = C_V dT + P dV \quad 5.8$$

Now, all equilibrium states are represented by $PV = nRT$. And, for an infinitesimal quasi-static process:

$$P dV + V dP = nR dT$$

Substituting this into 5.8, we get:

$$\begin{aligned} \bar{d}Q &= (C_V + nR) dT - V dP \\ \Rightarrow \frac{\bar{d}Q}{dT} &= C_V + nR - V \frac{dP}{dT} \end{aligned}$$

At constant pressure, the left side becomes C_p and $dP = 0$, therefore:

$$C_p = C_V + nR \quad \text{ideal gas}$$

So the heat capacity at constant pressure is always larger than the heat capacity at constant volume.

Since U is a function of T only for an ideal gas, it follows that:

$$\begin{aligned} C_V &= \frac{dU}{dT} = \text{function of only T} \\ C_P &= C_V + nR = \text{function of T only} \end{aligned}$$

One more useful equation can be obtained from $\bar{d}Q = (C_V + nR) dT - V dP$, we find:

$$\bar{d}Q = C_P dT - V dP$$

Experimental determination of heat capacities

To measure C_V , the gas is contained in a thin walled steel flask with a heating wire around it. By maintaining an electric current, an equivalent amount of heat is supplied to the gas. The same method is used to measure C_P , but using a piston to maintain constant pressure. The results of such measurements for ideal gases can be stated in terms of molar heat capacities, $c = C/n$:

- All ideal gases:
 - c_V is a function of T only
 - c_P is a function of T only and greater than c_V
 - $c_P - c_V = R$
 - $c_P/c_V = \gamma$ is a function of T only and is greater than 1.
- monoatomic gas:

-
- c_V is constant over a wide temperature range and nearly equal to $\frac{3}{2}R$
 - c_P is constant over a wide temperature range and is very nearly equal to $\frac{5}{2}R$
 - The ratio $c_P/c_V = \gamma$ is constant over a wide temperature range and is nearly equal to $5/3$

- **Diatom gas**

- c_V is mostly constant at ordinary temp, and equal to $\frac{5}{2}R$ and increases when T is raised
- c_P is mostly constant at ordinary temp, and equal to $\frac{7}{2}R$ and increases when T is raised
-
- $c_P/c_V = \gamma$ is mostly constant at ordinary temp, and equal to $\frac{7}{5}$ and decreases when T is raised

This are experimental results. Or maybe we can get it from statistical mechanics.
In general, c_V is equal to $K/2R$ where K is the number of freedoms of the molecule. And $c_P = c_V + R$

Quasi-static adiabatic

When a gas undergoes a quasi-static adiabatic process:

$$\begin{aligned}\bar{d}Q &= C_V dT + P dV \\ \bar{d}Q &= C_P dT - V dP\end{aligned}$$

In an adiabatic process, $\bar{d}Q = 0$, so:

$$\begin{aligned}V dP &= C_P dT \\ P dV &= -C_V dT\end{aligned}$$

Dividing the first by the second:

$$\begin{aligned}\frac{dP}{P} &= -\frac{C_P}{C_V} \frac{dT}{V} \\ \Rightarrow \frac{dP}{P} &= -\gamma \frac{dT}{V}\end{aligned}$$

For an ideal gas at certain temperatures, γ is constant, so $\ln P = \gamma \ln V + \ln cte$
So:

$$PV^\gamma = cte$$

The slope of any adiabatic curve is:

$$\left(\frac{\partial P}{\partial V}\right)_S = -\gamma \frac{P}{V}$$

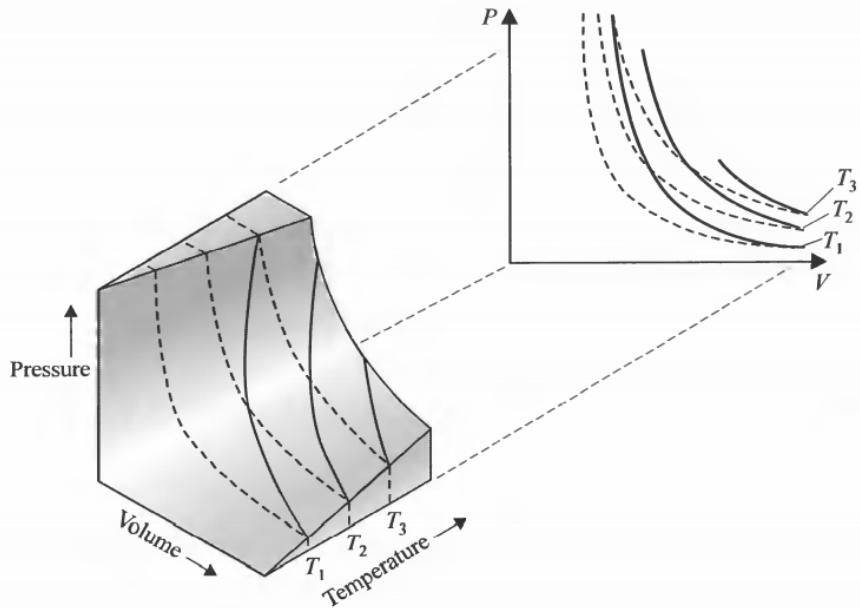


FIGURE 5-5

The PVT surface for the ideal gas and its projection onto a PV diagram. (Isotherms are shown as dashed curves, and adiabatics as full curves.)

quasi-static isothermal processes are represented by a family of equilateral hiperbolas obtained by assigning different values of T to $PV = nRT$. Since:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}$$

Kinetic Theory of The ideal Gas

Limited to monoatomic gases, we make several simplifying assumptions about the behavior of atoms in an ideal gas:

- Any small sample of gas consists of an enormous number of particles N . All atoms are identical and inert.
- The atoms of an ideal gas resemble small hard spheres that are in perpetual random motion.
- The atoms of an ideal gas are assumed to exert no forces or attraction or repulsion, they only collide
- When a particle collides with the wall, if it had speed w , the parallel speed remains constant, and the perpendicular changes sign.
- The atoms are distributed uniformly

-
- Not all atoms have the same speed.

Since the velocity vectors have no preferred direction, consider an arbitrary vector \vec{w} .

It can be found that for **monoatomic gasses**:

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

Consider an arbitrary direction of velocity vector \vec{w} , we are interested in finding the fraction of atoms with velocities in the neighborhood of \vec{w} . That is, velocities between w and $w + dw$ and directions within the solid angle $d\Omega = \sin \theta d\theta d\phi$ around \vec{w} .

Let dN_w be the number of atoms with speeds between w and $w + dw$, then the fraction of these atoms whose directions lie in the solid angle $d\Omega$ is $d\Omega/4\pi$.

So that the number of atoms within the speed range dw in the range $d\theta$ and $d\phi$ is given by:

$$d^3N_{w,\theta,\phi} = dN_w \frac{d\Omega}{4\pi}$$

An equation expressing the fact that atomic velocities have no preferred direction.

Now consider this group of atoms approaching a small area dA of the wall in a short interval of time dt such that all the $d^3N_{w,\theta,\phi}$ atoms will collide with dA . The volume of the cylinder of atoms is dV :

$$dV = wdt \cos \theta dA$$

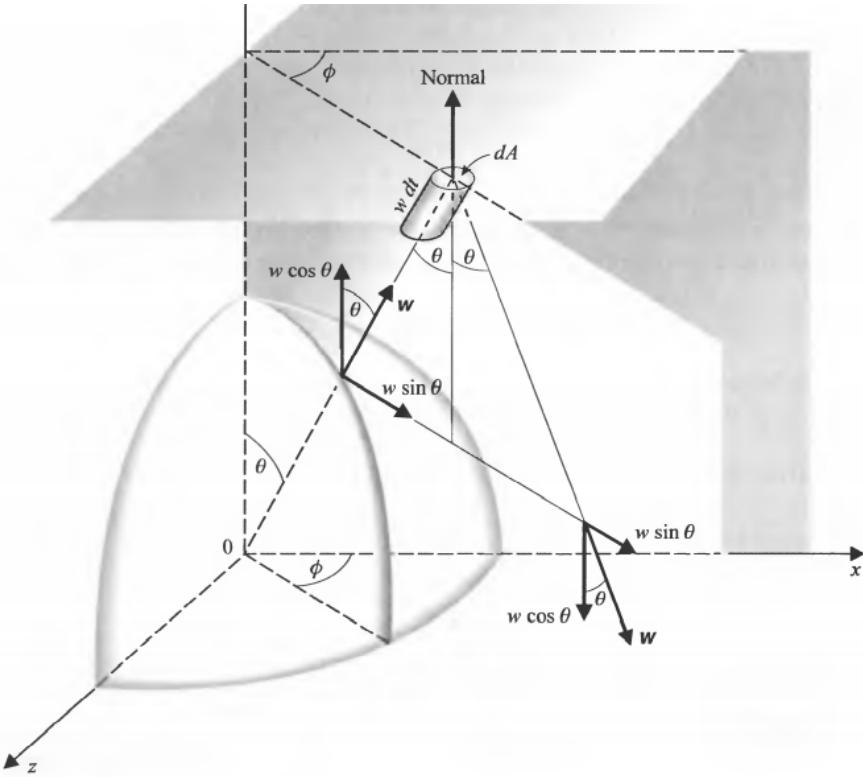


FIGURE 5-10

All the atoms in the cylinder of length $w dt$ strike the area dA at the angle θ to the normal. The perpendicular component of velocity $w \cos \theta$ is reversed, but the parallel component $w \sin \theta$ is unchanged.

If V is the volume of the container, only the fraction dV/V of the atoms will be contained in the cylinder. Therefore, the number of atoms of speed w and within the range $d\Omega$ impacting dA in time dt is expressed as:

$$d^3 N_{w,\theta,\phi} \frac{dV}{V}$$

An atomic collision is perfectly elastic. It follows that an atom moving with speed w in a direction making an angle θ to the normal will undergo a change only in its perpendicular component of velocity. The total change in momentum per collision is:

$$\text{Change of momentum per collision: } = -2mw \cos \theta$$

So the total change in momentum due to this cylinder colliding is:

$$\begin{aligned} \text{Tot chang in mom} &= (\text{No. atoms of speed } w \text{ in } d\Omega) (\text{Fraction of these atoms striking } dA \text{ in time } dT) (\text{change in mom per collision}) \\ &= \left(dN_w \frac{d\Omega}{4\pi} \right) \left(\frac{dV}{V} \right) (-2mw \cos \theta) \end{aligned}$$

$$\begin{aligned} &= \left(\frac{dN_w}{4\pi} \sin \theta d\theta d\phi \right) \left(\frac{1}{V} w dt \cos \theta dA \right) (-2mw \cos \theta) \end{aligned}$$

The change in momentum per unit time and per unit area due to collisions from all directions is the pressure dP_w exerted by the wall on the dN_w gas atoms. Reversing sign of the momentum change, we get the pressure dP_w exerted by the dN_w atoms on the wall (all directions):

$$dP_w = mw^2 \frac{dN_w}{V} \left(\frac{1}{2\pi} \int_0^{2\pi} d\phi \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta \right) = \frac{mw^2}{3V} dN_w$$

Then, the total pressure pressure due to atoms of all speeds is:

$$PV = \frac{1}{3}m \int_0^\infty w^2 dN_w$$

The average of the square of the atomic speeds $\langle w^2 \rangle$ is defined to be:

$$\langle w^2 \rangle = \frac{1}{N} \int_0^\infty w^2 dN_w$$

So we have:

$$PV = \frac{Nm}{3} \langle w^2 \rangle$$

Using the ideal gas law, this leads to:

$$PV = \frac{Nm}{3} \langle w^2 \rangle$$

So that T is related to the average kinetic energy of atoms:

$$T = \frac{2N}{3nR} \left(\frac{1}{2}m \langle w^2 \rangle \right)$$

Temperature is proportional to the average kinetic energy of the atoms in the **ideal gas**.

In kinetic theory, it is assumed that atoms are not interacting, so there is no potential energy. Therefore, the only form of energy is translational kinetic energy (the don't even possess rotational energy, we suppose they are monoatomic). Then:

$$U = \sum_j \frac{1}{2}mw_j^2 = N \left(\frac{1}{2}m \langle w^2 \rangle \right) = \frac{3}{2}nRT$$

So the internal energy is directly proportional to the temperature, which is consistent with experiment.

As a result, we may find that:

$$C_V = \frac{\partial U}{\partial T} = \frac{3}{2}nR$$

And $C_P = C_V + nR = \frac{5}{2}nR$

If we define $k = \frac{R}{N_A}$ (N_A is avogadro's number), then the equation can be written as:

$$U = \frac{3}{2} \frac{N}{N_A} RT = \frac{3}{2} N k T$$

So we can rewrite the average kinetic energy per particle as:

$$\frac{1}{2} m \langle w^2 \rangle = \frac{3}{2} k T$$

Summary

- **Important Definitions:**
 - **System:** What we will study, it is inside the boundaries and is surrounded by the **surroundings**.
 - **Types of Walls:**
 - * **Adiabtic:** A wall that seals off the system and doesn't let in any heat. A system that can only be changed by moving the boundary or creating an external field.
 - **Diathermic:** A wall that allows exchange of heat, that is, we can change its state without moving the boundaries.
 - **State:** A system can be characterized by a couple of variables. In the simplest case, by a generalized force X and a generalized displacement Y .
 - **Equilibrium State:** It's a state of a system in which the coordinates X, Y have definite values that remain constant as long as the external conditions are unchanged.
If two systems are separated by a diathermic wall, the values of X_1, Y_1, X_2, Y_2 will change until an equilibrium of the combined system is attained.
- **Zeroth Law:** If A is at equilibrium with C and B is at equilibrium with C , then A, B are in equilibrium.
This means that the relation 'is at equilibrium with' is a transitive (and reflexive and symmetric) relation.
Isotherm: The curve containing all states $X - Y$ that are at equilibrium with each other.
Temperature: The temperature of a system is a property that determines whether the system is at equilibrium with other systems. Two systems are at equilibrium if and only if they are at the same temperature. Temperature is a way of determining if two systems are at equilibrium.
Thermometer: An easy system in which we can graph all the isotherms and assign a specific value to each one.
- **Equation of State:** Because temperature T is a function of the variables X, Y , for a given state at equilibrium there is an equation $f(X, Y, T) = 0$ that relates the coordinates.

Mathematical Theorems:

$$\left(\frac{\partial X}{\partial Y}\right)_Z = \frac{1}{(\partial Y/\partial X)_Z}$$

$$\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \left(\frac{\partial Z}{\partial X}\right)_Y = -1$$

For example, for a **Hydrostatic system**, we have the variables V, P, T and the differential relation:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

And we can define the **Volume expansivity** $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$

And the **isothermal compressibility** $k = \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$

- **Work:** Work is done when a system undergoes displacement under the action of a force. It can be done by the system if the force is internal (The system loses energy) or on the system if the force is done by the surroundings (The system wins energy)
Quasistatic A process that happens infinitesimally slowly, so it is always at equilibrium.

For a hydrostatic system, work is $d'W = -PdV$, so:

$$W_{if} = - \int_{V_i}^{V_f} PdV$$

- **First Law:**

Adiabatic Work: Adiabatic work is the work done on a system while isolated by an adiabatic wall.

The **first law of thermodynamics** says that *If a closed system changes state by adiabatic means only, the work done is the same for all adiabatic paths connecting the two states.*

Therefore, we can define a potential:

$$W_{if}(\text{adiabatic}) = U_f - U_i$$

And the potential $U(T, P, V)$ is the **internal energy** and only depends on the state of the system. Positive work increases the internal energy.

Heat: When a system undergoes diathermic work, then the work done is not equal to $U_2 - U_1$, to account of the energy needed to balance the equation, we define heat as the energy needed:

$$U_f - U_i = Q + W$$

Differential Form of the First Law:

$$dU = d'Q + d'W$$

Heat Capacity: We define at temperature T_i it as:

$$C = \frac{d'Q}{dT}$$

evaluated at T_i . We can take the heat capacity at constant Pressure C_P or at constant volume C_V or make it molar like $c_P = C_P/n$, $c_V = C_V/n$

Heat Reservoir: A body of such large mass that it may absorb or reject an unlimited quantity of heat without a change in any thermodynamic coordinate.

- **Ideal Gas:**

The equation of state is:

$$\begin{aligned} PV &= nRT \\ \left(\frac{\partial U}{\partial P}\right)_T &= 0 \end{aligned}$$

The second condition is an idealization for the gas, and it implies that

$$U = U(T)$$

Kinetic Theory of Ideal Gas:

We suppose that the gas consists of an enormous amount of particles N that resemble small spheres without attraction or repulsion and distributed uniformly, with elastic collisions with the walls.

Then, it can be found that:

$$U(T) = \frac{f}{2}nRT$$

Where f is the amount of freedoms of the particles.

The total change in momentum due to a small cylinder dV of atoms traveling in the angular direction $d\Omega$ and with speed in $[w, w + dw]$ is:

$$\begin{aligned} \text{Totchange in mom} &= (\text{No. Atoms of speed } w \text{ in } d\Omega)(\text{Fraction of these atoms striking } dA \text{ in time } dT) \\ &= \left(dN_w \frac{d\Omega}{4\pi}\right) \left(\frac{dV}{V}\right) (-2mw \cos \theta) \\ &= \left(\frac{dN_w}{4\pi} \sin \theta d\theta d\phi\right) \left(\frac{1}{V} w dt \cos \theta dA\right) (-2mw \cos \theta) \end{aligned}$$

Where dN_w is the number of atoms with speeds between $w + dw$ and directed in the solid angle $d\Omega$.

dV is the volume of atoms in the cylinder $dV = wdt \cos \theta dA$

Then the momentum exerted by all the atoms can be found by integrating this over $\phi[0, 2\pi]$ and $\theta[0, \pi]$ and we find: $PV = \frac{1}{3}m \int_0^\infty w^2 dN_w$

So, if we define $\langle w^2 \rangle = \frac{1}{N} \int_0^\infty w^2 dN_w$, we get that: $PV = \frac{Nm}{3} \langle w^2 \rangle$.

Or, using the ideal gas law:

$$T = \frac{2N}{3nR} \left(\frac{1}{2}m \langle w^2 \rangle \right)$$

In kinetic theory we assume there is no potential between molecules, so U is the sum of kinetic energy:

$$U = \sum \frac{1}{2}mw_j^2 = N \left(\frac{1}{2}m \langle w^2 \rangle \right) = \frac{3}{2}nRT$$

or, in general:

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

- **Volume Heat Capacity:** The first law for a ideal gas says: $d'Q = dU + PdV$. But at constant volume, $d'Q = dU$ and therefore (and because $U = U(T)$), then $\left(\frac{dQ}{dT} \right)_V = \left(\frac{dU}{dT} \right)_V$. Therefore:

$$C_V = \frac{dU}{dT} = \frac{f}{2}nR$$

- **Heat Capacity constant pressure:** On the other hand, $PV = nRT$ so $PdV + VdP = nRdT$. And we can rewrite the first equation as $d'Q = (C_V + nR)dT - VdP \Rightarrow \frac{d'Q}{dT} = C_V + nR - V \frac{dP}{dT}$. At constant pressure, the left side is C_P and $dP = 0$, therefore:

$$C_p = C_V + nR \quad \text{ideal gas}$$

We also define $\gamma := C_p/C_V$.

Therefore:

$$\begin{aligned} -c_V &= \frac{f}{2}R \\ -c_P &= R + C_V = \frac{2+f}{2}R \\ -\gamma &= c_P/c_V = \frac{2+f}{f} \end{aligned}$$

This is only for ideal gases and in only a range of temperatures and pressures.

- **Quasi-Static Adiabatic:**

For an adiabatic process, $d'Q = C_V dY + PdV$ and $d'Q = C_p dT - VdP$.

But in adiabatic process, $d'Q = 0$ and therefore $VdP = C_p dT$ and $PdV = -C_V dT$.

Dividing the equations, we get $\frac{dP}{P} = -\gamma \frac{dV}{V}$. Therefore:

$$PV^\gamma = cte$$

- **Work and Heat in Ideal Gas Processes**

- **Isothermal ($T = T_0$):**

Work: The work is $W = - \int_{V_i}^{V_f} PdV = -nRT \log \frac{V_f}{V_i}$

Heat: Because $U = 0$, then $Q = -W$

Internal Energy: $U = 0$ (because it depends only in T)

- **Isobaric ($P = P_0$):**

Work: The work is $-P\Delta V$

Heat: $Q = nc_p\Delta T$

Internal Energy: $U = nc_V\Delta T$

- **Isocoric ($V = V_0$)**

Work: $W = 0$

Heat: $Q = nc_V\Delta T$

Internal Energy: $U = nc_V\Delta T$

- **Adiabatic ($PV^\gamma = k$):**

Work: $W = \frac{P_f V_f - P_i V_i}{\gamma - 1}$

Heat: $Q = 0$

Internal Energy: $U = nc_V\Delta T$

Not Ideal Gas

Compressibility Factor

We define:

$$Z = \frac{pV}{nRT} = \frac{P}{P_{id}}$$

Where P_{id} would be the pressure of an ideal gas if it had temperature T at volume V .
For an ideal gas, it is 1.

If $Z > 1$, pressure of the gas is greater than expected, so there is some kind of 'repulsion' ,
if $Z < 1$, then there is some kind of attraction.

Z is a function of P, T in general.

At low pressures, $Z \approx 1$ (the gas is nearly ideal), at medium pressure, generally $Z < 1$ and
at high pressures, $Z > 1$.

Also, at high temperatures, $Z \approx 1$

Virial series

We may write:

$$\begin{aligned} pv &= \bar{A}(T) + \bar{B}(T)p + \bar{C}(T)p^2 + \dots \\ pv &= A(T) \left[1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \dots \right] \end{aligned}$$

Where $v = \frac{V}{n}$ is the molar volume.

We see that when $p \rightarrow 0, \frac{1}{v} \rightarrow 0$, the expressions reduce to

$$pv = \bar{A}(T)$$

$$pv = A(T)$$

But in these limits, the behavior must be ideal, so $A = \bar{A} = nRT$

The other coefficients can be found experimentally or using some models.

Van Der Waals

This model has the following corrections:

- Molecule of the gas have a certain volume, so that $v = \frac{RT}{P} + b$ where b is the covolume or the molar volume of molecules, it is a fixed parameter for any given gas

- Attractive interaction between components of the gas.
What this does is diminish the gas pressure.

This gives the Wan der Waals equation:

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

Where a, b are different constants for every gas.

Then, we find:

$$Z = \frac{pv}{RT} = \frac{v}{v - b} - \frac{a}{RT} \frac{1}{v}$$

We see that the first part is > 1 so it is a repulsive part and the second is < 0 so it is attractive.

We can find the virial series to first order in p to be:

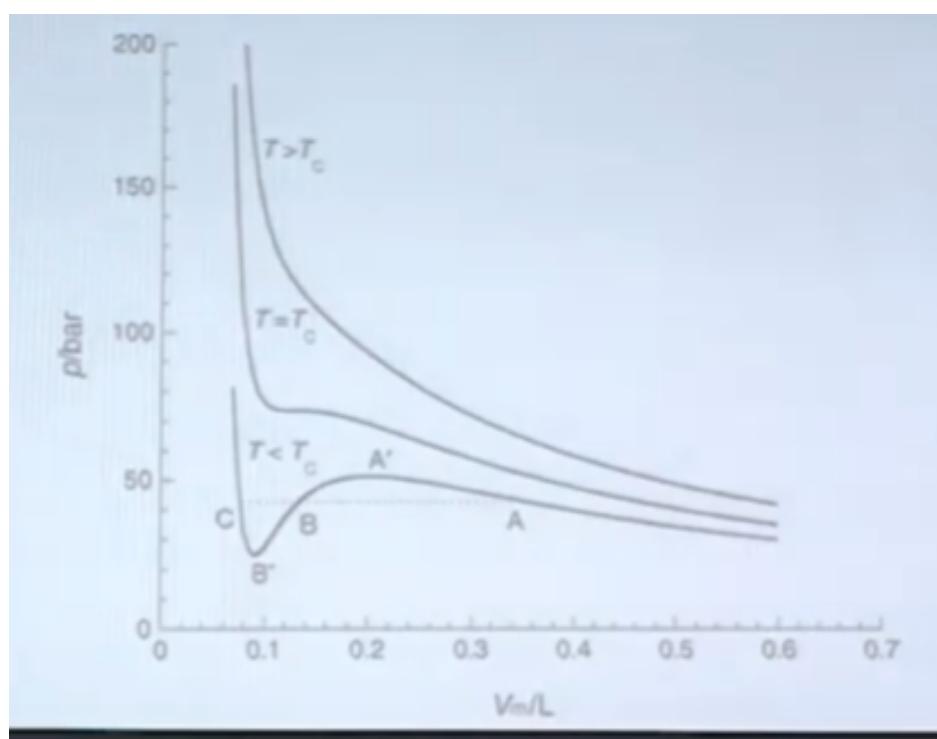
$$pv = RT + \left(b - \frac{a}{RT} \right) p$$

The expression for Z is then now given by:

$$Z = 1 + \left(b - \frac{a}{RT} \right) P$$

(to firs order in P).

Graphing the equation at different isotherms



We can see that for temperatures under a T_c critical temperature, the system has problems, since it has a positive $\partial V/\partial P)_T$ which makes no sense.

What happens is that the system between $A - C$ is unstable and as we now, these are the points were the system is a combination of water and gas.

The conditions of critical point are given by

$$\left(\frac{\partial P}{\partial v}\right)_T = 0 \quad , \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$$

And we can find it for the Van der Waals gas and get:

$$v_c = 3b \quad , \quad T_c = \frac{8a}{27Rb} \quad , \quad P_c = \frac{a}{27b^2}$$

And also $Z_c = \frac{p_c v_c}{RT_c} = \frac{3}{8}$

Second Law (B)

Let's analyze a couple of situations:

- **Free expansion:** We open a valve that connects a gas with an empty recipient, then intuitively the gas should expand.
- **Mixing:** We have two gasses separated by a wall and we remove the wall, so intuitively the gases mix.
- **Heat transfer:** We have a body at T_A and one at T_B with $T_B > T_A$. When we put them in contact, they will end up with the same temperature.
- **Reaction:** we have to substances A, B that can react to form C and we leave them in a closed recipient.

The first law doesn't say much about these systems. Energy is the same before and after the event in all systems.

So we need some kind of law that tells us the direction that the procedure will happen in. We can see that in general we go to a system with more distributed energy (more accessible microstates in the final system than in the initial one). But that is a statistic view, while the view we use is a thermodynamical one (macroscopic).

What we will use is called **entropy** and the second law says that **in an isolated system, entropy cannot decrease**.

Intro

Máquina: Is is an apparatus that permits transformation of heat into work (or vice versa) in a cyclical way (in order to repeat the cycle completely).

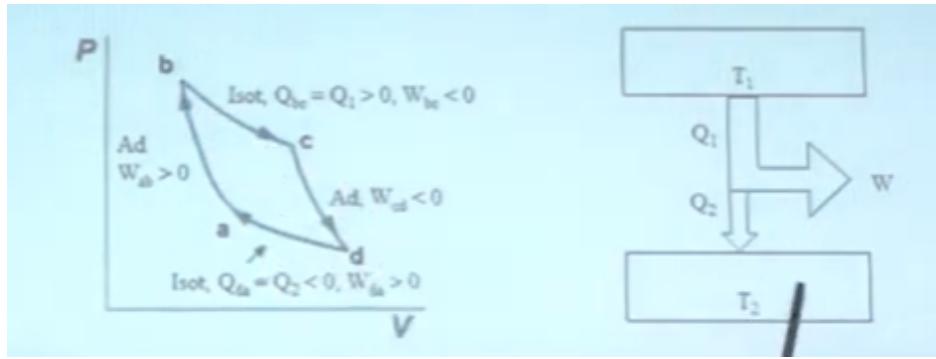
Machines work between different temperature sources.

The *simplest* machines work between 2 temperature sources (it is impossible to get work from only one).

Because the machine exchanges heat with only 2 sources, it must have two isothermal stages (when it exchanges heat with the sources) and two adiabatic stages (when it does something not in contact with a source, it cannot release or get heat from elsewhere).

This is the **Carnot Cycle** and is the simplest cycle we can device between two sources (or the only one).

In an ideal gas, it has the following diagram:



Efficiency

$$\eta = \frac{|W|}{|Q_1|}$$

Because energy has to be conserved at the end of the cycle (1st law and U is a state variable), then we must have that $|Q_1| = |W| + |Q_2|$, so:

$$\eta = \frac{|Q_1| - |Q_2|}{|Q_1|} = 1 - \frac{|Q_2|}{|Q_1|}$$

The machine can be operated in the opposite direction, to have a Carnot Freezer.

Second Law

- **Kelvin Planck:** It is impossible to construct a machine operating cyclically that doesn't produce any other effect other than realizing work by extracting heat for a unique temperature source.
- **Clausius:** It is impossible to build a machine operating cyclically that doesn't produce any effect other than extracting heat from a source and putting it in a source at higher temperature.

Theorem: KP == C

Carnot Theorem: No thermodynamic machine working between two temperature sources can have a better efficiency than a Carnot one working in those sources.

We can prove this showing that such a machine would contradict KP

Then, the best efficiency depends only on the two temperatures of the sources.

Corollary: All Carnot machines have the same efficiency no matter the material or procedure.

With that, we can define a **Thermodynamic temperature**:

$$\frac{T_2}{T_1} = \frac{|Q_2|}{|Q_1|}$$

And we take a reference $T_1 = T_{tp} = 273.15K$, so, we get:

$$T = 273.16K \frac{|Q|}{|Q_{tp}|}$$

So, to know the temperature of something, we have to construct a Carnot between that something and water at the triple point, then calculate the heat $|Q|$ and $|Q_{tr}|$ and we can calculate T .

A lucky fact is that this temperature is the same as the temperature defined in ideal gases.

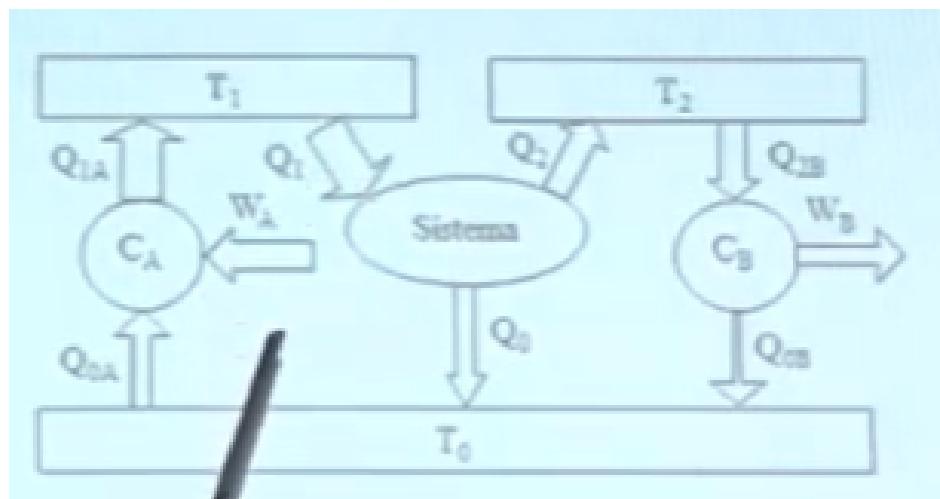
Clausius

Theorem: When a system exchanges heat quantities Q_i with a set of sources at T_i through a cyclical process (reversible or not), we get:

$$\sum_{i=1}^n \frac{Q_i}{T_i} \leq 0$$

Where Q_i includes the sign.

- **Proof (for 3 temperatures):** We have the following cyclical system (reversible or not or whatever) working in 3 temperatures



We build two Carnot Machines such that they compensate the heat given by T_1 and T_2 . In this case, one Carnot engine takes work W_A and gives heat Q_{1A} to T_1 to compensate, and machine B takes heat Q_{2B} from T_2 to compensate and creates work W_B .

We can think of this hole thing as a supermachine that produces work or gives work depending of W_B, W_A .

$$Q_1 + Q_{1A} = 0 \quad , \quad Q_2 + Q_{2B} = 0$$

$$Q_0 + Q_{0A} + Q_{0B} \leq 0$$

Because if it were positive, it means that the supermachine is taking heat from T_0 and producing work, which is impossible KP.

Now we use the efficiencies of the Carnot machines as $\frac{|Q_{1A}|}{|Q_{0A}|} = \frac{T_1}{T_0}$ and similarly for the other.

Then, after some algebra, we get:

$$\frac{Q_0}{T_0} + \frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0$$

This can be generalized for more systems

Then:

$$\sum \frac{Q_i}{T_i} \leq 0$$

We wrote this system for a machine working in a finite amount of sources (which is only possible using isotherms and adiabats), but for a system undergoing other kind of processes, we need an infinite number of sources (like a system undergoing an isobaric expansion or something like that). So we have in general:

$$\otimes \frac{dQ}{T} \leq 0$$

Where T is the temperature of the source.

Reversibility

If the system where reversible, we could run it the other way around and therefore get the opposite inequality, for both to hold, we need:

$$\text{For reversible processes: } \oint \frac{dQ}{T} = 0$$

This means that for reversible processes, $\frac{dQ}{T}$ is the differential of a state function (because it doesn't matter the direction of integration), therefore, we can define:

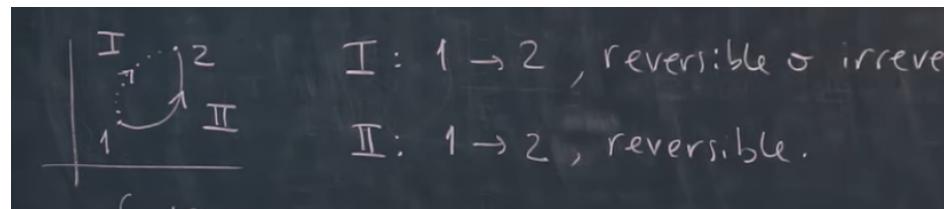
$$dS = \frac{dQ}{T}_{rev}$$

And S will be a function of state.

More on Entropy

Say we have two states 1, 2 in an arbitrary diagram for a system with two variables. In this diagram, we have two paths going from 1 to 2.

Where one of the paths is arbitrary (reversible or not), and the other is reversible.



Then, we can make a cycle and use the Clausius theorem:

$$\int_{1-I}^2 \frac{dQ}{T} + \int_{2-II}^1 \frac{dQ}{T} \leq 0$$

Since the second path is reversible, we can substitute $dS = dQ/T)_{rev}$, then:

$$\int_{1-I}^2 \frac{dQ}{T} \leq \int_1^2 dS = \Delta S = S(2) - S(1)$$

So that we conclude:

$$\boxed{\Delta S \geq \int \frac{dQ}{T}}$$

And for an infinitesimal change:

$$\boxed{dS \geq \frac{dQ}{T}}$$

Where the equals sign is valid iff it is a reversible path.

This is a reformulation of the **Second Law of Thermodynamics**.

Theorem: Saying $dS \geq \frac{dQ}{T}$ is equivalent to the KP principle, so it is truly a reformulation of the 2nd law

- $KP \rightarrow dS \geq \frac{dQ}{T}$

We have already proved this, since KP leads to Clausius theorem and this leads to $dS \geq \frac{dQ}{T}$

- Prove $dS \geq \frac{dQ}{T} \Rightarrow KP$

We will prove by contradiction.

Suppose KP is not met, then there exists a machine that takes heat Q from a single source at T_1 and gives out work W in a cyclical way.

Because it operates cyclically, we have $\Delta S = 0$ (because entropy is a state function).

On the other hand, we have by hypothesis that:

$$0 = \Delta S \geq \int \frac{dQ}{T} = \frac{1}{T} \int dQ = \frac{Q}{T} > 0$$

So $0 > 0$, a contradiction.

So $dS > \frac{dQ}{T}$ is a reformulation of the second law.

For Isolated System

For an isolated system, we have that $Q = 0$ (since it is isolated), so the second law for an isolated system is now:

$$dS \geq 0$$

So, in an isolated system, entropy can only increase (or stay the same)

So isolated systems will only change in a way that increases (or leaves the same) the entropy. Then, an isolated system might change until reaching a maximum of S , which means that it can't continue changing, and is in an equilibrium state.

Turns out this formulation, though only valid for isolated systems, is equivalent to the second law.

Theorem: KP is equivalent to $dS \geq 0$ for isolated systems

-
- KP $\Rightarrow dS \geq 0$

We have already proved this in the development of the theory.

- $dS \geq 0$ implies KP

We consider a motor that violates the KP formulation. The motor takes heat Q from a single source at T and produces work W .

The motor isn't an isolated system, since it receives heat, but the complete system (motor + source +) is isolated.

So we can calculate its change in entropy:

$$\Delta S_{total} = \Delta S_{motor} + \Delta S_{source}$$

Since the machine is cyclical and returns to initial condition after one cycle, $\Delta S_{motor} = 0$, and since the source gives heat Q at constant temperature T , its entropy change is

$$\Delta S_{source} = \frac{Q}{T}$$

Where Q is the heat seen by the point of view of the source, so it is negative.

$$\text{Therefore, } \Delta S_{total} = \frac{Q}{T} < 0$$

Which contradicts that $dS \geq 0$ for isolated systems.

Thus, we can see that it is impossible to create a machine with only one source (a KP machine) since only the heat source changes in entropy, and it actually loses entropy.

Examples

- **Change in entropy on a adiabatic reversible:**

It is simply:

$$dS := \frac{dQ}{T}_{rev} = 0$$

- **Change in entropy in a reversible cyclical process**

Since it is cyclical, and the entropy is a state function, then $\Delta S = 0$ (for only the system).

- **Reversible isothermic**

$$\Delta S = \int dS = \int \frac{dQ}{T}_{rev} = \frac{1}{T} \int dQ_{rev} = \frac{Q_{rev}}{T}$$

- **Isothermic and isobaric reversible process**

If the process where reversible isothermal, then $\Delta S = \frac{Q_{rev}}{T}$

But since it is isobaric, then $Q_{rev} = Q_p = \Delta H$

Therefore:

$$\Delta S = \frac{\Delta H}{T}$$

This equation involves only state functions.

So if there is a reversible path between the two states, the change of entropy in this reversible path should be the same to the change of entropy in any irreversible path connecting the same points.

So this is valid for **irreversible paths** two.

This one is useful for a phase change, since it happens at constant temperature and pressure.

- **Isolated reversible process**

For a reversible process in an isolated system stays the same.

- **Isobaric process in a monophasic substance**

We have that $dQ_{rev} = dQ_p = C_p dT$, so that

$$\Delta S = \int \frac{dQ}{T}_{rev} = \int \frac{C_p(T)}{T} dT$$

So:

$$\Delta S = \int \frac{C_p(T)}{T} dT$$

As before, to calculate it, we used a reversible process, but if we can imagine a reversible system with the same end states, the entropy is the one just calculated.

And then, since S is a state function, the change of entropy is the same for irreversible systems.

- **Isochoric processes for a monophasic substance**

It can be done analogously to before and get:

$$\Delta S = \int \frac{C_v(T)}{T} dT$$

- **Reversible process between two states (P_1, V_1, T_1) of an ideal gas (P_2, V_2, T_2)**

We have that

$$dQ_{rev} = dU - dW =_{ideal} C_V dT - P dV = C_v dT + \frac{nRT}{V} dV$$

Then:

$$\Delta S = \int dS = \int \frac{dQ_{rev}}{T} = \int \frac{C_V dT}{T} + \int \frac{nR}{V} dV$$

So that:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V(T) dT}{T} + nR \log \frac{V_2}{V_1}$$

And if additionally, C_V is constant:

$$\Delta S = nc_V \log \frac{T_2}{T_1} + nR \log \frac{V_2}{V_1}$$

Or, using the state equation, it is equal to $nc_p \log \frac{T_2}{T_1} + nR \log \frac{P_1}{P_2}$

$$\text{Or } \Delta S = nc_V \log \frac{P_2}{P_1} + nc_p \log \frac{V_2}{V_1}$$

This is true also for irreversible processes, so long as we can connect them reversibly and use that S is a state function.

Sub examples

– Joule Expansion:

1 Mol of gas in a volume V expands to double its volume by filling empty space. Since it is an isolated irreversible process, entropy must increase by the increase of entropy theorem.

We use the formula:

$$\Delta S = nc_v \log \frac{T_1}{T_2} + nR \log \frac{V_2}{V_1} = R \log 2 > 0$$

Clausius inequality

We have calculated that $\Delta S = R \log 2$.

$$\text{And } \int \frac{dQ}{T}$$

So we have that $\Delta S \geq \int \frac{dQ}{T}$, as we should.

– Reversible isothermal Joule expansion of the gas

We consider the same experiment but now we use a piston and move it very slowly, always at contact with a source T , so that it is reversible.

$$\text{Therefore: } \Delta S = \int \frac{dQ}{T}_{rev} = - \int \frac{dW}{T} = + \int \frac{pdV}{T} = \int \frac{RT}{VT} dV = R \log 2$$

Where we used that energy is constant in this case (for an ideal gas U depends only on T), so $dQ = dW$.

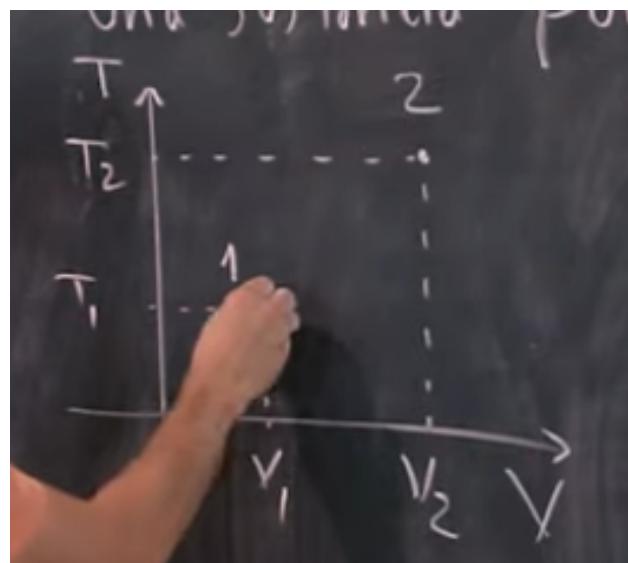
We get the same solution as before, since S is state function.

In this case, the system is not isolated (it is in contact with a source), so the principle of increase in entropy is not valid.

However if we consider the complete system, since it is reversible, the change in entropy of the now isolated system should be 0.

So we know that the source is loosing entropy at $R \log 2$ to compensate this.

- Process between states (V_1, T_1) and (V_2, T_2) for a pure simple substance (expansive work)



$$\begin{aligned} dQ_{rev} &= dU - dW = \frac{\partial U}{\partial T})_V dT + \frac{\partial U}{\partial V})_T dV + pdV \\ &= C_V dT + \left[-p + T \frac{\partial P}{\partial T})_V \right] dV + pdV \\ \text{so that } dS &= \frac{dQ_{rev}}{T} = \frac{C_V}{T} dT + \frac{\alpha}{k_T} dV \end{aligned}$$

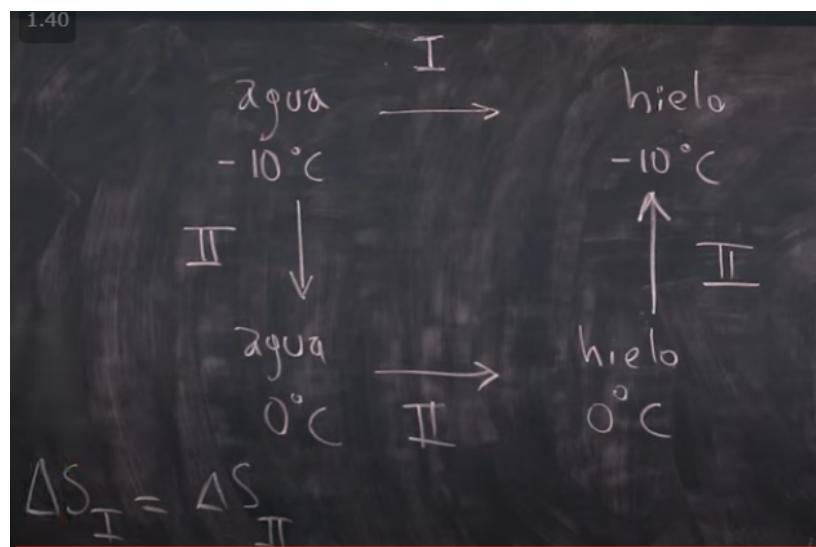
We have to integrate it in any way that joins the two states, we choose a broken path parallel to the axes.

So we get

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V(V_1, T) dT}{T} + \int_{V_1}^{V_2} \frac{\alpha(T_2, V)}{k_T(T_2, V)} dV$$

- Irreversible Isobaric phase change

For example, we have supercooled liquid water at -10°C and by a small perturbation, it becomes ice, this is clearly irreversible.



Then, we calculate the changes of entropy in the 3 paths, that we already actually know.

$$40 \quad \Delta S_{II} = \int_{-10^\circ C}^{0^\circ C} \frac{C_p(T) dT}{T} + \frac{\Delta H}{T} + \int_{0^\circ C}^{-10^\circ C} \frac{C_p(T) dT}{T}$$

Formulation of the second law as a balance of entropy

From the second law, we know that $dS - \frac{dQ}{T} \geq 0$

But we can define new thing $d_iS \geq 0$ called (**Entropy production**) and define it as:

$$dS - \frac{dQ}{T} = d_iS$$

Where T is the temperature of the point at which the system exchanges heat with the medium, we call $\frac{dQ}{T}$ the **Flux of entropy**

So, the new equation is:

$$dS = d_eS + d_iS$$

Where d_eS is the flux of entropy and d_iS the production of entropy.

Then, a system has two ways of changing entropy, either exchanging with the medium (d_eS) or by entropy production (d_iS)

We also see that a process is reversible iff $d_iS = 0$.

Where, as we know:

$$\begin{aligned} dS &= \frac{dQ}{T}_{rev} \\ d_eS &= \frac{dQ}{T} \end{aligned}$$

dQ_{rev} is the reversible heat and dQ the real one when the process is irreversible.

In the second equation T is the temperature of the point where the system is exchanging heat with the surroundings.

So now the second law is simply $d_iS \geq 0$, which says that entropy cannot be lost, only produced.

In general, we could calculate dS, d_eS using a reversible path and a the real one, and then use this to calculate d_iS

40 Formulación tradicional	Balance de entropía
$dS \geq \frac{dQ}{T_f}$	$dS = d_eS + d_iS$ $d_eS = \frac{dQ}{T}$ $d_iS \geq 0$

Proceso reversible

$$dS = \frac{dQ}{T} \Big|_{rev}$$

$$\left. \begin{array}{l} d_i S = 0 \\ \Rightarrow dS = d_e S = \frac{dQ}{T} = \frac{dQ}{T} \Big|_{rev} \end{array} \right.$$

1.40 Proceso irreversible

$$dS > \frac{dQ}{T_f} \quad \checkmark$$

$$\left. \begin{array}{l} dS = \frac{dQ}{T} + d_i S \\ \boxed{dS > \frac{dQ}{T} > \frac{dQ}{T_f}} \quad \checkmark \\ T_f > T \Rightarrow dQ > 0 \\ \frac{1}{T} > \frac{1}{T_f} \Rightarrow \frac{dQ}{T} > \frac{dQ}{T_f} \end{array} \right.$$

Sistema aislado

$$dS \geq 0$$

$$\left. \begin{array}{l} dS = d_e S + d_i S \\ = 0 \\ dS = d_i S \geq 0 \end{array} \right.$$

Proceso isentrópico

$$0 \geq \frac{dQ}{T_f}$$

$$dQ \leq 0$$

$$\left. \begin{array}{l} 0 = d_e S + d_i S \\ = \frac{dQ}{T} + d_i S \\ \geq 0 \end{array} \right.$$

Proceso cíclico

$$\int dS \geq \int \frac{dQ}{T_f}$$

$$\Rightarrow 0 \geq \int \frac{dQ}{T_f}$$

$$\int dS = \int d_e S + \int d_i S$$

$$0 = \int \frac{dQ}{T} + \Delta_i S$$

$$\int \frac{dQ}{T} = -\Delta_i S < 0$$

Formulation of both laws in terms of balance

For a closed system (no change of mass)

$$dU = d_e U + d_i U$$

$$dS = d_e S + d_i S$$

Where d_e means flux and d_i means production.

The laws would then be

$$d_e U = d'Q + d'W , \quad d_i U = 0$$

$$d_e S = \frac{dQ}{T} , \quad d_i S \geq 0$$

Examples

- **Machine that goes against KP**

We have a machine that takes heat Q from a single source T and produces work W .

In this case, as the machine operates cyclically, $\Delta U = 0$ so $Q + W = 0 \Rightarrow Q = -W$

Looking at entropy, $\Delta S = 0 = \Delta_e S + \Delta_i S = \frac{Q}{T} + \Delta_i S > 0 + \geq 0 > 0!$

- **Reversible motor**

We have a motor that takes heat Q_1 at T_1 and gives heat Q_2 to T_2 and produces heat W .

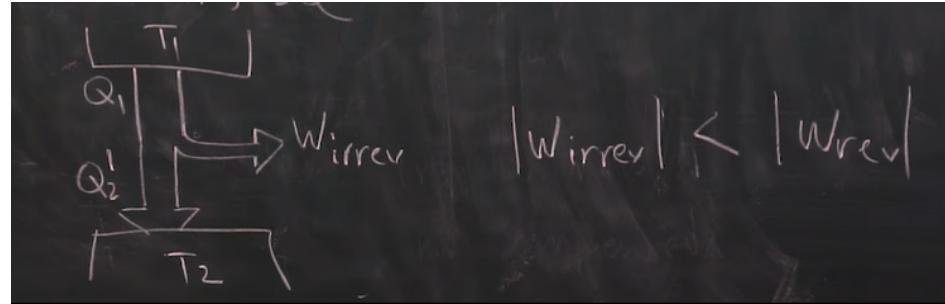
We have $\Delta U = 0 = \Delta_e U = Q_1 + Q_2 + W$

On an entropy point of view, we have $\Delta S = 0 = \Delta_e S + \Delta_i S = \Delta_e S = \frac{Q_1}{T_1} + \frac{Q_2}{T_2}$

$\Delta_i S = 0$ because of reversible, and we recover the Clausius theorem for reversible.

- Comparison of reversible and irreversible cycle work

We have an irreversible motor like the following:



Where W_{rev} is the work that would be done if the cycle were reversible and, Q_2 is the heat that would be lost in reversible.

So we have for irreversible

$$\begin{aligned}\Delta U &= 0 = Q_1 + Q'_2 + W_{irrev} \\ \Delta S &= 0 = \Delta_e S + \Delta_i S = \frac{Q_1}{T_1} + \frac{Q'_2}{T_2} + \Delta_i S\end{aligned}$$

And for reversible:

$$\begin{aligned}\Delta U &= Q_1 + Q_2 + W_{rev} \\ \Delta S &= 0 = \frac{Q_1}{T_1} + \frac{Q_2}{T_2}\end{aligned}$$

Combining these 4 equations, we can get:

$$W_{irrev} = W_{rev} + T_2 \Delta_i S$$

Remember $W < 0$ in a motor, so this means the irreversible work is lower (in module) because $\Delta_i S, T$ are positive.

Then, the entropy generation $\Delta_i S$ tells us how much possible work we are losing. From this we can get:

$$\eta_{irrev} = \eta_{rev} \left(1 - \frac{T_2 \Delta S_2}{|W_{rev}|} \right)$$

The Second Law Of Thermodynamics

The transformation of heat into work

In general any kind of W may be done on a system in contact with a heat reservoir (a big reservoir at a given temperature), it causes heat Q to leave the system without altering the state of the system.

It is apparent from the first law that $W = Q$, so work is transformed into heat with a 100 percent efficiency and it can be continued indefinitely.

We are also interested in the opposite process, conversion of heat into work. We can think of isothermal expansion of an ideal gas as a possible process.

In this case there is no change of internal energy, since the temperature is constant and therefore $Q = W$, so heat has been converted completely into work.

Nevertheless, the process involves a change of state of the gas, so it can not be continued indefinitely.

What is needed is a series of processes in which a system is brought back to its initial state, a **cycle**.

Each process in the cycle involves either a performance of work or a flow of heat between the system and surroundings, which consists of a heat reservoir at a higher temperature and a heat reservoir at the lower temperature.

For one complete cycle, we define:

- $|Q_H|$: represents the heat exchanged between the high temperature reservoir and the system.
- $|Q_L|$ represents the heat exchanged between the low temperature reservoir and the system.
- $|W|$ represents the work exchanged between the system and the surroundings.

We put the absolute values because we are only interested in the amount of heat.

Heat Engine:

If $|Q_H| > |Q_L|$ and if $|W|$ is the work done by the system. The heat engine delivers work continuously to the surroundings. The net work in the cycle is the output, and the heat absorbed from the high temperature reservoir is the input.

The **thermal efficiency** of the engine is defined as:

$$\eta = \frac{\text{work output}}{\text{heat input}} = \frac{|W|}{|Q_H|}$$

Applying the first law to the completed cycle (which doesn't change internal energy at completion), we get that:

$$|Q_H| - |Q_L| = |W|$$

And therefore:

$$\eta = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|}$$

We can see that η will be 1 (100 percent) if $Q_L = 0$, that is if there is no loss of heat in the cycle.

The Gasoline Engine

The gasoline engine is done in 6 steps:

- **Intake stroke:** The system is a mixture of gasoline vapor and air, which moves into a cylinder due to suction as a piston enlarges because of pressure difference.
- **Compression stroke:** The mixture is compressed until its pressure and temperature rise, this is done by advancing the piston.
- **Combustion:** With an electric spark, the hot mixture is ignited. This generates a high pressure but the volume remains unchanged for a very short time interval.
- **Power Stroke:** The hot production products expand and push the piston away, thus increasing the volume and decreasing the pressure. The system thus produces work on the surroundings.
- **Exhaust:** The combustion products are still at a higher temperature than the surroundings and they are allowed to escape.
- **Exhaust stroke:** The piston pushes all the remaining combustion products out of the cylinder.

This is called an **Otto cycle**

The behavior of the system can be approximated by assuming a couple of conditions:

- The working substance is at all times air, which behaves like an ideal gas with constant heat capacities.
- All processes are quasi-static
- There is no friction or turbulence
- There is no loss of heat through the walls.
- The processes are reversible

This idealized process is now plottable in a *PV* diagram as shown below.

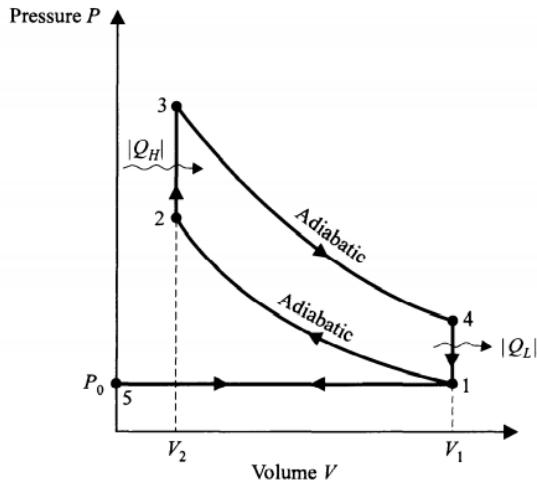


FIGURE 6-1
Idealized Otto cycle for gasoline engines shown on a PV diagram.

The process $5 \rightarrow 1$ represents a quasi-static intake stroke, isobaric at atmospheric pressure. The volume goes from 0 to V_1 and gets to n moles.

Process $1-2$ represents a quasi-static, adiabatic compression stroke. There is no friction, and no loss of heat through the walls. The temperature rises from ambient T_1 to T_2 according to the adiabatic law $PV^\gamma = cte$ which is equivalent to:

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

Process $2-3$ represents a quasi-static isochoric increase of temperature and pressure due to the explosion, but modeled by an absorption of heat $|Q_H|$ from a series of external high-temperature reservoirs whose temperatures range from T_2 to T_3 .

Process $3-4$ represents a quasi-static adiabatic power stroke, involving a drop an expansion and a drop in temperature from T_3 to T_4 according to the equation:

$$T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$$

Process $4-1$ represents a quasi-static isochoric drop in temperature due to the exhaust of air. We model it as a rejection of heat $|Q_L|$ to a series of low temperature external reservoirs ranging from T_4 to T_1 .

Process $1-5$ represents a quasi-static exhaust stroke, isobaric at atmospheric pressure.

There is an absorption of $|Q_H|$ heat from $2-3$ and a rejection of $|Q_L|$ from $4-1$.

Assuming C_V to be constant along line $2-3$, we find that the heat that enters the system is:

$$|Q_H| = \int_{T_2}^{T_3} C_V dT = C_V(T_3 - T_2)$$

Similarly for process 4-1 the heat leaving the system is:

$$|Q_L| = - \int_{T_4}^{T_1} C_V dT = C_V(T_4 - T_1)$$

So the efficiency is therefore:

$$\eta = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

We now use the relations $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$ and $T_4 V_1^{\gamma-1} = T_3 V_2^{\gamma-1}$

Which after some work leads to: $\frac{T_4 - T_1}{T_3 - T_2} = \frac{T_4}{T_3}$

SO the thermal efficiency is:

$$\eta = 1 - \frac{T_1}{T_2}$$

Where the temperatures are those at the beginning and end of the compression stroke.

0.1 Diesel Engine

In the Diesel engine, only air is admitted on the intake stroke. The air is compressed adiabatically until the temperature is high enough to ignite oil that is sprayed into the cylinder after compression.

The combustion takes place approximately isobarically, the rest of the cycle is the same.

If we make the same assumptions as before, the line 2-3 is horizontal instead of vertical, resulting in

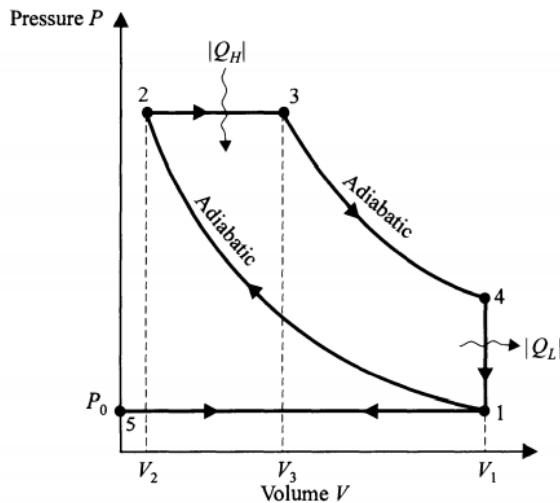


FIGURE 6-2
Idealized Diesel cycle for oil-fired engines shown on a PV diagram.

Line 2-3 represents the quasi-static isobaric absorption of heat from a series of external reservoirs ranging in temperature from T_2 to T_3 . This process approximates the isobaric burning of the oil.

Assuming C_p to be constant along the line 2-3, we get:

$$|Q_H| = \int_{T_2}^{T_3} C_p dT = C_p(T_3 - T_2)$$

And as in the Otto cycle:

$$|Q_L| = C_V(T_4 - T_1)$$

So the efficiency is:

$$\eta = 1 - \frac{1}{\gamma} \frac{T_4 - T_1}{T_3 - T_2}$$

Which can be simplified to:

$$\eta = 1 - \frac{1}{\gamma} \frac{(r_E^\gamma - 1) T_1}{(r_E - 1) T_2}$$

Where $r_E = \frac{V_1}{v_3}$ is the expansion ratio and $r_C = \frac{V_1}{V_2}$ is the compression ratio (which doesn't appear)

Steam Engine

The steam engine was the first engine driven by heat

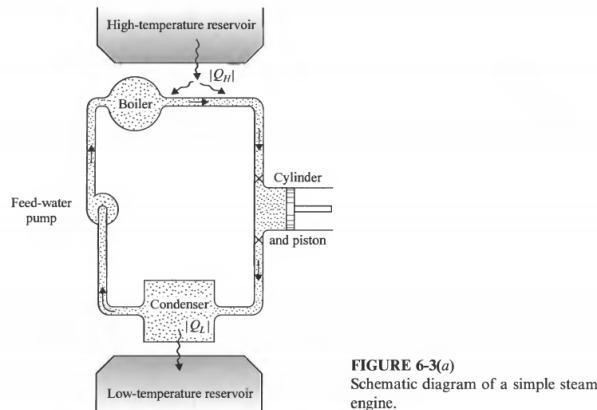


FIGURE 6-3(a)
Schematic diagram of a simple steam engine.

Water flows in the inner tubes. The water in the condenser is at a pressure less than atmospheric and at a temperature less than the normal boiling point.

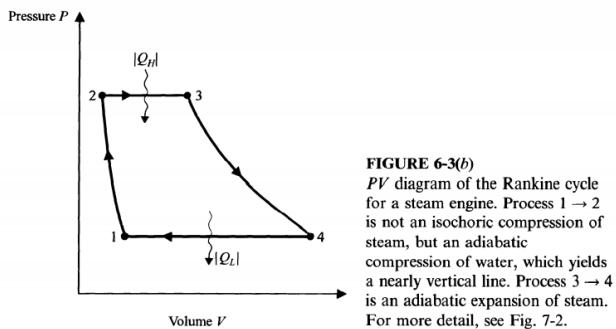
By means of a pump, it is introduced into the boiler, which is at much higher pressure and temperature. In the boiler, the water is first heated to its boiling point and then vaporized

at constant pressure.

The steam is then raised to a temperature greater than the normal boiling point at same pressure. It is then allowed to flow into the cylinder, where it expands approximately adiabatically against a piston or a set of turbine blades, until its temperature and pressure drop to that of the condenser.

In the condenser, finally, the steam condenses into water at the same state than at the beginning.

We make a few assumptions ignoring turbulence and etc.



The ranking cycle has the following processes:

- 1-2: Adiabatic compression of water to the pressure of the boiler. (only very small changes of temperature and volume)
- 2-3: Isobaric heating of water to the boiling point, vaporization of water into saturated steam and superheating of steam to a temperature T_H above boiling point.
- 3-4: Adiabatic expansion of the superheated steam into wet steam.
- 4-1: Isobaric, isothermal condensation of steam into saturated water at temperature T_L

During the process 2-3, heat $|Q_H|$ enters the system from the hot reservoir.

During process 4-1, heat $|Q_L|$ is rejected to the atmosphere.

Since heat is always rejected during the condensation of water, $|Q_L|$ cannot be 0, so there is no perfect efficiency.

The actual operating efficiency is about 30-40 percent.

Stirling Engine

Stirling designed a hot air engine that could convert some of the energy liberated by a burning fuel into work.

The steps of operation of an idealized Stirling engine are shown:

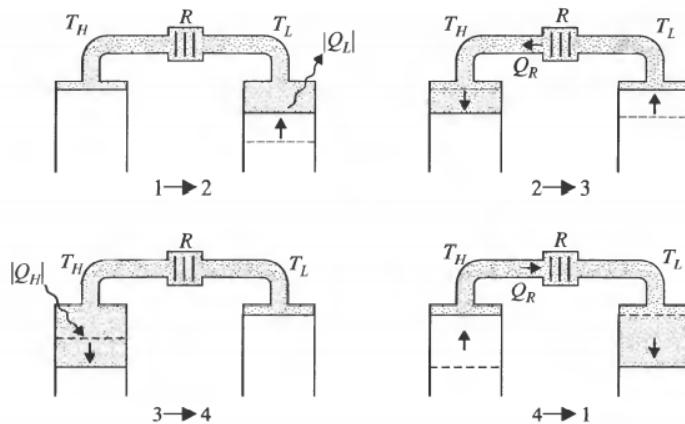


FIGURE 6-4(a)

Schematic diagram of the steps in the operation of an idealized Stirling engine. The numbers under each diagram refer to the processes shown in Fig. 6-4(b).

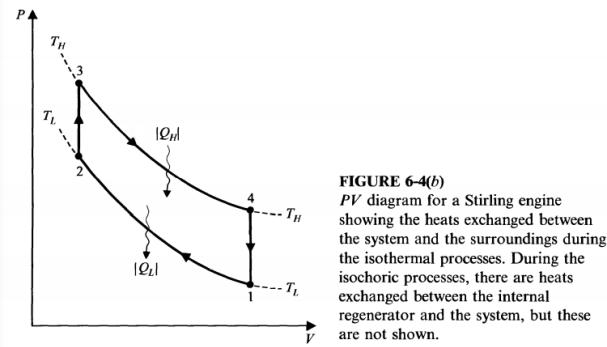


FIGURE 6-4(b)

PV diagram for a Stirling engine showing the heats exchanged between the system and the surroundings during the isothermal processes. During the isochoric processes, there are heats exchanged between the internal regenerator and the system, but these are not shown.

Two pistons are connected to the same shaft. As the shaft rotates, these pistons move out of phase. The space between the pistons is filled with gas which is recycled from one cylinder to the other.

The left-hand portion of the space is kept at T_H high (burning fuel), while the right hand is in contact with a low temperature reservoir (atmosphere).

between the two cylinders is a device R , called a regenerator, consisting of a packing of fine wire screens to form a kind of metal sponge.

The regenerator serves as an internal reservoir, which exchanges heat with the gas as it passes back and forth through the regenerator.

The **Stirling cycle** consists of four processes:

- 1-2: The left piston remains at the top of the cylinder. Meanwhile, the right piston moves halfway up its cylinder, compressing low temperature gas that is in contact with the low temperature reservoir, therefore causing heat $|Q_L|$ to leave. This is an approximately isothermal compression at T_L
- 2-3: The left piston moves down and the right piston up, so that there is no change in volume occupied by the gas. However, gas is forced through the regenerator from the low temperature side to the high temperature side and enters the left hand side at the higher temperature T_H . The regenerator supplies heat $|Q_R|$ to the gas.

- 3-4: The right piston remains stationary. The left piston continues moving down while in contact with the high-temperature reservoir, so the gas expands isothermally, additional heat $|Q_H|$ is absorbed at temperature T_H .
- 4-1: Both pistons move in opposite directions, thereby forcing gas through the regenerator from HT to LT and giving up approximately the same amount of gas $|Q_R|$, canceling with step 2-3.

The net result is the absorption of $|Q_H|$ and rejection of $|Q_L|$. And the delivery of work $|W| = |Q_H| - |Q_L|$ to the surroundings.

The efficiency ranges in 35-45 percent

Heat Engine: Kelvin-Planck Statement of the second law

The important characteristics of heat engine cycles may be summed up as:

- There is some process or series of processes during which there is an absorption of heat from an external reservoir at a higher temperature.
- There is some process or series of processes during which heat is rejected to an external reservoir at lower temperature

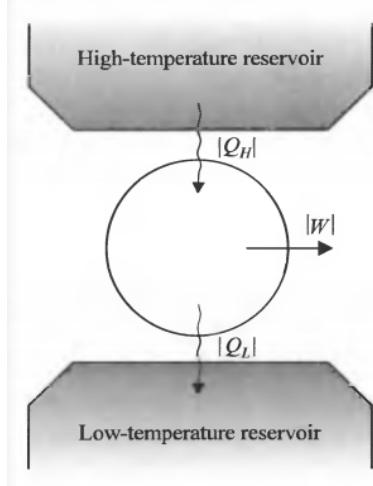


FIGURE 6-5
Schematic representation of the generalized heat engine.

It is a fact of experience that no heat engine has ever been developed that converts the heat extracted from a reservoir at a higher temperature into work without rejecting some heat to a reservoir at lower temperature.

This is the second law of thermodynamics and there are several ways of writing it.

Kevin-Planck statement of second law:

It is impossible to construct an engine that, operating in a cycle, will produce no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work.

The operation of a machine that utilizes the internal energy of only one heat reservoir (which is impossible) is called a perpetual motion machine.

Refrigerator: Clausius' statement

If we imagine a cycle performed in a sequence opposite to that of an engine, then some heat is absorbed by the system from a hear reservoir at a low temperature, a larger amount of heat is rejected to a heat reservoir at a high temperature and a net amount of work is done on the system by the surroundings. This is called a refrigerator.

We write:

- $|Q_H|$: Amount of heat rejected by the refrigerant to the high temperature reservoir.
- $|Q_L|$ amount of heat absorbed by the refrigerant from the low temperature reservoir.
- $|W|$ work done on the refrigerant by the surroundings.

Since there is no total change in internal energy:

$$|Q_L| - |Q_H| = |W|$$

$$|Q_H| = |Q_L| + |W|$$

The purpose is to extract as much heat $|Q_L|$ as possible from the low-temperature reservoir and expend as little work $|W|$ as possible.

The **Clausius statement of the second law is:**

It is impossible to construct a refrigerator that, operating in a cycle, will produce no effect other than the transfer of heat from a lower-temperature reservoir to a higher-temperature reservoir.

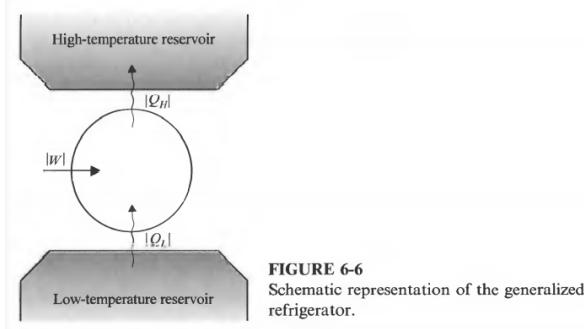


FIGURE 6-6
Schematic representation of the generalized refrigerator.

Equivalence of Kelvin - Planck and Clausius Statements

We adopt the following notation:

- K = truth of the Kelvin - Planck Statement
- C = Truth of the Clausius statement

To prove: $-C \Rightarrow -K$: Consider a refrigerator, that requires no work to transfer $|Q_L|$ units of heat from a low-temperature reservoir to a high temperature reservoir ($-C$). Suppose that a heat engine also operates between these two reservoirs in such a way that heat $|Q_L|$ is delivered to the low temperature reservoir. The refrigerator and engine together constitute a self-contained machine that takes heat $|Q_H| - |Q_L|$ from the high temperature and converts all this heat into work without producing any change in the low-temperature reservoir, therefore violating K-P.

To prove $-K \rightarrow -C$: consider an engine that rejects no heat to the low temperature reservoir so it violates KP. Suppose a refrigerator works in the same reservoirs. The engine and

refrigerator together violate the Clausius.

Therefor $C \Leftrightarrow K$

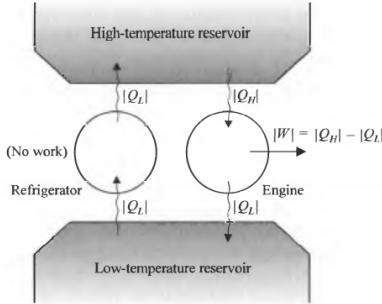


FIGURE 6-7
Proof that $-C \supset -K$. The refrigerator on the left is a violation of C ; the refrigerator and the heat engine acting together violate K .

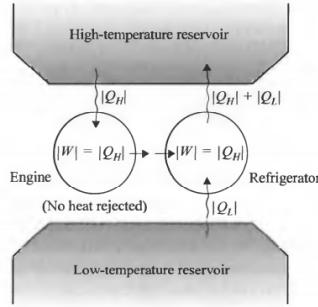


FIGURE 6-8
Proof that $-K \supset -C$. The heat engine on the left is a violation of K ; the heat engine and refrigerator acting together violate C .

Reversibility and Irreversibility

Imagine, for simplicity, a suspended object coupled, by means of pulleys and things, to a system so that any work done by or on the system can be described in terms of the raising or lowering of the object.

Imagine further a series of reservoirs which may be put in contact with the system and in terms of which any flow of heat to or from the system may be described.

We refer to the suspended object and the reservoirs as the *local surroundings*.

Now suppose a process in which:

- 1) The system proceeds from an initial state i to a final state f .
- 2) The suspended object is lowered to an extent that W units of work are performed on the system
- 3) A transfer of heat $|Q|$ takes place from the system to the series of reservoirs

If at the end of this process, the system may be restored to its initial state i , the object lifted to its former level and the reservoirs caused to part with the same amount of heat $|Q|$,

without producing any changes in any other device in the universe, the original process is said to be **reversible**.

Reversible: A process that is performed in such a way that, at the conclusion of the process, both the system and the local surroundings may be restored to their initial states **without producing any changes in the rest of the universe.**

External Mechanical Irreversibility

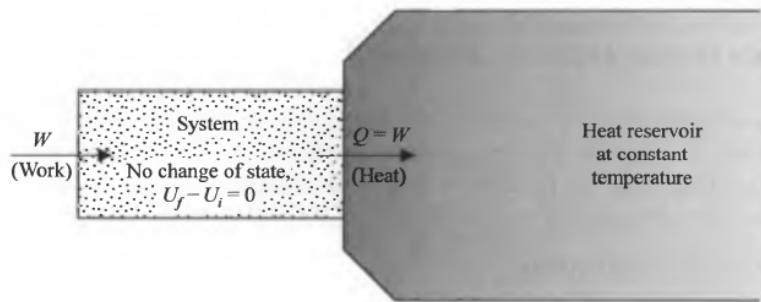


FIGURE 6-9
Isothermal transformation of work through a system (which remains unchanged) into internal energy of a reservoir.

There is a large class of processes involving the isothermal transformation of work through a system into internal energy of a reservoir, for example:

- Friction from rubbing two solids in contact with a reservoir.
- Inelastic deformation of a solid in contact with a reservoir.
- Transfer of charge through a resistor in contact with a reservoir.

In order to restore the system and its local surroundings to their initial states without producing changes elsewhere, $|Q|$ units of heat would have to be extracted from the reservoir and converted completely into work, but this is impossible according to Kelvin Statement. So all of the above processes are irreversible.

Another set of processes involves the adiabatic transformation of work into energy of a system. This is represented:

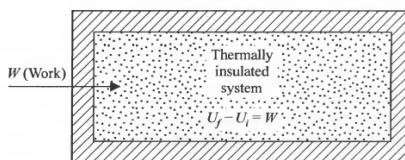


FIGURE 6-10
Adiabatic transformation of work into internal energy of a system.

For example:

- Friction from rubbing two thermally insulated solids.
- Inelastic deformation of a thermally insulated solid
- Transfer of charge through a thermally insulated resistor.

A process of this type is accompanied by a rise of temperature of the system from, say T_i to T_f .

In order to restore the system and its local surroundings to their initial states without producing changes elsewhere, the internal energy of the system would have to be decreased by extracting $U_f - U_i$ units of heat, thus lowering the temperature from T_f to T_i , and this heat would have to be completely converted into work. This violates the second law, so all these processes are irreversible.

The transformation of work into internal energy either of a system or of a reservoir is seen to take place through the agency of such phenomena as friction, viscosity, resistance, etc. These effects are known as dissipative and the work is said to be dissipated.

Processes involving the dissipation of work into internal energy are said to exhibit external mechanical irreversibility.

Friction renders a process irreversible, since heat is produced by friction in whichever direction the process is traversed

Internal Mechanical irreversibility

The following involve the transformation of internal energy of a system into mechanical energy and then back into internal energy:

- Ideal gas rushing into a vacuum (free expansion)
- Gas flowing through a porous plug.
- Snapping of a stretched wire after it's cut.
- Collapse of a soap film after punctured.

These are all irreversible.

In a stretched wire cut, there is first a transformation of internal energy into kinetic of irregular motion and of vibration, and then the dissipation of this energy into internal energy again.

chemical irreversibility:

Some examples:

- Form of chemical compounds after a reaction.
- Mixing of substances.
- freezing a supercooled liquid.

They are irreversible.

Conditions for Reversibility

From the second law, we are led to conclude that:

All natural spontaneous processes are irreversible

A careful inspection of the various types of natural process shows that all involve one or both of the following features:

- The conditions for mechanical, thermal, or chemical equilibrium are not satisfied
- Dissipative effects (friction, inelasticity, resistance, etc) are present.

For a process to be reversible it must not possess these features. We are led to the conclusion that a process is reversible when:

- 1) It is performed quasi-statically (so that it is always in equilibrium)
- 2) It is not accompanied by dissipative effects

It is impossible to satisfy both conditions perfectly, so a reversible process is purely very ideal.

A **heat reservoir** is a large body capable of absorbing or rejecting an unlimited supply of heat without suffering appreciable changes in its thermodynamic coordinates.

The changes that do happen are very minute and slow and so there is no dissipation.

Therefore, when heat enters or leaves a reservoir, the changes that take place **in the reservoir** are the same as those which would take place if the same quantity of heat were transferred reversibly.

It is possible to approximate reversible processes, like with a well lubricated piston and a gas allowed to expand very slowly against an opposing force.

All four idealized cycles in this chapter were assumed to be quasi-static without dissipation, hence reversible.

Work and Heat in Ideal Gas Processes

- **Isothermal** ($T = T_0$):

Work: The work is $W = - \int_{V_i}^{V_f} P dV = -nRT \log \frac{V_f}{V_i}$

Heat: Because $U = 0$, then $Q = -W$

Internal Energy: $U = 0$ (because it depends only on T)

- **Isobaric** ($P = P_0$)

Work: The work is $-P\Delta V$

Heat: $Q = nc_p\Delta T$

Internal Energy: $U = nc_V\Delta T$

- **Isocoric** ($V = V_0$)

Work: $W = 0$

Heat: $Q = nc_V\Delta T$

Internal Energy: $U = nc_V\Delta T$

- **Adiabatic** ($PV^\gamma = k$)

Work: $W = \frac{P_f V_f - P_i V_i}{\gamma - 1}$

Heat: $Q = 0$

Internal Energy: $U = nc_V\Delta T$

The Carnot Cycle and the Thermodynamic Temperature Scale

Carnot Cycle

During a part of the cycle of an engine, some heat is absorbed from the hot reservoir. During another part of the cycle, a smaller amount of heat is rejected to a cooler reservoir (it is a fact of experience that some heat is always rejected to the cooler reservoir, so efficiency is never 100%).

If we have at our disposal two heat reservoirs at given temperatures we ask ourselves what is the best efficiency we can get.

A Carnot cycle is such a cycle. And it can be done by any thermodynamic system. We begin with the system at equilibrium with a heat reservoir of temperature T_L .

- 1) A reversible adiabatic process is performed in such a direction that the temperature rises to the one of the hot reservoir T_H
- 2) The working substance is maintained in contact with the reservoir T_H and a reversible isothermal process is performed and heat $|Q_H|$ absorbed.
- 3) A reversible adiabatic process is performed in opposite direction of 1 until reaching a temperature T_L
- 4) The working substance is maintained in contact with T_L and a reversible isothermal process is performed in direction opposite to 2 until reaching the initial state. During the process, heat $|Q_L|$ is rejected to the low temperature reservoir.

Notice that all heat enters at the high temperature reservoir and leaves at the low temperature. There are not multiple reservoirs like in the other cycles.

The Carnot engine is reversible

The difference with other cycles we have studied is that now there are only 2 reservoirs instead of infinite.

Examples of Carnot Cycles

The simplest example is that of a has as depicted in the following image.

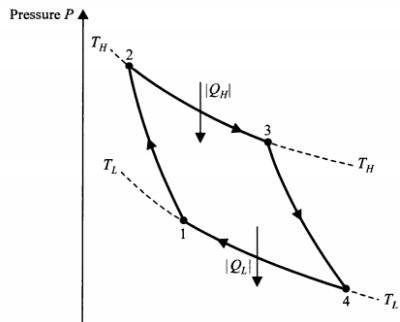


FIGURE 7-1
Carnot cycle of a real gas.

Or it can be done with other substances like a mixture of liquid and vapor

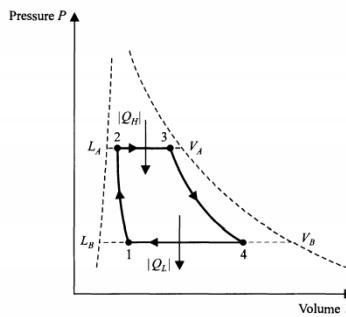


FIGURE 7-2
Carnot cycle of a mixture of liquid and vapor, such as water, plotted with pressure as a function of volume. To the left of the dashed line marked $L_A L_B$, the substance is completely liquefied; to the right of the dashed line marked $V_A V_B$, the substance is completely vaporized.

Or using a electrochemical cell

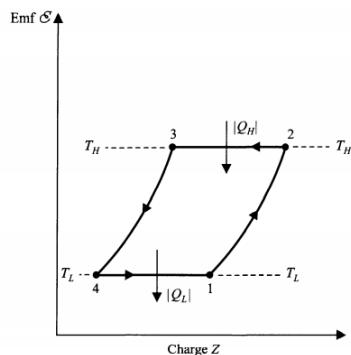


FIGURE 7-3
Carnot cycle of an electrochemical cell.

Or even using a paramagnet

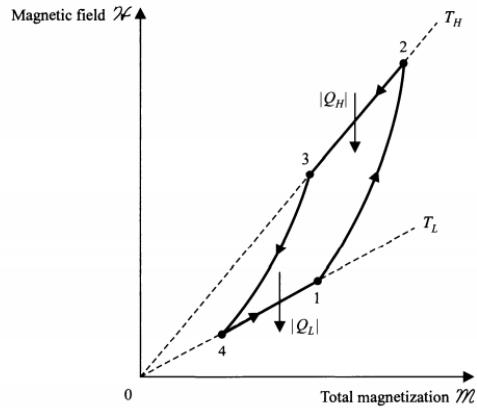


FIGURE 7-4
Carnot cycle of a paramagnetic substance.

Carnot Refrigerator

When the Carnot cycle is performed in opposite direction, it is a refrigerator cycle. The important feature of the Carnot cycle refrigerator, which distinguishes it from any general reversed engine cycle is that the quantities $|Q_H|$, $|Q_L|$, $|W|$ are numerically equal to those quantities when the cycle is performed in the opposite direction.

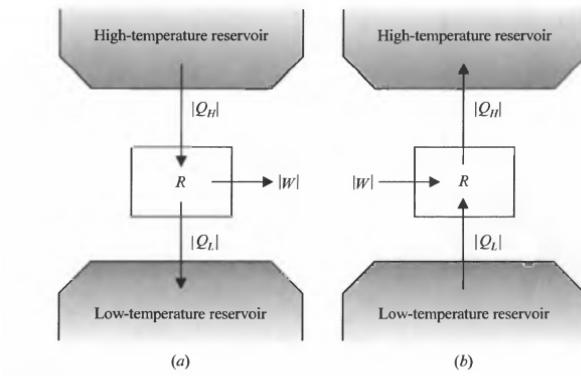


FIGURE 7-5
Schematic representation of (a) the Carnot engine, and (b) the Carnot refrigerator.

Carnot's Theorem and Corollary

Theorem: No heat engine operating between two given reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.

Proof: Imagine a Carnot engine R , which is reversible, and any other engine I , which is irreversible, working between the same two reservoirs and adjusted such that both produce work $|W|$. Then:

- **Carnot R:**

- 1) Absorbs heat $|Q_H|$ from the high temperature

- 2) Performs work $|W|$
- 3) Rejects heat $|Q_H| - |W|$ to the low-temperature reservoir.
- 4) Efficiency $\eta_R = |W|/|Q_H|$

- **Irreversible I**

- 1) Absorbs heat $|Q'_H|$ from the high temperature reservoir
- 2) Performs work $|W|$
- 3) Rejects heat $|Q'_H| - |W|$ to the low temperature reservoir.
- 4) Efficiency $\eta_I |W|/|Q'_H|$

Let us assume that $\eta_I > \eta_R$, so $|Q_H| > |Q'_H|$

Now, we put Carnot's engine backward into a refrigerator.

The engine and refrigerator in this way create an isolated system.

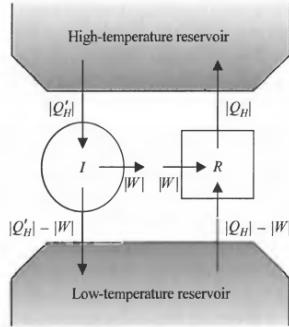


FIGURE 7-6
Irreversible engine I operating a Carnot refrigerator R .

The net heat extracted from the low temperature reservoir is $|Q_H| - |Q'_H|$ which is positive. The net heat delivered to the high temperature reservoir is $|Q_H| - |Q'_H|$.

Therefore, the machine transfers perfectly $|Q_H| - |Q'_H|$ units of heat from low temperature to high temperature without work done by the surroundings, this violates the Clausius statement.

Corollary: All carnot engines operating between the same two reservoirs have the same efficiency.

The important thing of the Carnot cycle is that it takes or gives heat only at 2 different temperatures. Other reversible processes usually take or give heat at more temperatures.

Efficiency: The efficiency of the Carnot Cycle can be found to be:

$$\eta = \frac{|W|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H}$$

The Thermodynamic Temperature Scale

In chapter one the Zeroth law allowed us to define a temperature. But an empirical temperature scale must be defined in terms of some thermometric property of an specific system such as an ideal gas.

We are looking for an **absolute** temperature scale that is not depending on the nature of the working substance.

The Carnot engine and the theorem proven above (the corollary specifically) allows us to define something that only depends on the temperature of two reservoirs and not on the system.

A Carnot engine absorbing $|Q_H|$ from a heat reservoir T_H and rejecting $|Q_L|$ units of heat to a reservoir at T_L has an efficiency η_R independent of substance given by:

$$\eta_R = 1 - \frac{|Q_L|}{|Q_H|}$$

What's more, the efficiency depends only on the temperatures:

$$\eta_R = \phi(T_H, T_L)$$

Rearranging the equations, we have:

$$\frac{|Q_H|}{|Q_L|} = \frac{1}{1 - \phi(T_H, T_L)} := f(T_H, T_L)$$

Where we don't know $f(T_H, T_L)$

To discover f , we apply the equation to three Carnot cycles working at temperatures $T_1 > T_3 > T_2$

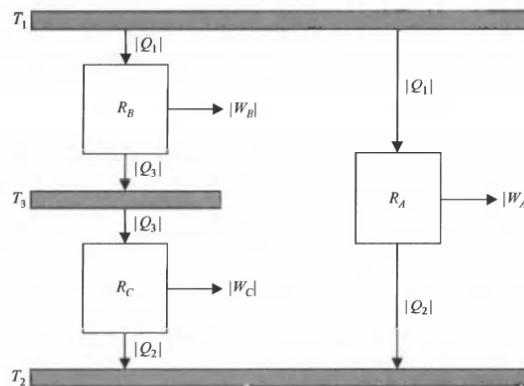


FIGURE 7-7
Schematic diagram of Carnot engines used to demonstrate the thermodynamic temperature scale.

For engine R_A we have:

$$\frac{|Q_1|}{|Q_2|} = f(T_1, T_2)$$

Now, the second Carnot engine and third working together are put in such a way that they exchange the same heat with T_3 . Therefore, the hole $R_A + R_B$ can be seen as a Carnot engine from T_1 to T_3 .

Which makes it equivalent to R_A , and so we have the same values of $|Q_1|, |Q_2|$.

We also have:

$$\frac{|Q_1|}{|Q_3|} = f(T_1, T_3) \quad , \quad \frac{|Q_3|}{|Q_2|} = f(T_3, T_2)$$

Now, since $\frac{|Q_1|}{|Q_2|} = \frac{|Q_1|/|Q_3|}{|Q_2|/|Q_3|}$, we have that:

$$f(T_1, T_2) = \frac{f(T_1, T_3)}{f(T_2, T_3)}$$

Since T_3 doesn't appear on the left, it must cancel out in the ratio. After cancellation, we can write the ratio as:

$$\frac{|Q_1|}{|Q_2|} = \frac{\psi(T_1)}{\psi(T_2)}$$

This ration on the right of two temperatures is denoted by T_1/T_2 , we have finally:

$$\frac{|Q_1|}{|Q_2|} = \frac{T_1}{T_2}$$

Thus, we have defined the ratio of two temperatures:

Two temperatures in the thermodynamic scale are to each other as the absolute value of the heats absorbed and rejected, by a Carnot engine operating between these temperatures. This scale is independent of the substance used and so is **absolute**.

To complete the definition, we proceed to define the temperature of the triple point of water as:

$$T_{TP} = 273.16K$$

Therefore, to determine the temperature of anything, we can theoretically make a Carnot cycle between a reservoir at equilibrium with this thing and one at equilibrium with the triple point.

Then $\frac{|Q|}{|Q_{Tp}|} = \frac{T}{T_{TP}}$ and so:

$$T = 273.16 \frac{|Q|}{|Q_{TP}|}$$

Absolut 0 and Carnot efficiency

It follows that the smaller the value of $|Q|$, the smaller the corresponding T . The smallest value of $|Q|$ is zero.

Thus, if a system undergoes a reversible isothermal process without transfer of heat, the temperature at which the process takes place is called absolute zero.

Now, the efficiency of a Carnot cycle becomes:

$$\eta_R = 1 - \frac{T_L}{T_H}$$

Equivalence of Gas temperature and Carnot temperature

A Carnot cycle in a ideal gas takes a heat $|Q_1| = nR\theta_1 \log \frac{V_3}{V_2}$ and $|Q_2| = nR\theta_2 \log \frac{V_4}{V_1}$

After doing some calculations and using the formulas for the processes, it can be found that:

$$\frac{|Q_1|}{|Q_2|} = \frac{\theta_1}{\theta_2}$$

But this quantity should be equal to $\frac{T_1}{T_2}$ according to the Carnot definition.

So $\theta = T$

Entropy

Reversible Part of the second law

Let Y represent any generalized force and X any generalized displacement.

We can plot a generalized process in a Y vs X diagram.

Consider a reversible process represented by the smooth curve $i \rightarrow f$ on the generalized work diagram

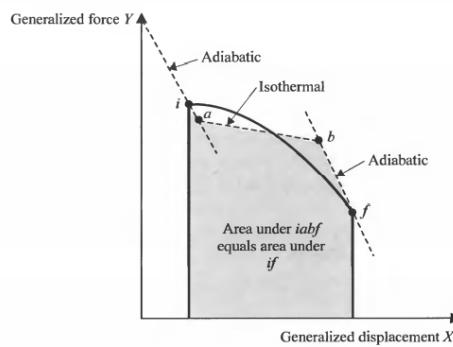


FIGURE 8-1
Generalized work diagram, where $i \rightarrow f$ is any reversible process; $i \rightarrow a$ is a reversible adiabatic process; $a \rightarrow b$ is a reversible isothermal process; and $b \rightarrow f$ is a reversible adiabatic process.

The dashed curves through i and f represent portions of adiabatic processes

The curve $a \rightarrow b$ is a isothermal process drawn in such a way that the area under if is equal to that under $iabf$.

Then, the work done is the same:

$$W_{if} = W_{iabf}$$

From the first law:

$$\begin{aligned} Q_{if} &= U_f - U_i - W_{ig} \\ Q_{iabf} &= U_f - U_i - W_{iabf} \\ \Rightarrow Q_{if} &= Q_{iabf} \end{aligned}$$

But since no heat is transferred in ia and bf , we have:

$$Q_{if} = Q_{ab}$$

Then, given any reversible process in which the temperature may change in any manner, it is always possible to find a reversible zigzag path between the same two states consisting of two adiabatic paths and an isothermal in the middle. Such that the heat transferred during the isothermal is the same as in the original process (and the total work is the same).

Cycle:

Now, we will consider a general cycle in a generalized work diagram.

Since no adiabatic lines can intersect, a number of adiabatic lines may be drawn and divide the cycle on adjacent strips.

Now we may draw a zigzag path by joining the adiabatic lines with isotherms, such that the heat transferred in the isothermal paths is the same as the heat transferred in the original cycle.

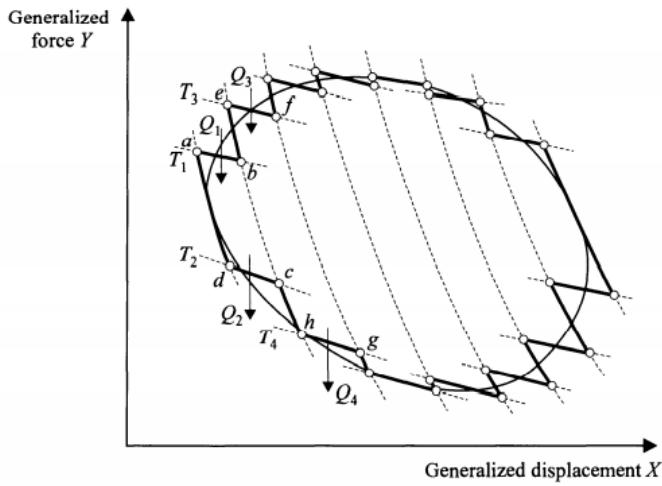


FIGURE 8-2

Generalized work diagram, where the smooth closed curve is a reversible cycle and the zigzag closed path is made up of alternating reversible isothermal and reversible adiabatic processes.

Consider the isothermal process ab at temperature T_1 with heat Q_1 absorbed, and cd at temperature T_2 with heat Q_2 rejected.

Since ab, cd are bounded by the same adiabats, then $abcd$ is a Carnot cycle.

As we know from Carnot cycles, we have that:

$$\frac{|Q_1|}{T_1} = \frac{|Q_2|}{T_2}$$

We regard Q as an algebraic symbol, positive for heat absorbed and negative for heat rejected from a system. We may then write:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

Where Q_1 is a positive number and Q_2 is a negative number.

We can do the same for the cycle $efgh$, and get:

$$\frac{Q_3}{T_3} + \frac{Q_4}{T_4} = 0$$

If we write similar equations for all strips, we get:

$$\sum_j \frac{Q_j}{T_j} = 0$$

If we divide the cycle in infinite strips with heat dQ and temperature T , we get:

$$\oint_R \frac{d'Q}{T} = 0$$

The integrations takes place over the complete cycle, and R means that it is reversible. This is known as **Clausius' Theorem**.

Entropy

Let an initial equilibrium state be i and a final equilibrium state by f .

It is possible to take the system from i to f along any number of different reversible paths, since i, f are equilibrium states.

Suppose we take the system along the reversible path R_1 and then back along another path R_2 , the two paths together form a cycle, so:

$$\begin{aligned} & \oint_{R_1 R_2} \frac{d'Q}{T} = 0 \\ \Rightarrow & \int_{i R_1}^f \frac{d'Q}{T} + \int_{f R_2}^i \frac{d'Q}{T} = 0 \\ \Rightarrow & \int_{i R_1}^f \frac{d'Q}{T} = - \int_{f R_2}^i \frac{d'Q}{T} \end{aligned}$$

Since R_2 is a reversible path.

Then, finally:

$$\int_{i R_1}^f \frac{d'Q}{T} = \int_{i R_2}^f \frac{d'Q}{T}$$

Therefore: $\int_{i R}^f \frac{d'Q}{T}$ is **independent of path connecting i and f** , this is just a consequence of Clausius theorem.

Therefore, there exists a function of only thermodynamic coordinates that is in some sense the potential of $d'Q/T$. This state function was named **entropy** by Clausius and denoted by S .

Therefore, from the definition, we have:

$$S_f - S_i = \int_{iR}^f \frac{d'Q}{T}$$

Where the integral is **independent of path**. Although the heat entering the system depends on the path, the entropy change does not depend on the path.

So both U and S are state functions, which means that the difference of them between two states is independent of path.

If we make the states i, f infinitesimally near, then we get the differential equation:

$$dS = \frac{d'Q_R}{T}$$

Where dS is now an exact differential.

Entropy is measured in J/K

We can write it also as:

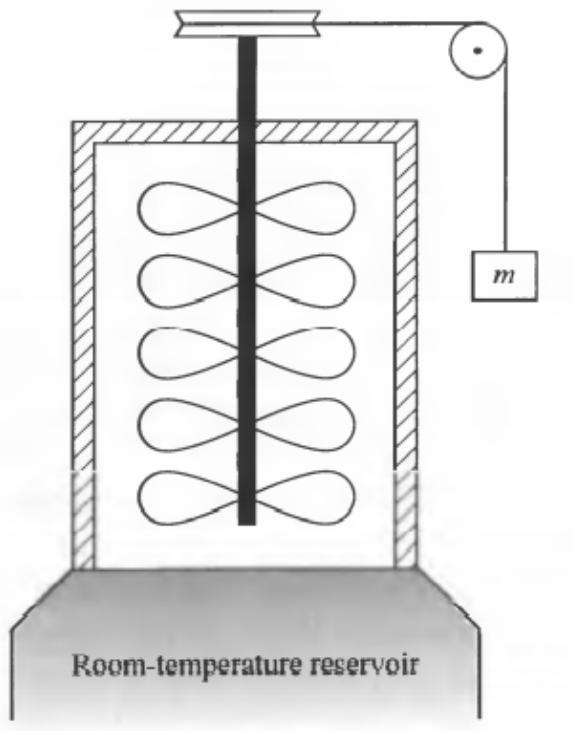
$$d'Q_R = TdS$$

Which deals with the inexact differential of Q just as $d'W = -PdV$ deals with the inexact differential of W .

For now, we have S, P, V, T as thermodynamic variables.

Example:

Consider the Joule paddle wheel apparatus. The system is a kilogram of water at room temperature T and the cylinder of water is surrounded by an adiabatic cylindrical wall. The bottom is diathermic and in contact with a heat reservoir at temperature T



A slowly falling mass m causes the paddle wheels to turn, the falling mass does work on the system, which tends to experience an increase in the temperature of the water. However, the diathermic bottom prevents the temperature from rising by removing energy in the form of heat.

The change of entropy of the **reservoir** (knowing that T is constant) is:

$$\Delta S = \int \frac{d'Q_R}{T} = \frac{Q}{T}$$

Which is also the total change of entropy for the composite system of liquid plus reservoir, since the state of the water in the apparatus is unchanged at the end.

Furthermore, since the state is unchanged at the end, the internal energy is unchanged too. This means that the work done by the falling mass equals the heat that enters the reservoir, so we can calculate the change in entropy easily.

Let's say that the mass was 29.9kg and moved a meter:

$$\Delta S = \frac{W}{T} = \frac{(29.9\text{kg})(9.8\text{m/s}^2)(1\text{m})}{293\text{K}} = 1\text{J/K}$$

The entropy is generated by the conversion of work into heat.

Principle of Caratheodory

We can give a more axiomatic definition.

In 1909 Caratheodory proved the following mathematical **theorem**:

Imagine a space of three dimensions with rectangular coordinates x, y, z . Then, in the neighborhood of an arbitrary point P_0 , there are points that are not accessible from P_0 along solution curves to the equation:

$$A(x, y, z)dx + B(x, y, z)dy + C(x, y, z)dz = 0$$

if and only if, the equation is integrable.

The equation is said to be integrable if there exist functions $\lambda(x, y, z)$ and $F(x, y, z)$ such that:

$$Adx + Bdy + Cdz = \lambda dF$$

Now we use this theorem in Thermodynamics. Consider a system whose states are determined by three coordinates x, y, z . Then, the first law in differential form may be written as:

$$d'Q = Adx + Bdy + Cdz$$

Where A, B, C are functions of x, y, z .

Then, the adiabatic, reversible transitions are subject to the condition:

$$d'Q = Adx + Bdy + Cdz$$

Now, Caratheodory's version of the **second law** is:

In the neighborhood of any arbitrary initial state P_0 of a physical system, there exist neighboring states that are not accessible from P_0 along quasistatic adiabatic paths.

Therefore, the Caratheodory theorem states that there exists functions T, S such that:

$$d'Q = Adx + Bdy + Cdz = TdS$$

Entropy of Ideal Gas

If a system absorbs an infinitesimal amount of heat $d'Q_R$ during a reversible process, the entropy change of the system is:

$$dS = \frac{d'Q_R}{T}$$

Although $d'Q_R$ is inexact, the ratio $d'Q_R/T$ is exact. That is, $1/T$ is the integrating factor of $d'Q_R$.

For an **ideal gas**, the differential of heat is:

$$d'Q_R = C_p dT - V dP$$

And therefore:

$$\begin{aligned} dS &= C_p \frac{dT}{T} - \frac{V}{T} dP \\ &= C_p \frac{dT}{T} - nR \frac{dP}{P} \end{aligned}$$

now we may calculate ΔS between an arbitrary reference state r with coordinates T_r, P_r and any other state with coordinates T, P . Integrating between the states, we get:

$$\begin{aligned} \Delta S &= \int_{T_r}^T C_p \frac{dT}{T} - nR \log \frac{P}{P_r} \\ &= C_p \log \frac{T}{T_r} - nR \log \frac{P}{P_r} \quad \text{if } C_p \text{ is constant} \end{aligned}$$

Suppose the reference state has entropy S_r and choose an arbitrary numerical value for this quantity. Then, the entropy S of point with coordinates T, P is:

$$\begin{aligned} S &= S_r + \Delta S \\ &= S_r + C_p \log \frac{T}{T_r} - nR \log \frac{P}{P_r} \\ &= C_p \log T - nR \log P + (S_r - C_p \log T_r + nR \log P_r) \\ &:= C_p \log T - nR \log P + S_0 \end{aligned}$$

Let us calculate the change of entropy of the ideal gas as a function of T and V :

$$\begin{aligned} \frac{d'Q_R}{T} &= C_V \frac{dT}{T} + \frac{P}{T} dV \\ \Rightarrow dS &= C_V \frac{dT}{T} + nR \frac{dV}{V} \end{aligned}$$

Where C_V is the heat capacity at constant volume. Integrating, we get:

$$\begin{aligned} S &= \int C_V \frac{dT}{T} + nR \log V + S_0 \\ &= n \int_i^f c_V \frac{dT}{T} + nR \log \frac{V_f}{V_i} \end{aligned}$$

Similarly, we can write it as a function of T and P as before:

$$\Delta S = n \int_i^f c_p \frac{dT}{T} + nR \log \frac{P_f}{P_i}$$

TS diagram

Any thermodynamic process can also be graphed in a *TS* diagram.
As we have seen:

$$Q_R = \int_i^f T dS$$

So in this diagram, the heat is the area under the curve.

In this case, an isothermal process is a horizontal line.

In an adiabatic process, $d'Q = 0$, so $dS = \frac{d'Q}{T} = 0$, therefore, S is constant.

That is, in the *TS* diagram, adiabatic processes are vertical lines with constant entropy.
This process is called an **isentrope**

Therefore, a Carnot cycle in a *TS* diagram looks like a rectangle regardless of the nature of the working substance.

Entropy and Reversibility

If we have a process of a system, we can calculate the entropy change of the system itself as well as the entropy change of the surroundings.

The sum of these changes is the **entropy change of the universe** due to the process.

When a finite amount of heat is absorbed or rejected by a reservoir, extremely small changes in the coordinates occur to every unit of mass in the reservoir.

The entropy change of a unit mass is therefore very small.

However, since the reservoir is very big, the total entropy change is finite.

Suppose that a reservoir is in contact with a system and heat Q is absorbed irreversibly by the reservoir at temperature T .

The reservoir undergoes nondissipative changes determined entirely by the quantity of heat absorbed.

Exactly the same changes in the reservoir would occur if the same amount of heat Q were transferred reversibly.

Therefore, whenever a reservoir absorbs heat Q at the temperature T from any system during any kind of process, the entropy change of the **reservoir** is Q/T .

Now consider the entropy change of the universe during a reversible process. The process will in general be accompanied by a flow of heat between a system and a set of reservoirs ranging in temperature from T_i to T_f .

During any infinitesimal portion of the process, an amount of heat $d'Q_R$ is transferred between the system and one of the reservoirs at temperature T . If $d'Q_R$ is absorbed by the system, then:

$$dS \text{ of the system} = +\frac{d'Q_R}{T}$$

$$dS \text{ of the reservoir} = -\frac{d'Q_R}{T}$$

And the entropy change of the universe is 0.

If $d'Q_R$ is rejected by the system, then:

$$dS \text{ of the system} = -\frac{d'Q_R}{T}$$

$$dS \text{ of the reservoir} = +\frac{d'Q_R}{T}$$

And the entropy change of the universe is again 0.

If no heat is transferred, then $d'Q_R = 0$ and neither system change entropy.

Then, for a general (not infinitesimal) **reversible process**, the change of entropy of the **universe is zero**.

However, all natural processes are irreversible and this is only for ideal processes that are reversible.

Entropy and Irreversibility

During an irreversible process, it is different.

When a system undergoes an irreversible process between an initial equilibrium state and a final equilibrium state, the irreversible process is replaced by a reversible one. This replacement is permitted when the initial and final states are of equilibrium.

No integration is performed over the original irreversible path, since the path is not known. The entropy change of the system is equal to:

$$S_f - S_i = \int_{iR}^f \frac{d'Q}{T}$$

Where R indicates any arbitrarily chosen reversible process by which the system is brought from the initial eq state to the final eq state (it doesn't matter which, that is why we can change the irrev process to a rev one when the edge states are of equilibrium).

When either the initial or final states are not of equilibrium, we need special techniques.

- **Processes exhibiting external mechanical irreversibility**

Examples are those processes involving the isothermal dissipation of work through a system (which remains unchanged) into internal energy of a reservoir, such as:

- Friction from two solids in contact with a reservoir
- Irregular stirring of a viscous liquid in contact with a reservoir (like the Joule paddle)
- Inelastic deformation of a solid in contact with a reservoir.
- Transfer of charge through a resistor in contact with a reservoir.

In the case of any process involving the isothermal transformation of work W done by a system into internal energy of a reservoir, there is no entropy change of the system because the thermodynamic coordinates of the system do not change.

Heat Q is absorbed by the reservoir, where $Q = W$ from the work done on the reservoir. Since the reservoir absorbs $+Q$ units of heat at the temperature T , the entropy change of the reservoir is $+Q/T$ or $+W/T$.

The entropy change of the universe is therefore $+W/T$, which is positive.

- Processes involving the adiabatic dissipation of work into internal energy of a system open to the atmosphere, such as

- Friction from rubbing thermally insulated liquids
- Irregular stirring of a viscous thermally insulated liquid
- Inelastic deformation of a thermally insulated solid
- Transfer of charge through a thermally insulated resistor.

In the case of any process involving the adiabatic transformation of work W into internal energy of a system whose temperature rises from T_i to T_f at constant atmospheric pressure, there is no flow of heat to or from the surroundings, and, therefore, the entropy change of the local surroundings is zero.

To calculate the entropy change of the system, the original irreversible process must be replaced by a reversible one that will take the system from the given initial state (temperature T_i , pressure P) to the final state (temperature T_f , pressure P).

Let us replace the irreversible performance of work by a reversible isobaric flow of heat from a series of reservoirs in temperature ranges from T_i to T_f .

The entropy change of the system will then be:

$$S_f - S_i \text{ (system)} = \int_{T_i R}^{T_f} \frac{d'Q}{T}$$

For an isobaric process, $dQ' = C_p dT$, so:

$$S_f - S_i \text{ (system)} = \int_{T_i}^{T_f} C_p \frac{dT}{T}$$

And if C_p is constant, then:

$$S_f - S_i \text{ (system)} = C_p \log \frac{T_f}{T_i}$$

Thus, the entropy change of the universe is $C_p \log \frac{T_f}{T_i}$, which is positive.

- **Process exhibiting internal mechanical irreversibility**

Examples are those processes involving the transformation of internal energy of a system enclosed by adiabatic walls into mechanical energy and then back into internal energy again, such as:

- Ideal gas rushing into vacuum (free expansion)
- Gas flowing through a porous plug
- Snapping of a stretched wire after it is cut
- Collapse of a soap film after punctured

In the case of a free expansion, the entropy change of the local surroundings is zero, because there is no heat transfer through the adiabatic walls. In order to calculate the entropy change, we must replace it by a reversible process with same initial (volume V_i , temperature T) and final states (volume V_f , temperature T).

We can replace it for a reversible isothermal expansion at temperature T from volume V_i to volume V_f .

Then, the entropy change of the system is:

$$S_f - S_i \text{ (system)} = \int_{V_i}^{V_f} \frac{d'Q}{T}$$

For an isothermal process of the ideal gas, $d'Q_R = PdV$, therefore $\frac{d'Q_R}{T} = nR \frac{dV}{V}$. So the entropy change of the system is:

$$S_f - S_i \text{ (system)} = nR \log \frac{V_f}{V_i}$$

The entropy change of the universe is therefore $nR \log \frac{V_f}{V_i}$, which is positive.

This may be puzzling because there is no heat entering the system in the original process.

However, the original process is not reversible, and that is why we change it with the reversible one, which does let heat in.

Irreversible processes always have a positive net change in entropy of the universe

- **Processes exhibiting external thermal irreversibility**

Examples are those processes involving a transfer of heat by virtue of a finite temperature difference, such as:

- Conduction or radiation of heat from a system to its cooler surroundings
- Conduction or radiation of heat through a system (which remains unchanged) from a hot reservoir to a cooler one.

In the case of conduction of Q units of heat from one end to the other end of the system (which remains unchanged) from a hotter reservoir at T_1 to a cooler reservoir at T_2 the following steps are obvious:

- $S_f - S_i$ (system) = 0
- $S_f - S_i$ (hotter reservoir) = $-Q/T_1$
-
- $S_f - S_i$ (cooler reservoir) = $+Q/T_1$
- $S_f - S_i$ (universe) = $\frac{Q}{T_2} - \frac{Q}{T_1}$

The entropy change of the universe is positive, since $T_2 < T_1$.

- **Processes exhibiting chemical irreversibility**

Examples are:

- Diffusion of two dissimilar inert ideal gasses.
- Mixing of alcohol and water.
- Osmosis
- chemical reaction
- Dissolution of a solid in water

We can see it as two free expansions, with total entropy change $2nR \log \frac{V_f}{V_i}$

TABLE 8.1
Entropy change of the universe due to natural processes

Type of irreversibility	Irreversible process	Entropy change of the system	Entropy change of the local surroundings	Entropy change of the universe
External mechanical irreversibility	Isothermal dissipation of work through a system into internal energy of a reservoir	0	$\frac{W}{T}$	$\frac{W}{T}$
	Adiabatic dissipation of work into internal energy of a system	$C_P \ln \frac{T_f}{T_i}$	0	$C_P \ln \frac{T_f}{T_i}$
Internal mechanical irreversibility	Free expansion of an ideal gas	$nR \ln \frac{V_f}{V_i}$	0	$nR \ln \frac{V_f}{V_i}$
External thermal irreversibility	Transfer of heat through a medium from a hotter to a cooler reservoir	0	$\frac{Q}{T_2} - \frac{Q}{T_1}$	$\frac{Q}{T_2} - \frac{Q}{T_1}$
Chemical irreversibility	Diffusion of two dissimilar inert ideal gases	$2nR \ln \frac{V_f}{V_i}$	0	$2nR \ln \frac{V_f}{V_i}$

Irreversible Part of the second law

The first part of the second law considered only reversible processes. The second part deals with irreversible processes. Recall that for a reversible cycle, we have:

$$\oint_R \frac{d'Q}{T} = 0 \quad (\text{reversible})$$

We now consider an irreversible cycle and calculate its closed integral

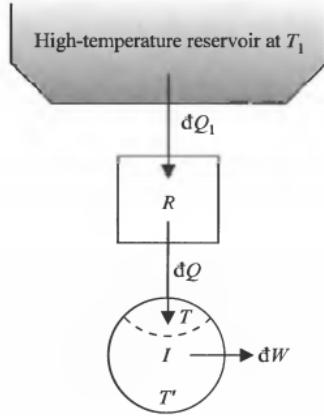


FIGURE 8-7

A high-temperature reservoir at temperature T_1 supplies heat $d'Q_1$ to an auxiliary reversible engine R . Irreversible engine I receives heat dQ at temperature T , even though the system was initially at temperature T' .

The figure shows a high temperature reservoir at T_1 supplying a small quantity of heat $d'Q_1$ to an auxiliary reversible engine R .

The purpose of R is to provide reversible heat for the reversible engine I . Engine R rejects a small amount of heat $d'Q$ at temperature T that is supplied to the irreversible engine I . Engine I does a small amount of work $d'W$ during an irreversible cycle, so the combined system of engine R and engine I also performs an irreversible cycle.

The net work of the combined system, according to the first law equals $\oint d'Q_1$.

But the net work cannot be positive, according to Kelvin Planck, since the combined system exchanges heat with a single reservoir.

So $\oint d'Q_1$ cannot be positive.

Moreover, if $\oint d'Q_1$ equals zero, then, at the end of the cycle, engine I and its surroundings have returned to their original state, which contradicts the irreversibility of engine I . Therefore:

$$\oint_R d'Q_1 < 0$$

That is, engine I generates heat that flows out of the system. From the definition of thermodynamic temperature scale, we have for reversible engine R :

$$\frac{d'Q_1}{T_1} = -\frac{d'Q}{T}$$

And integrating:

$$\oint_R -\frac{d'Q}{T} = \oint_R \frac{d'Q_1}{T_1}$$

However, T_1 is the constant temperature of the reservoir, so:

$$-\oint_R \frac{d'Q}{T} = \frac{1}{T_1} \oint_R d'Q_1$$

The heat $d'Q$ rejected from R is absorbed by I , so $-d'Q_R = d'Q_I$.

Substituting this expression and recognizing that the closed integral on the left now applies to the irreversible system, we obtain:

$$\oint_I \frac{d'Q}{T} = \frac{1}{T_1} \oint_R d'Q_1$$

So:

$$T_1 \oint_I \frac{d'Q}{T} = \oint_R d'Q_1 < 0$$

Since $T_1 > 0$, the result is:

$$\oint_I \frac{d'Q}{T} < 0 \quad \text{irreversible}$$

This is the second part of the second law, known as **inequality of Clausius**.

It states that for an internally irreversible cycle, the closed integral $\oint_I d'Q/T$ of the ratio of the heat absorbed by a system to the temperature **at which the heat is received** is always less than 0.

The integral is less than 0 for irreversible and equal to zero for reversible.

So, Clauisus mathematical statement of the second law is:

$$\boxed{\oint \frac{d'Q}{T} \leq 0}$$

T represents the temperature of the reservoir or reversible engine that provides the small quantity of heat $d'Q$, and is not necessarily equal to the temperature T' of the system that receives the heat.

Heat and entropy in irreversible processes

In order to relate change of entropy to heat in irreversible processes, consider a cycle in which a system begins in an initial equilibrium state i , passes during an irreversible process I to a final equilibrium state f and then returns by a reversible process R to the initial state i .

since entropy is a state function, its closed integral is always zero:

$$\oint dS = \int_{iI}^f dS + \int_{fR}^i dS = 0$$

From Clausius inequality, we obtain:

$$\oint_I \frac{d'Q}{T} = \int_{iI}^f \frac{d'Q}{T} + \int_{fR}^i \frac{d'Q}{T} < 0$$

But, by the definition of entropy:

$$\int_{iR}^f \frac{d'Q}{T} = \int_{iR}^f dS$$

So, in the two equations above, the reversible parts are equal, which must mean that the irreversible parts follow:

$$\int_{iI}^f dS > \int_{iI}^f \frac{d'Q}{T}$$

So the change of entropy in an irreversible process is greater than the integral of the heat divided by the temperature of the auxiliary reservoirs.

For small changes is state:

$$dS_I > \left(\frac{d'Q}{T} \right)_I$$

And in general:

$$dS \geq \frac{d'Q}{T}$$

With equality for reversible processes.

Entropy and Nonequilibrium state

The processes seen earlier were simple because both the initial and final states were equilibrium states and S is a state variable, so we can change the path to a suitable reversible one.

Consider however, the following process involving internal thermal irreversibility with equilibrium only in the final state.

A thermally conducting bar has a nonuniform temperature distribution by connecting one end to a high temperature reservoir and one to a low temperature reservoir.

The bar is removed from the reservoirs and is thermally insulated with adiabatic walls at constant pressure.

An internal flow of heat will finally bring the bar to a uniform temperature, so the irreversible state is from a nonequilibrium state to a equilibrium one.

Now it is impossible to replace the irreversible process with a reversible one, because the initial state is nonequilibrium to begin with. So what meaning can be given to the entropy

change.

We consider the bar to be made of an infinite number of thin slices of different initial temperature (but same final temperature).

WE imagine the slices are insulated from one another and all are kept at the same pressure, and then each slice is put in contact successively with a series of reservoirs ranging in temperature from the initial temperature of the particular section to the common final temperature.

This model defines an infinite number of reversible isobaric processes for each slice.

We define the entropy change as the result of integrating $d'Q/T$ over all of these reversible processes. So we conceive of an infinite number of reversible processes for each volume element.

Consider a uniform bar of length L as depicted, a typical volume element at x has a mass

$$dm = \rho Adx$$

With ρ the density and A the cross sectional area.

The heat capacity of the volume element is:

$$c_p dm = d_p \rho A dx$$

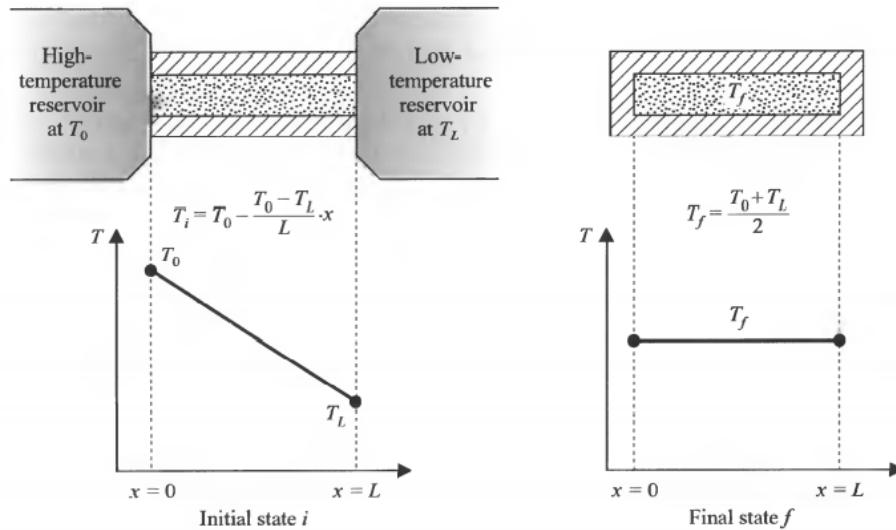


FIGURE 8-9
Process exhibiting internal thermal irreversibility.

Let us suppose that the initial temperature distribution is linear, so the volume element at x has an initial temperature of:

$$T_i = T_0 - \frac{T_0 - T_L}{L}x$$

There T_0 is the temperature at $x = 0$ and T_L is the temperature at $x = L$.

If no heat is lost and if we assume for the sake of simplicity that the thermal conductivity, density and heat capacity of all volume elements remain constant, then the final temperature of the entire length of the bar will be:

$$T_f = \frac{T_0 + T_L}{2}$$

Integrating $d'Q/T$ over a reversible isobaric transfer of heat between a particular volume element and a series of reservoirs ranging in temperature from T_i to T_f , we get the entropy of this one volume element:

$$\begin{aligned} S_f - S_i \text{ (volume element)} &= c_p \rho A dx \int_{T_i}^{T_f} \frac{dT}{T} \\ &= c_p \rho A dx \log \frac{T_f}{T_i} \\ &= c_p \rho A dx \log \frac{T_f}{T_0 - \frac{T_0 - T_L}{L} x} \\ &= -c_p \rho A dx \log \left(\frac{T_0}{T_f} - \frac{T_0 - T_L}{LT_f} x \right) \end{aligned}$$

We now integrate over x from 0 to L to get the complete difference in entropy:

$$S_f - S_i \text{ (system)} = C_p \left[1 - \log \frac{T_L}{T_f} + \frac{T_0}{T_0 - T_L} \log \frac{T_L}{T_0} \right]$$

Since the bar is enclosed by an adiabatic enclosure, there is no entropy change of the surroundings. Hence, the entropy change of the universe is the same.

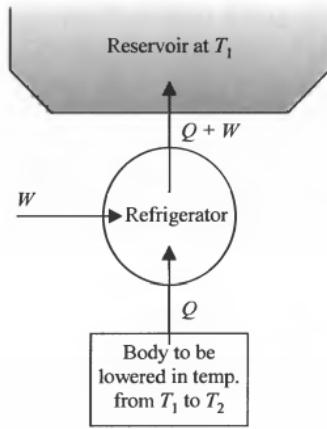
It can be seen that this change is positive.

Principle of Increase of Entropy

We lead to believe that whenever an irreversible process occurs, the entropy of the universe increases. This is known as the **entropy principle**.

We have seen that this is true for all processes involving the irreversible transfer of heat, so we can confine our attention to adiabatic processes only. We start considering the special case of an adiabatic irreversible process between two equilibrium states of a system.

- 1) Let the initial state be represented by the point i on a generalized work diagram, and suppose it undergoes an irreversible adiabatic process to the state f , then the entropy change is $\Delta S = S_f - S_i$


FIGURE 8-11

Operation of a refrigerator in lowering the temperature of a body from that of its surroundings T_1 to any desired temperature T_2 .

A temperature change may or may not have occurred. Let us cause the system to undergo a reversible adiabatic process $f \rightarrow k$ in a sequence of steps that brings the temperature of the system to the temperature of an arbitrary reservoir, say T' . Then, since $S_f = S_k$, the change in entropy becomes:

$$\Delta S = S_k - S_i$$

Suppose that the system is brought into contact with the reservoir at T' and the system undergoes a reversible isothermal process $k \rightarrow j$ until its entropy is the same in state j as in the initial state i . A final reversible adiabatic process $j \rightarrow i$ will now bring the system back to i with no change in entropy, and since $S_j = S_i$, the last equation is:

$$\Delta S = S_k - S_j$$

The only heat transfer Q_R occurred in the cycle during the reversible isothermal process $k \rightarrow j$, where:

$$Q_R = T'(S_j - S_k)$$

A net amount of work has been done in the cycle, where:

$$W = Q_R$$

From the second law, Q_R cannot be positive, for then we have a cyclic process where the only effect is the absorption of heat from a single reservoir and the performance of an equivalent amount of work. Therefore $Q_R \leq 0$ and:

$$T'(S_j - S_k) \leq 0$$

Therefore:

$$S_k - S_j = \Delta S \geq 0$$

2) If we assume that the original irreversible adiabatic process occurred without any change of entropy, then it would be possible to bring the system back to i by means of one reversible adiabatic process.

Moreover, since the net heat transferred in the cycle is zero, the net work would also be 0.

Therefore, the system and its surroundings would have been restored to the initial states without changes elsewhere, so the original process was reversible. This is a contradiction, so the entropy of the system cannot remain unchanged, therefore:

$$\Delta S > 0$$

So, in any kind of process, we have:

$$\Delta S \text{ (universe)} \geq 0$$

Application of the entropy Principle

We have seen that whenever irreversible processes occur, the entropy of the universe increases. In the actual operation of a machine, it is possible to calculate the sum of all the entropy changes.

And the principle is useful

For example: Suppose one wants to cool an object with a refrigerator to a desired low temperature T_2 from a temperature T_1 of the surroundings.

A refrigerator operating between the reservoir at T_1 and the body itself is used. After several complete cycles, a quantity of heat Q has been removed from the body, a quantity of work W has been supplied to the refrigerator and a quantity of heat $Q + W$ has been rejected to the reservoir.

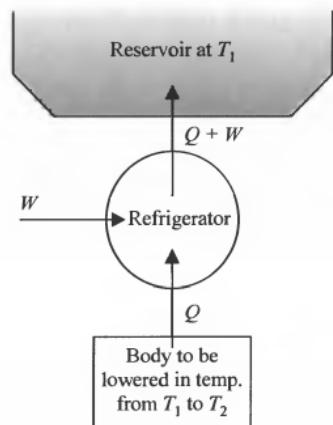


FIGURE 8-11
Operation of a refrigerator in lowering the temperature of a body from that of its surroundings T_1 to any desired temperature T_2 .

The changes of entropy are:

$$\begin{aligned}\Delta S \text{ of the body} &= S_2 - S_1 \\ \Delta S \text{ of the refrigerant} &= 0 \\ \Delta S \text{ of the reservoir} &= \frac{Q + W}{T_1}\end{aligned}$$

Applying the entropy principle, we get:

$$S_2 - S_1 + \frac{Q + W}{T_1} \geq 0$$

We multiply by T_1 we get:

$$W \geq T_1(S_1 - S_2) - Q$$

So the smallest possible value for W is:

$$W(\min) = T_1(S_1 - S_2) - Q$$

We can use tables to obtain $S_1 - S_2$, and if the process is isobaric, we get Q . The calculated value of $W(\min)$ gives an approximation of the minimum amount of work done.

Entropy and disorder

Unlike most quantities in physics and chemistry, the change of entropy of the system and its surroundings is not conserved, rather it increases.

First order phase changes are irreversible, isothermal processes that lend themselves to a descriptive discussion of entropy.

The use of disorder as a synonym for entropy can be seen in the following examples:

- The temperature of an ideal gas does not change and heat is not added to the system during a free expansion, yet entropy increases. Also, there is more 'dissorder'
- The entropy increases in the transition from ferromagnetism to paramagnetism (in the disorder of magnetic moments).
- Entropy increases in the conduction of heat from high to low temperature

Exact Differentials

We know that:

$$dU = d'W + d''Q$$

We see that heat and work are not differentials of a mathematical function, they are inexact, but their sum is exact!

And heat can be expressed as:

$$d'Q = TdS$$

Now, the first law can be written as:

$$dU = -PdV + TdS$$

Pure Substances

PV Diagram for a pure Substance

Let us investigate pure water.

The experiment consists of measurements of P, V at equilibrium for pure water.

The sample is placed in a cylinder closed at one end and contained by a piston, ovens and refrigerators control the temperature.

If 1g of water at $94C$ is introduced into the cylinder of 2 liters in which all air has been removed, it will evaporate completely and the system will be unsaturated vapor, this is state A in the diagram.

If the vapor is compressed slowly and isothermally, the volume is decreasing and the pressure will rise until it reaches a saturated vapor at point B on the isotherm.

If the compression is continued, condensation occurs to form droplets of water. During compression, the pressure now is constant (isobaric) as long as the temperature is constant. This is the line BC thr isothermal isobaric condensation of water vapor as the volume decrease, this constant pressure called **vapor pressure**.

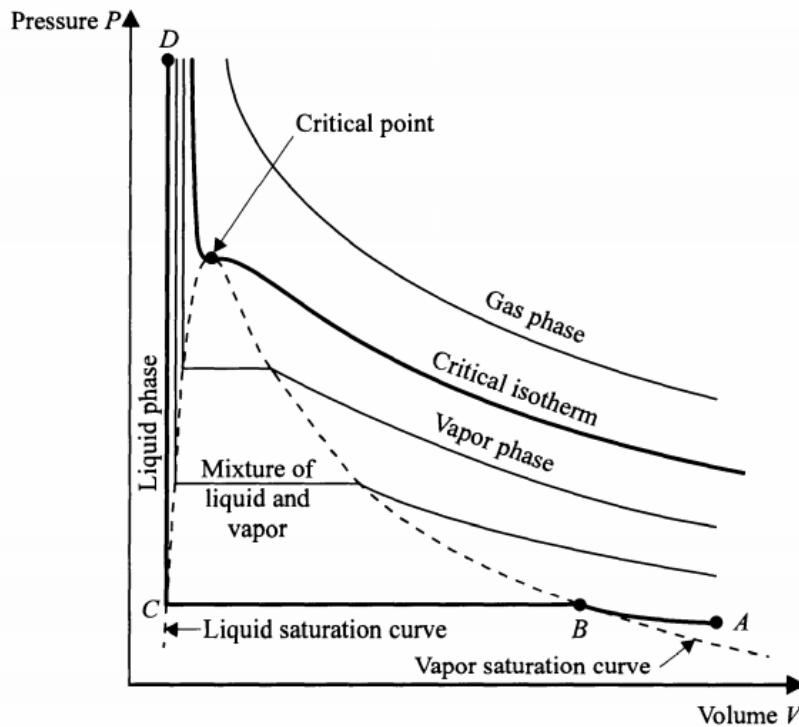
Alternately, as the volume increases, the vaporization line BC represents the isothermal isobaric evaporation of water vapor.

At any point in BC, water and vapor coexist in equilibrium.

At point C, the sample is just liquid water, or **saturated liquid**.

In order to compress the liquid slightly, we need a very large pressure, that is why CD is almost vertical, at any point on CD, the water is liquid phase (just as any point in BC is vapor face)

The curve ABCD is a typical isotherm of a pure substance.



At other temperatures, the **isotherms** have different forms, but we can see they are very similar:

- We begin with a pure vapor (unsaturated)
- We increase the pressure, therefore decreasing the volume.
- Then some vapor transforms into water (just there, we have saturated vapor) and we have a mix.
- We keep on moving the piston, but as long as we have a mix, the pressure doesn't change, and the only thing that happens is that more vapor is transformed to water.
- When all is water, we have a saturated liquid.
- We continue moving the piston, and now we need a very large pressure to barely change the volume.

We see that at higher temperatures, the mix part is smaller.

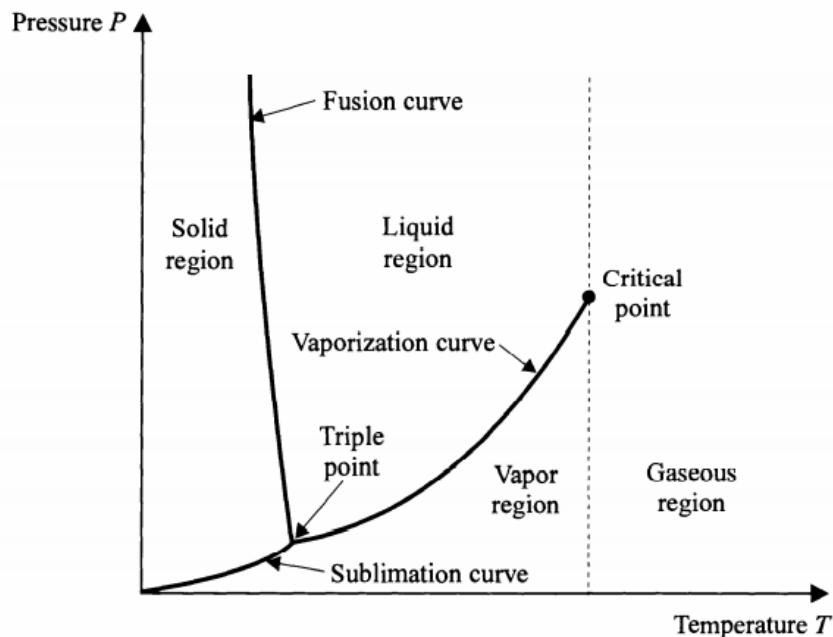
We see that we can draw a curve of the vapor saturation points.

There is a critical temperature in the **critical isotherm** where there is no mixture at all, and it transforms to water without passing through the mixture state in the **critical point**. Where the two saturation curves meet.

Higher than this temperature, the element is in gas phase and approach hyperbolas (just as the ideal Gas law says)

PT diagrams, phase diagram

Consider a solid at very low temperature. If the vapor pressure of a solid is measured at various temperatures until the triple point is reached, we can plot the results in a PT diagram, called a **phase diagram**.



E 9-3

The coexistence of solid and vapor lie on the **sublimation curve**

The coexistence of solid and liquid lies on the **fusion curve**

The coexistence of liquid and vapor on the **vaporization curve** which is bounded by the critical point and the triple point.

The temperatures along the vaporization curve are the boiling points as a function of pressure, in 101325 PA it is 373.124 K.

In the phase diagram, no two phase regions are shown as in the PV diagram. Rather, all two phase states collapse into one of the three curves on the PT diagram, away from the curves there are only single phase equilibrium states.

Vapor is a gas below its critical temperature (that is at a temperature at which it can transform to water isothermally)

The slope of the sublimation and vaporization curves are always positive. For the fusion curve, water is one of the only cases with a negative slope fusion curve (a consequence of the expansion of water when solidifying).

Only on a phase PT diagram is the triple point represented by a single point, on a PV diagram, the triple phase is a line.

At triple point, the three phases coexist at equilibrium.

PVT surface

We can draw the complete surface of equilibrium states of water, and the diagrams are just projections of this.

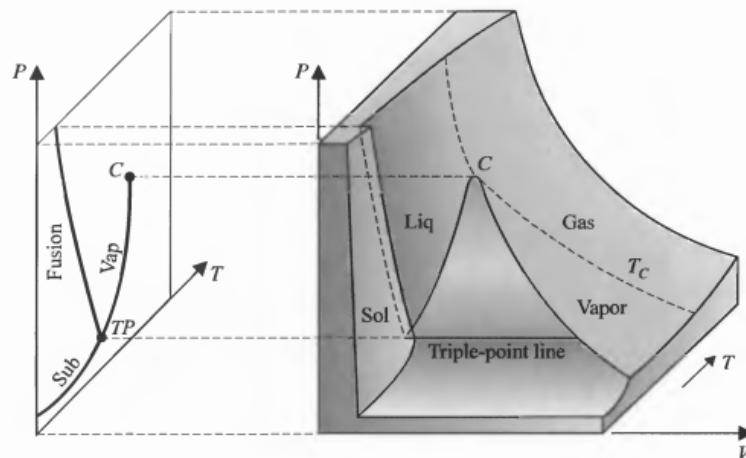


FIGURE 9-4
PVT surface for H_2O , which contracts while melting.

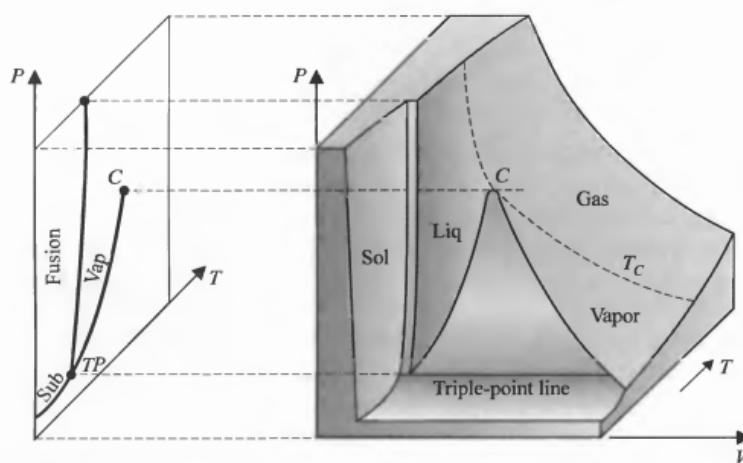


FIGURE 9-5
PVT surface for CO_2 , which expands while melting.

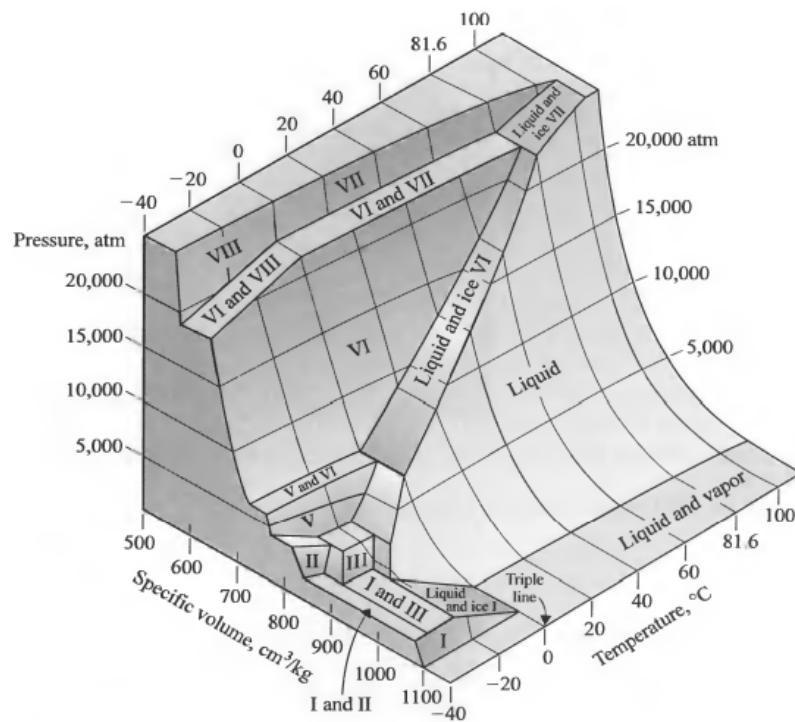


FIGURE 9-6
PVT surface for H_2O , showing all the equilibrium states. A triple line is a line parallel to the axis of specific volume.

Different substances have different diagrams like this one

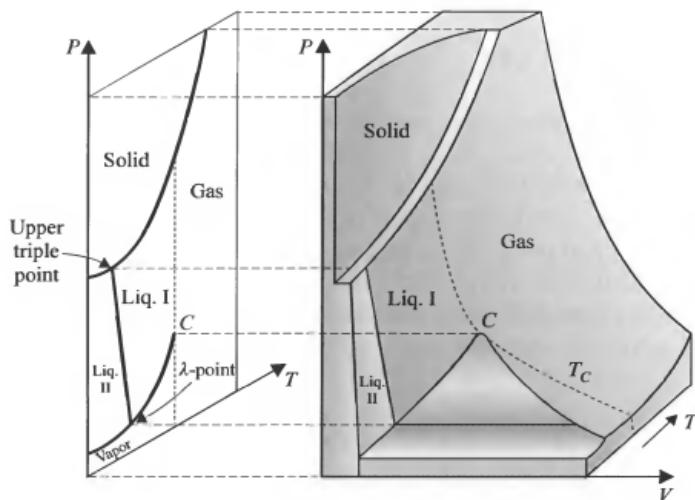


FIGURE 9-7
PVT surface and phase diagram for ${}^4\text{He}$.

Equations of State

It is impossible to express the complete behaviour over the whole measured values of P, V, T with one simple equation.

We need many equations generally.

From the PV diagram, it follows that at the critical point:

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0$$

Also, the critical point is a point of inflection on the critical isotherm, hence:

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0$$

This equations along with the state equation itself allows us to find the critical value.

For example, the Van der Waals eq of state is $P = \frac{RT}{v-b} - \frac{a}{v^2}$ where $v = V/n$. (this equation is valid near the critical point).

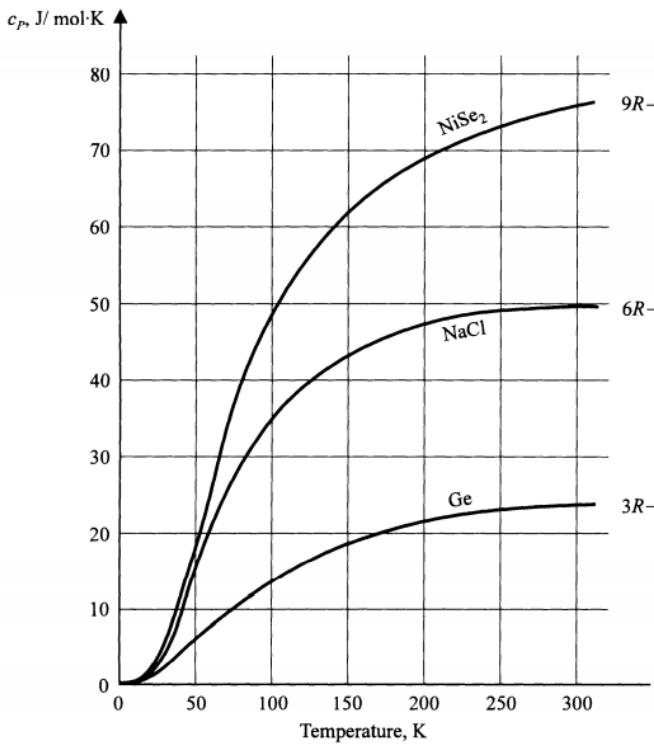
Then, from the equations derived earlier, we can get two equations with variables v_C and T_C .

And we get $v_C = 3b$, $T_C = \frac{8a}{27bR}$ and $P_C = \frac{a}{27b^2}$

We can thus calculate $\frac{RT_C}{P_C v_C} = 2.67$

Molar heat capacity at constant pressure

$c_p = C_p/n = (\partial Q/\partial T)_P/n$ is in general not constant, but we can graph its behaviour experimentally

**FIGURE 9-8**

Molar heat capacity at constant pressure of three crystalline nonmetals. (Ge: P. H. Keesom and G. Seidel: *Physical Review*, vol. 113, pp. 33–39, 1959. NaCl: K. Clusius, J. Goldmann, and A. Perlick: *Zeitschrift für Naturforschung*, vol. 4a, pp. 424–432, 1949. NiSe_2 : F. Grønvold and E. F. Westrum: *Inorganic Chemistry*, vol. 1, pp. 36–48, 1962.)

We can see that in general, the heat capacity c_p is higher at higher temperatures. At higher temperatures, a small change in T has a big effect on Q .

Volume expansivity

The volume expansivity $\beta = 1/V(\partial V/\partial T)_P$ is measured directly.

But the linear expansion coefficient may be useful too.

It can be proven that if α_i is the linear expansion coefficient in the i th direction, then:

$$\beta = \alpha_1 + \alpha_2 + \alpha_3$$

Compressibility

Isothermal compressibility is:

$$k = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

We can also define **reversible adiabatic compressibility**:

$$k_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S$$

it results that:

$$c_p - c_V = \frac{Tv\beta^2}{k}$$

And the ration of molar heat capacities is:

$$\gamma = \frac{c_p}{c_V} = \frac{k}{k_S}$$

So, we can find:

$$k - k_S = \frac{Tv\beta^2}{c_p}$$

Molar Heat capacity at constant volume

We can measure c_p, β, k and so use:

$$c_p - c_V = \frac{Tv\beta^2}{k}$$

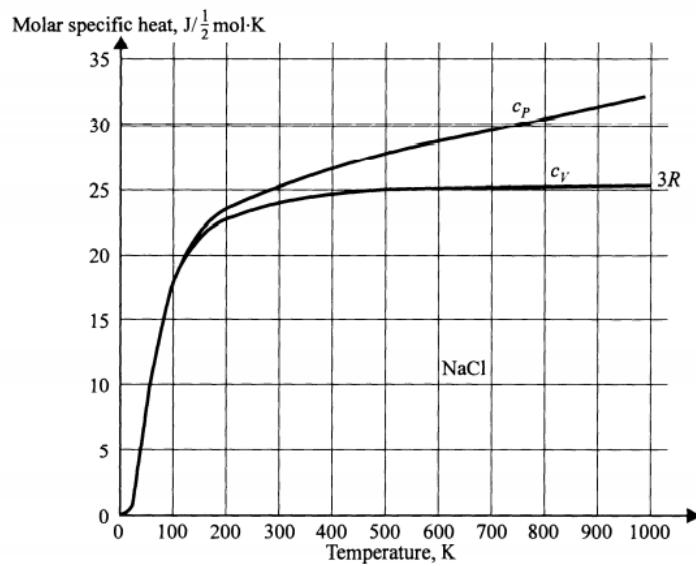
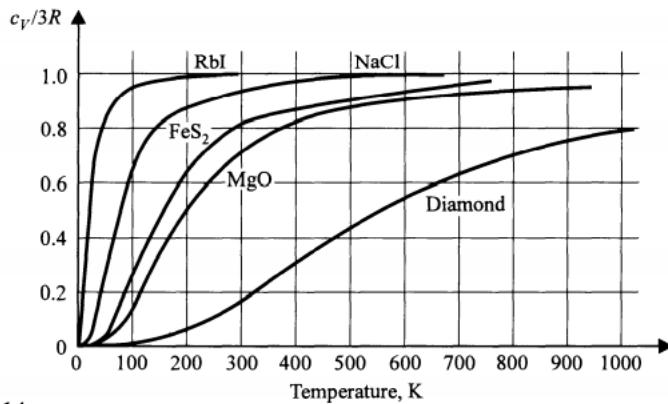


FIGURE 9-13

Temperature variation of c_p and c_V of $\frac{1}{2}$ mol of NaCl. The value of c_V is close to $3R$ at high temperatures.

**FIGURE 9-14**

Temperature variation of $c_V/3R$ of nonmetals. (1 mol of diamond, $\frac{1}{2}$ mol of RbI, NaCl, and MgO; and $\frac{1}{3}$ mol of FeS₂.)

TS diagram for a pure substance

We know that entropy is a function of thermodynamic coordinates whose difference in equilibrium states is:

$$S_f - S_i = \int_{i-R}^f \frac{d'Q}{T}$$

If the equilibrium states are very close:

$$\begin{aligned} d'Q &= TdS \\ \Rightarrow \frac{d'Q}{dT} &= T \frac{dS}{dT} \end{aligned}$$

So, at **constant pressure**:

$$\left(\frac{d'Q}{dT} \right)_P = C_p = T \left(\frac{\partial S}{\partial T} \right)_P$$

So, at **constant volume**:

$$\left(\frac{d'Q}{dT} \right)_V = C_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

The entropy change during a

If the temperature variation of C_V is known, the entropy change during an isobaric process may be calculated from the equation

$$S_f - S_i \text{ (isobaric)} = \int_i^f \frac{C_P}{T} dT.$$

Similarly, for an isochoric process,

$$S_f - S_i \text{ (isochoric)} = \int_i^f \frac{C_V}{T} dT.$$

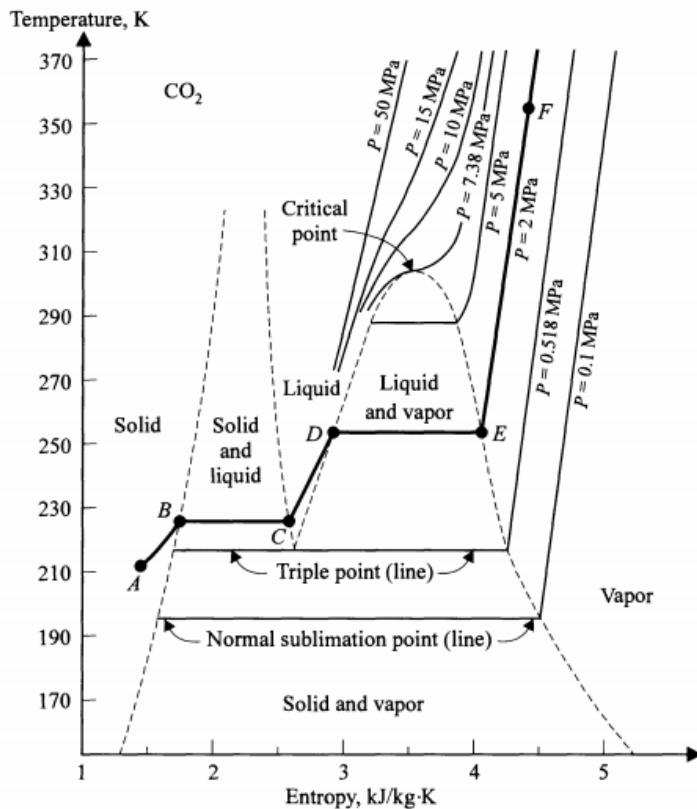


FIGURE 9-15
TS diagram for CO_2 showing isobaric process ABCDEF.

- $AB =$ isobaric heating of solid to its melting point,
- $BC =$ isobaric isothermal melting,
- $CD =$ isobaric heating of liquid to its boiling point,
- $DE =$ isobaric isothermal vaporization,
- $EF =$ isobaric heating of vapor (superheating).

The area under the curve is $\int TdS = Q$.

So, the area under the segment BC is the latent heat of fusion at the particular temperature

and under DE it is the latent heat of vaporization.

And for curves with temperature under the triple line, it is a direct sublimation, whose area is then the latent heat of vaporization.

We see that the heat needed decreases at higher temperatures for the three processes

Only at the triple point is latent heat of sublimation equal to the sum of the other two.

Mathematical functions

Characteristic Functions

If the state of a system is described by a function of two variables $f(x, y)$, which satisfies the equation:

$$df = udx + vdy$$

And we wish to change the description to one involving a new function $g(u, y)$ satisfying a similar equation in terms of du and dy , then it is necessary to define the **Legendre transform** $g(u, y)$ as:

$$g := f - ux$$

Therefore, we find that:

$$\begin{aligned} dg &= df - udx - xdu \\ &= udx + vdy - udx + xdu \\ &= -xdu + vdy \end{aligned}$$

Consider the first law of thermodynamics for a hydrostatic system expressed in terms of temperature and entropy:

$$dU = -PdV + TdS$$

We define a new function H , called **Enthalpy** as the Legendre transform of U , that is, we define it as:

$$H := U + PV$$

Since U, P, V are state functions, H is a **state function**.

And in differential form, just as the Legendre transform says, we get:

$$dH = VdP + TdS$$

H is a state function of characterized by P and S .

On the other hand, if we write U as:

$$dU = TdS - PdV$$

And apply the Legendre transform but now differently, we define the **Helmholtz function** \mathbf{A} as:

$$A := U - TS$$

Which is also a state function, depending on T and V in differential form:

$$dA = -SdT - PdV$$

Where A is a function of T and V .

If we now begin with the enthalpy differential and apply a Legendre transform:

$$dH = TdS + VdP$$

Then, the transform is the **Gibbs function** G defined as:

$$G := H - TS$$

Which is a state function characterized by P and T with differential:

$$dG = VdP - SdT$$

So, we have four differential equations that are formulations of the first law, namely:

$$\begin{aligned} dU &= -PdV + TdS \\ dH &= VdP + TdS \\ dA &= -PdV - SdT \\ dG &= VdP - SdT \end{aligned}$$

These form a complete set of functions based on successive Legendre transformation of the four thermodynamic variables P, V, T, S for a hydrostatic system.

The characteristic functions $U(V, S), H(P, S), A(V, T), G(P, T)$ are the **thermodynamic potential functions**.

If the functions are expressed in terms of the appropriate thermodynamic variables, then all the thermodynamic properties of a system can be calculated by differentiation only.

For instance, if the internal energy function U is known as a function of V and S for a system, then we can calculate the other thermodynamic properties are obtained by differentiation, because we may write:

$$dU = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS$$

From which it follows that:

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad , \quad \left(\frac{\partial U}{\partial S}\right)_V = T$$

However if U were chosen to be a function of V and T , we could not obtain the rest of the properties without integration (and therefore introducing constants)
So it is important to have the equation defined in the right way.

For other systems, we replace volume with the other extensive variable and replace $-P$ with the intensive one. For example

site system of an ideal paramagnetic gas was considered. Its four characteristic functions are:

$$\begin{aligned} dU &= -P dV + \mu_0 \mathcal{H} dM + T dS, \\ dH &= V dP - M \mu_0 d\mathcal{H} + T dS, \\ dA &= -P dV + \mu_0 \mathcal{H} dM - S dT, \end{aligned} \quad (10.12)$$

and

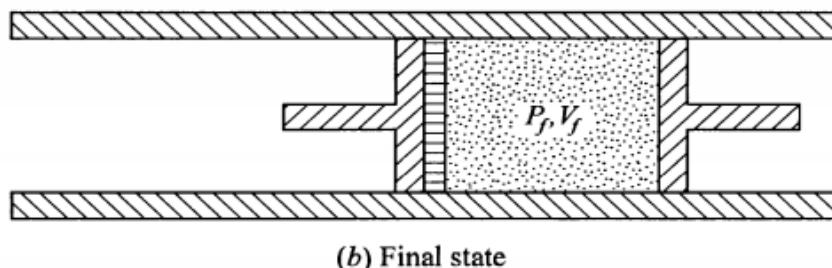
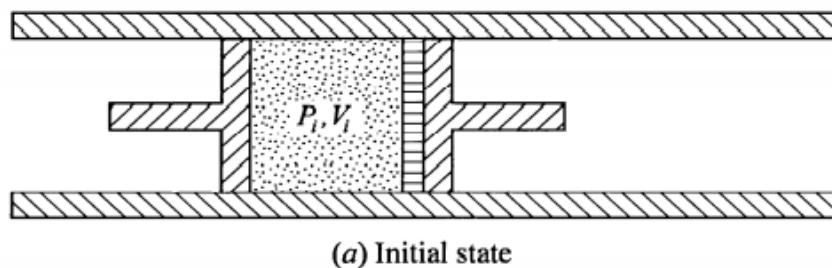
$$dG = V dP - M \mu_0 d\mathcal{H} - S dT.$$

Obviously in a simple system of a paramagnetic solid the terms involving the

Enthalpy

In the study of ideal gases, the sum $U + PV$ appeared several times.

In order to investigate this sum, imagine a cylinder, thermally insulated and equipped with two adiabatic pistons on opposite sides of a porous wall that is also adiabatic



The porous wall permits mass to flow from one chamber to another while controlling the pressure.

Between the left piston and the wall, there is a gas at pressure P_i and volume V_i and at the beginning, all the gas is to the left of the wall.

Now both pistons move simultaneously at different speeds to the right such that a constant higher pressure P_i is maintained on the left hand side of the porous plug and a constant lower pressure P_f is maintained on the right hand side.

After all the gas has gone through the wall, the final stage is in figure b).

This is a **porous plug process or a Joule Thomson Expansion**.

The process is irreversible, because of the friction in the porous. in the process, the gas passes through dissipative nonequilibrium states on its way from the initial equilibrium state to the final equilibrium state.

The intermediate states cannot be described by thermodynamic coordinates.

From the first law, seeing the initial and final states, we have:

$$(U_f - U_i) = W + Q$$

The process occurs in adiabatic enclosure, so $Q = 0$

The net work done by the pistons on the gas causes the gas to flow across the boundary of the system enclosing the porous plug, that is,

$$W = - \int_{V_f}^0 P_f dV - \int_0^{V_i} P_i dV$$

Since both pressures remain constant on either side, we have:

$$W = -(P_f V_f - P_i V_i)$$

Therefore, we see that the initial and final equilibrium states have different internal energy.

But we can device a state function that has the same values in the end states for the Joule Thomson expansion.

We have that:

$$\begin{aligned} (U_f - U_i) &= -(P_f V_f - P_i V_i) \\ \Rightarrow U_i + P_i V_i &= U_f + P_f V_f \end{aligned}$$

Therefore, if we define:

$$H = U + PV$$

as the **enthalpy**.

And we see that for a **Throttling process**, we have:

$$\text{Property 1)} \quad H_i = H_f$$

We see that it is equal in initial and final state, though that doesn't mean that H is conserved along the process.

To determine the properties of enthalpy, we see that:

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= d'Q + VdP \end{aligned}$$

We can divide by dT to obtain:

$$\frac{dH}{dT} = \frac{d'Q}{dT} + V \frac{dP}{dT}$$

And therefore, at constant P , we have:

$$\text{Property 2: } \left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{d'Q}{dT} \right)_P = C_P$$

Notice that H is a function of T, P to make this derivative.

Furthermore, for **all processes** we have:

$$H_f - H_i = \int_i^f C_P dT$$

For example, for an ideal gas, $H_f - H_i = C_P(T_f - T_i)$

Again, as $dH = d'Q + VdP$, we have that

For an **isobaric** process:

$$\text{property 3)} \quad H_f - H_i = Q_P$$

Therefore, for isochoric process, heat is the flow of internal energy. Whereas for an isobaric process, heat is the flow of enthalpy.

If heat is added during a first order phase transition (e.g. melting, boiling, sublimation), then the change of enthalpy of the system is called 'latent heat'. The word 'latent' acknowledges that there is no change in temperature of the system, we could better call it latent enthalpy.

The change in enthalpy of a system that undergoes a reversible **adiabatic** process is, starting from $dH = d'Q + VdP$:

$$\text{Property 4)} \quad H_f - H_i = \int_i^f VdP \quad \text{Adiabatic}$$

This is the area to the left of a curve for an isentropic process on a PV diagram

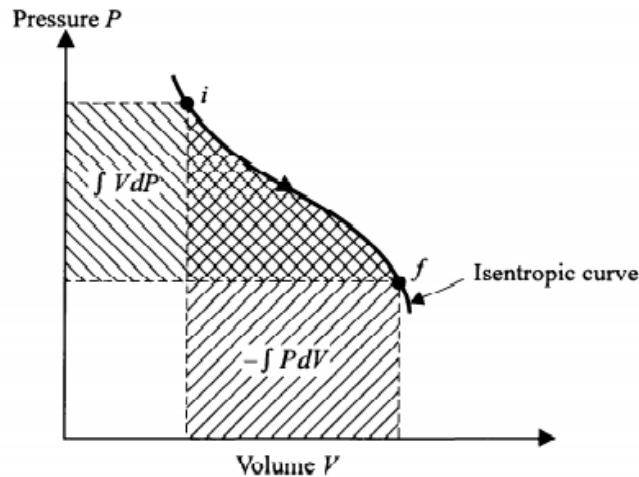


FIGURE 10-3
 PV diagram illustrating the difference between work and flow-work.

If a pure substance undergoes an infinitesimal reversible process, then we can write:

$$dH = TdS + VdP$$

Which of course, means that we can use partial differentiation to get:

$$\left(\frac{\partial H}{\partial S} \right)_P = T \quad , \quad \left(\frac{\partial H}{\partial P} \right)_S = V$$

We can summarize:

Comparison of properties of U and H for a hydrostatic system

Internal energy $U(V, S)$	Enthalpy $H(P, S)$
Free expansion (irreversible) $U_i = U_f$	Throttling process (irreversible) $H_i = H_f$
In general $dU = dQ - P dV$ $\left(\frac{\partial U}{\partial T}\right)_V = C_V$	In general $dH = dQ + V dP$ $\left(\frac{\partial H}{\partial T}\right)_P = C_P$
Isochoric process $U_f - U_i = Q_V$	Isobaric process $H_f - H_i = Q_P$
For an ideal gas $U_f - U_i = \int_i^f C_V dT$	For an ideal gas $H_f - H_i = \int_i^f C_P dT$
Adiabatic process $U_f - U_i = - \int_i^f P dV$	Adiabatic process $H_f - H_i = \int_i^f V dP$
Nearby equilibrium states $dU = T dS - P dV$ $\left(\frac{\partial U}{\partial S}\right)_V = T$ $\left(\frac{\partial U}{\partial V}\right)_S = -P$	Nearby equilibrium states $dH = T dS + V dP$ $\left(\frac{\partial H}{\partial S}\right)_P = T$ $\left(\frac{\partial H}{\partial P}\right)_S = V$

Helmholtz and Gibbs Functions

The Helmholtz function $A(V, T)$ is given by:

$$A = U - TS$$

For an infinitesimal reversible process, the Helmholtz function is:

$$dA = -PdV - SdT$$

So it follows:

- For a reversible isothermal process

$$dA = -PdV$$

Or:

$$(A_f - A_i)_T = - \int_i^f (PdV)_T$$

Hence, the *increase* of the Helmholtz function during a reversible isothermal process equals the work done *on* the system.

Alternatively, in a reversible isothermal process, the decrease in Helmholtz function is the maximum amount of work done by the system.

That is why it is called the **Helmholtz free energy**.

For any finite isothermal process, we may write:

$$\begin{aligned}\Delta A_T &= \Delta U_T - T\Delta S_T \\ \Rightarrow \Delta A_T &= \Delta U_T - \Delta Q_T = \Delta W_T\end{aligned}$$

The decrease of the Helmholtz energy ΔA_T equals the maximum amount of isothermal work ΔW_T that is performed by the system.

The internal energy also decreases ΔU_T , but the decrease is not equal to the work that the system can perform.

$$\Delta W_T \geq \Delta U \quad \text{depending on} \quad \Delta Q_T \geq 0$$

2) For a **reversible isothermal and isochoric process**:

$$dA = 0$$

So

$$A = cte$$

So the Helmholtz function has the same initial and final values when the initial and final temperatures and volumes are unchanged.

From the differential of the Helmholtz function:

$$dA = -PdV - SdT$$

Then, the pressure and entropy can be calculate by simple differentiation:

$$\left(\frac{\partial A}{\partial V} \right)_T = -P \quad , \quad \left(\frac{\partial A}{\partial T} \right)_V = -S$$

Gibbs function:

The Gibbs function $G(P, T)$ is:

$$G = H - TS$$

Or, differentially

$$dG = VdP - SdT$$

So the volume and the entropy may be calculated by differentiation:

$$\left(\frac{\partial G}{\partial P} \right)_T = V \quad , \quad \left(\frac{\partial G}{\partial T} \right)_P = -S$$

So, in the case of a **reversible isothermal and isobaric process**:

$$\begin{aligned} dG &= 0 \\ G &= cte \end{aligned}$$

This is important for processes involving change of phase. Sublimation, fusion and vaporization take place isothermally and isobarically. Hence, during such processes, the Gibbs function of the system remains constant.

We denote by the symbols g' , g'' , g''' the molar Gibbs functions of a saturated solid, saturated liquid and saturated vapor, then the equation of the fusion curve is:

$$g' = g''$$

The equation of the vaporization curve is:

$$g'' = g'''$$

The equation of the sublimation curve is:

$$g' = g'''$$

And the equation of the triple point is:

$$g' = g'' = g'''$$

All the g s are functions of P and T only. And hence, this last equations serves to find the pressure and temperature of the triple point (triple line of different volumes).

this is extremely important in chemistry, since chemical reactions begin and end at the same equilibrium atmospheric pressure and ambient temperature.

Two Mathematical Theorems

Theorem 1: If a relation exists among x, y, z , then we may imagine z written as a function of x, y , whence:

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

Then, if we let $M = \left(\frac{\partial z}{\partial x} \right)_y$ and $N = \left(\frac{\partial z}{\partial y} \right)_x$

Then $dx = M dx + N dy$

Where z, M, N are all functions of x, y .

Differentiating, we get:

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$$

This is the **condition for an exact differential** and applies for all 4 characteristic functions.

Theorem 2: If f is a function of x, y, z and a relation exists between x, y, z , then f can be regarded as a function of any two of x, y, z . Similarly, any other x, y, z can be considered as a function of f and the other x, y, z .

Then we can find that:

$$\left(\frac{\partial x}{\partial y} \right)_f \left(\frac{\partial y}{\partial z} \right)_f \left(\frac{\partial z}{\partial x} \right)_f = 1$$

Notice that it is different from the equation that gave -1, that is because there are now 4 variables instead of 3.

Also:

$$\left(\frac{\partial x}{\partial f} \right)_z = \left(\frac{\partial x}{\partial f} \right)_y + \left(\frac{\partial x}{\partial y} \right)_f \left(\frac{\partial y}{\partial f} \right)_z$$

Maxwell's Relations

We have seen that for a hydrostatic system of a pure substance, we have that:

$$\begin{aligned} dU &= -PdV + TdS \\ dH &= VdP + TdS \\ dA &= -PdV - SdT \\ dG &= VdP - SdT \end{aligned}$$

Since they are all state functions, the differentials are exact, so we can use the first theorem to get:

1. $dU = T dS - P dV$; hence, $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$.
 2. $dH = T dS + V dP$; hence, $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$.
 3. $dA = -S dT - P dV$; hence, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$.
 4. $dG = -S dT + V dP$; hence, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$.
- (10.33)

These are Maxwell's Relations

these relations hold at any equilibrium state of a hydrostatic system.

They provide relationships between measurable quantities and difficult to measure quantities. for example, the 4th Maxwell relation can be combined with the volume expansivity β of a pure substance to provide information concerning the statistical interpretation of entropy

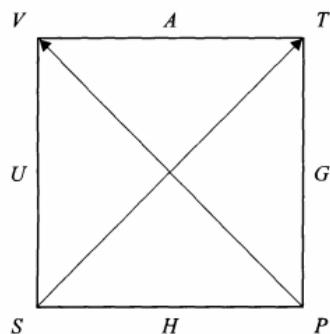


FIGURE 10-4
The VAT-VUS diagram; a mnemonic device for writing the differential forms of the four thermodynamic potentials.

T dS equations

The entropy of a pure substance can be considered as a function of any two variables, such as T, V , thus:

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

And then:

$$TdS = T \left(\frac{\partial S}{\partial T} \right)_V dT + T \left(\frac{\partial S}{\partial V} \right)_T dV$$

Since $TdS = d'Q$. Then, for a reversible isochoric process:

$$T \left(\frac{\partial S}{\partial T} \right)_V = C_V$$

And from Maxwell's 3rd relation, $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$, so:

$$TdS = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV$$

This is the **First TdS equation**.

Example: 1 mol of van der Waals gas undergoes a reversible isothermal expansion from an initial molar volume v_i to a final molar volume v_f . How much heat is transferred? For 1 mol:

$$Tds = c_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dv$$

Where all underscore quantities are molar.

We use the molar van der Waals equation:

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

And $\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{v - b}$

Hence, the equation is:

$$TdS = c_V dT + RT \frac{dv}{v - b}$$

Since T is constant, $dT = 0$, and since the process is reversible, $q = \int Tds$. Therefore:

$$q = RT \int_{v_1}^{v_f} \frac{dv}{v - b} = RT \log \frac{v_f - b}{v_i - b}$$

Second TdS equation

We regard $S = S(T, P)$ and write it as $dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

Then, $TdS = T \left(\frac{\partial S}{\partial T}\right)_P dT + T \left(\frac{\partial S}{\partial P}\right)_T dP$.

But $T \frac{\partial S}{\partial T} = C_p$.

And from Maxwell's 4th, we have $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

So finally:

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T}\right)_P dP$$

This is the **Second TdS equation**.

Example: For reversible isothermal change of pressure, when T is constant, we have:

$$Q = -T \int \left(\frac{\partial V}{\partial T}\right)_P dP = -T \int V \beta dP$$

This equation is even better if β and V are nearly constant, for $Q = -TV\beta(P_f - P_i)$

Similarly, for an isothermal process we can find:

$$W = - \int \left(\frac{\partial V}{\partial P}\right)_T P dP = \int_{P_i}^{P_f} V k P dP$$

Which, if volume and k are nearly constants, then $W \simeq \frac{1}{2}V k P_f^2$

Reversible adiabatic change of pressure

Since entropy is constant in this process, $TdS = 0 = C_P dT - T \left(\frac{\partial V}{\partial T}\right)_P dP$

$$\text{So } dT = \frac{TV\beta}{C_P} dP$$

Internal energy equations

We begin with $dU = TdS - PdV$ and divide by dV .

If T is **constant**, and using Maxwell 3rd, we get:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

This is the **first internal energy equation**.

Example:

- Ideal gas.

As $P = \frac{nRT}{V}$, we have $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$ and therefore:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{nR}{V} - P = 0$$

So U doesn't depend on V .

- For Van der Waals gas (1 mol)

We have $P = \frac{RT}{v-b} - \frac{1}{v^2}$, so substituting, we get:

$$\left(\frac{\partial u}{\partial v}\right)_T = \frac{a}{v^2}$$

Consequently, $du = c_V dT + \frac{a}{v^2} dv$, so

$$u = \int c_V dT - \frac{a}{v} + cte$$

So the internal energy of Wan der Walls does depend on volume.

Second Internal energy equation

$$\left(\frac{\partial U}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T$$

Heat capacity equations

We begin with the first and second TdS and equate them.

After some work, we get:

$$C_p - C_V = -T \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right) T$$

From this, we conclude:

- Since $\partial P/\partial V)_T$ is positive for all known substances, then C_p is greater than C_V

- As $T \rightarrow 0$, then $C_p \rightarrow C_V$
- $C_p = C_V$ when $\partial V / \partial T)_P = 0$

Using k, β , we may write:

$$c_p - c_V = P \frac{T v \beta^2}{k}$$

Open Systems

Joule Thomson Expansion

The Joule Thomson expansion or Throttling process was already defined before in last chapter.

The experiment is the following. The pressure P_i and temperature T_i on the high pressure side of the plug are chosen arbitrarily.

The pressure P_f on the other side of the plug is then set at any value less than P_i , and the temperature of the gas T_f is measured.

Next, P_i and T_i are kept the same, P_f is changed to another value and the corresponding T_f measured in each case.

The final pressure P_f is the independent variable of the experiment and T_f the dependent variables.

The results provide a set of discrete points on a phase diagram one point being (P_i, T_i) and the others being the various corresponding P_f and T_f

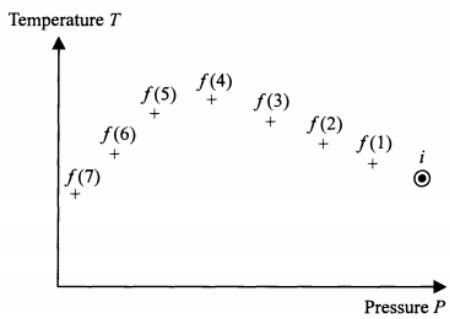


FIGURE 11-1
Isenthalpic states of a gas undergoing the Joule-Thomson expansion.

We see that, if a throttling process takes place between the states (P_i, T_i) and (P_f, T_f) (4), there is a rise in temperature.

However, between (P_i, T_i) and (P_f, T_f) (7) there is a drop of temperature.

According to the discussion of enthalpy, the eight points plotted represent equilibrium states of a certain amount of the gas (say, 1 mol), for which the gas has the same enthalpy at the initial equilibrium state and at the final equilibrium state.

A **Isenthalpic curve** is the locus of all points representing equilibrium initial and final states of the same molar enthalpy.

Notice, it is just all points with same molae enthalpy, it is not the process of any system.

Now, the temperature T_i on the high pressure side is now change to another value with P_i the same.

The final pressure P_f is again varied, and the corresponding T_f s are measured.

So we plot (P_i, T_i) and all the (P_f, T_f) to get another isenthalpic curve.

The numerical value of the slope of an isenthalpic curve on a TP diagram at any point, is called the **Joule-Thomson coefficient** and is denoted by μ . Thus:

$$\mu = \left(\frac{\partial T}{\partial P} \right)_h$$

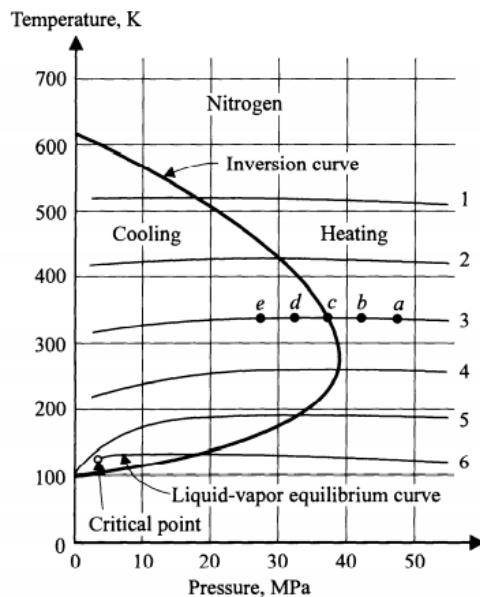


FIGURE 11-2
Isenthalpic curves, labeled 1–6, and inversion curve for nitrogen. In the region below the liquid–vapor curve, the substance is in the liquid phase.

that is, the Joule Thomson coefficient is the slope at a point on the isenthalpic expansion curve.

The locus of all points at which $\mu = 0$ (the locus of maxima of the isenthalpic curves) is known as the **inversion curve**.

The region inside the inversion curve, where $\mu > 0$, is called the **region of cooling**, that is the final temperature of the curve is less than the initial.

The region outside the curve, where μ is negative, is called the **region of heating**, that is, the final temperature is more than the initial temperature.

for example, a expansion from (a) to (b) or (c) raises the temperature of the gas, whereas movement from points (c) or (d) to (e) lowers the temperature of the gas.

Since the Joule Thomson coefficient involves T, P, h , we seek a relation among the differentials of T, P, h . In general, the difference in molar enthalpy between two neighboring equilibrium states is:

$$dh = Tds + v dP$$

And according to the second Tds equation, $Tds = c_p dT - T \left(\frac{\partial v}{\partial T} \right)_P dP$

Substituting for dS_s and using $\mu = (\partial T / \partial P)_h$ gives:

$$\mu = \frac{1}{c_p} \left[T \left(\frac{\partial v}{\partial T} \right)_P - v \right]$$

This is the thermodynamic equation for the Joule Thomson coefficient. The condition for the inversion curve, $\mu = 0$ is met when the term in brackets vanishes.

Liquefaction of Gases by the Joule-Thomson Expansion

An inspection of the isenthalpic curves and the inversion curve shows that, for the Joule Thomson expansion to give rise to cooling, the initial temperature of the gas must be below the point where the inversion curve intercepts the temperature axis, that is, below the maximum inversion temperature. Otherwise, the Joule Thomson expansion raises the temperature of the gas.

That way, Joule Thomson cooling can be used to cool a gas, but sometimes some precooling is necessary, because it must be first below the maximum inversion temperature.

Once a gas has been precooled, the optimum pressure from which to start corresponds to a point on the inversion curve, because it is the last point we can begin to cool in. Starting at this pressure and ending at atmospheric pressure, the process produces the largest temperature drop.

After successive throttling, the gas may become partly liquified.

First Order Phase Transitions; Clausius-Clapeyron Equation

In phase transitions, the temperature and pressure remain constant, while volume and entropy change. Consider n_0 moles of material in phase i with molar entropy $s^{(i)}$ and molar volume $v^{(i)}$, both are functions of T and P , and hence remain constant during the phase transition that ends with the material in phase f with molar entropy s^f and molar volume v^f .

Let x be the fraction of the **initial phase** that has been transformed into the final phase at any moment. Then, the entropy S and volume V of the mixture at any moment are given by:

$$S = n_0(1-x)s^i + n_0x s^f$$

$$V = n_0(1-x)v^i + n_0x v^f$$

If the phase transition takes place reversibly at constant pressure, then the change of enthalpy per mole is:

$$\Delta h = T(s^f - s^i)$$

The change in molar enthalpy, therefore means there is a change of molar entropy, since $dg = -sdT + vdP$, then $s = -\left(\frac{\partial g}{\partial T}\right)_P$ and $v = \left(\frac{\partial g}{\partial P}\right)_T$.

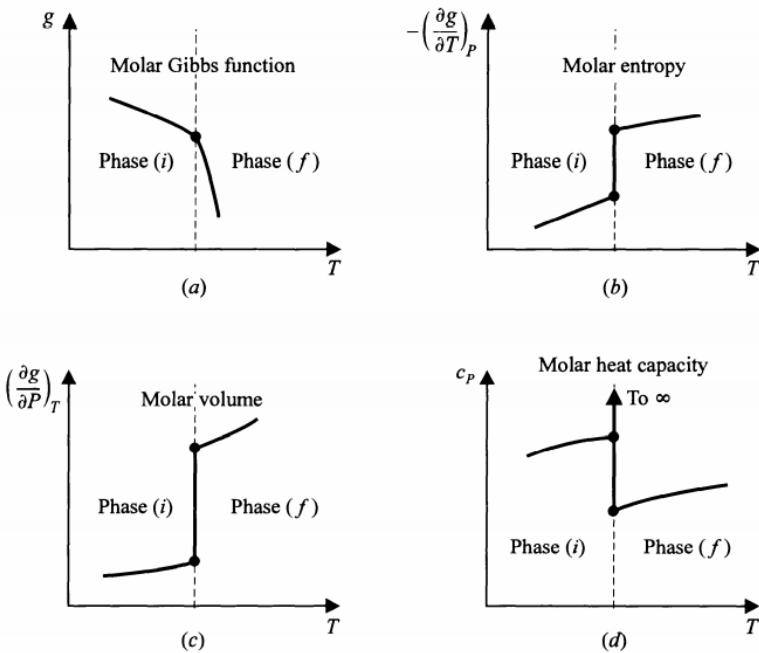
So, we may characterize the familiar phase transitions by the following equivalent statements:

- There are changes of molar entropy and molar volume
- The first order derivatives of the molar Gibbs function change discontinuously

Any phase change that satisfies these requirements is a **phase change of the first order**

Any phase change that satisfies these requirements is known as a *phase change of the first order*. For such a phase change, the temperature variation of g , s , v , and c_p are shown by four graphs in Fig. 11-9, which shows a phase change from liquid to vapor. The phase transition may be regarded as accomplished reversibly in either direction. Notice that the molar Gibbs function has a single value at the vaporization temperature, but the slope is discontinuous

The fourth graph, showing the behavior of molar heat capacity c_p , is particularly significant in that *the c_p of a mixture of two phases during the*



Clausius Clapeyron equation

$$\boxed{\frac{dP}{dT} = \frac{s^f - s^i}{v^f - v^i} = \frac{h^f - h^i}{T(v^f - v^i)}}$$

This equation applies for any first order change of phase or any transition that occurs at constant T and P .

The difference in molar enthalpies at a fixed pressure $h^f - h^i$ is also known as the **molar latent heat**.

We can derive it as follows:

For a change of phase at T and P , the molar Gibbs functions are equal at the end states, so $g^i = g^f$.

And for a phase change at $T + dT$ and $P + dP$, $g^i + dg^i = g^f + dg^f$

Subtracting, we get:

$$\begin{aligned} dg^i &= dg^f \\ \Rightarrow -s^i dT + v^i dP &= -d^f dT + v^f dP \\ \Rightarrow \frac{dP}{dT} &= \frac{s^f - s^i}{v^f - v^i} = \frac{h^f - h^i}{T(v^f - v^i)} \end{aligned}$$

Clausius Clapeyron Equation and Phase Diagrams

The equation is important to the understanding of the coexistence curves in phase diagrams, such as the following one, that is a PT diagram of H_2O and of CO_2

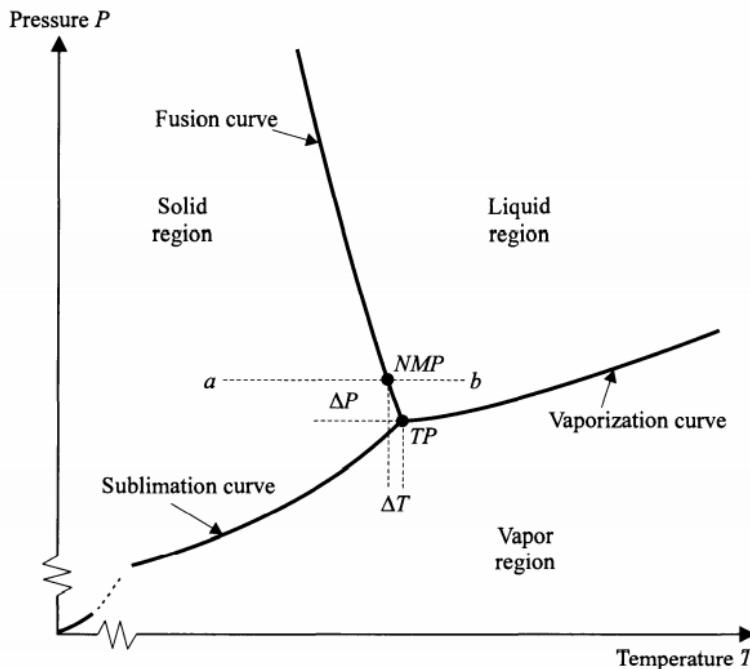


FIGURE 11-10

Phase diagram for H_2O in the region of the triple point and normal melting point.

A system in a point on a coexisting curve of the diagram is a system made of coexisting phases.

The Clausius Claperyon equation, however is not concerned with the coordinates, but the slope.

Consider a sample of ice with initial temperature T below the melting temperature and open to atmospheric pressure P , which remains constant.

Heating that increases the enthalpy also rises the temperature. A system in the solid state such as a) moves horizontally until it reaches the fusion curve (remember constant pressure) Additional heat melts the ice to produce liquid water, but with no change of temperature, which is the normal melting point T_{NMP} .

After enough heating has melted the ice, the temperature of the system rises again moving towards b and the vaporization curve.

A sample of ice at the T_{NMP} coexists with water and air at standard atmospheric pressure. If the sample is placed in a chamber and the air pressure of the system is lowered, then there has been a small change in pressure ΔP and the state of the system would no longer lie on the fusion curve. As a result, the temperature of the system will change by ΔT to return the state to the fusion curve.

For a small order approximation, the change in temperature is $\Delta T = \Delta P/(dP/dT)$

The negative slope of the fusion curve for H_2O partially explains why the triple point temperature $T_{TP} = 273.16K$ is higher than the normal melting temperature $T_{NMP} = 273.15K$. At the normal melting point, ice and water are in equilibrium with air at a pressure of 101,325 Pa. At the triple point, however, ice and water are in equilibrium with water vapor, which has a vapor pressure of only 612 Pa.

Then, we obtain that (assuming that enthalpies and molar volumes are constant):

$$\Delta T = \frac{T(v'' - v')}{h'' - h'} \Delta P$$

Where single primed quantities refer to the solid phase and double to the liquid phase.

Take the triple point of water to be the initial point.

The change in temperature by increasing the pressure from essentially zero to the triple point to the atmospheric pressure for the normal melting point can be calculated to the three significant figures using $T = 273K$, $v' = 19.64 \times 10^{-6}m^3/mol$, $v'' = 18.02 \times 10^{-6}m^3/mol$, $h'' - h' = 6.01Kj/mol$ and $\Delta P = 1.01 \times 10^5Pa$, which yields:

$$\begin{aligned} \Delta T &= \frac{273K(18.02 \times 10^{-6}m^3/mol - 19.64 \times 10^{-6}m^3/mol)}{6.01 \times 10^3 J/mol} (1.01 \times 10^5 Pa) \\ &= -7.27 \times 10^{-3} K \\ &= -0.0073 K \end{aligned}$$

So the increase of the pressure depresses the temperature by 0.0073 K.

Clausius Clapeyron Equation and the Carnot Engine

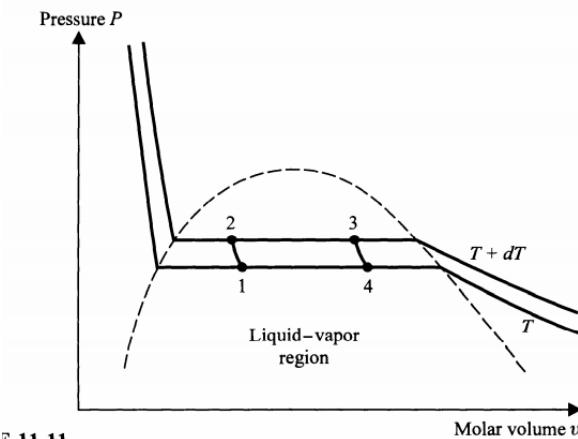
The Clausius-Clapeyron equation may also be derived from a study of the Carnot engine, which operates using a two phase hydrostatic system.

Consider a Carnot engine operating in the two phase region of the water vapor region. It follows the reversible cycle 1-2 and 3-4 are adiabatic and 2-3 and 4-1 are isothermal and isobaric.

During the process 2-3, at temperature $T + dT$, n moles of liquid are converted to vapor at pressure $P + dP$, while during process 4-1, at temperature T , n moles of vapor are converted back to liquid at pressure P .

The efficiency η is:

$$\eta = \frac{|W|}{|Q_H|}$$



E 11-11 Diagram showing a Carnot cycle in the liquid-vapor region.

And:

$$\eta = 1 - \frac{T}{T + dT} = \frac{dT}{T}$$

So:

$$\frac{|W|}{|Q_H|} = \frac{dT}{T}$$

The work done on the system is the area $dP(n\Delta v)$ where Δv is the change of molar volume at temperature T .

The heat absorbed by the system during the isothermal process 2-3 is $n\Delta h$, where Δh is the molar enthalpy of vaporization. Thus, we can write it as:

$$\frac{(dP)(n\Delta v)}{n\Delta h} = \frac{dT}{T}$$

Or, within the coexistence region,

$$\left(\frac{dP}{dT}\right)_{coexist} = \frac{\Delta h}{T\Delta v}$$

Statistical Mechanics

Fundamental Principles

The particles of an ideal gas are indistinguishable and quasi-independent.

Suppose that a closed system contains a monatomic ideal gas consisting of N weakly interacting atoms, where N is enormous number.

Let the gas be contained in an adiabatic cubical enclosure of lengths L , and let ϵ the energy of any particle be entirely kinetic of translation.

In the x direction, the energy ϵ_x is given by:

$$\epsilon_x = \frac{p_x^2}{2m}$$

If the particle is quantic, this energy is given by:

$$\epsilon_x = n_x^2 \frac{h^2}{8mL^2}$$

Where n_x is an integer.

It was shown that the average energy of a monoatomic ideal gas is $\frac{3}{2}kT$ per particle. That means that the average energy associated with each translational degree of freedom is $\frac{1}{2}kT$. For example, for energy ϵ_x , it is: $\epsilon_x = \frac{1}{2}kT$.

For three dimensions, quantum says that:

$$\epsilon = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

Given by the three integers n_x, n_y, n_z that characterize the state we are in.

Degeneracy: If an energy level ϵ_i has g_i quantum states to get it, we say the energy has a **degeneracy** of g_i

For example, an energy of $\epsilon_i = 66h^2/8mL^2$ can be achieved in $g_i = 12$ different ways.

In general, for the energies we are using, this number is extremely large

We denote by N_i the number of particles in state ϵ_i . Generally, degeneracy is so large that $g_i \gg N_i$

At one moment, some particles are moving rapidly and others slowly, so that the particles are distributed among a large number of quantum states.

Fundamental Assumption: All quantum states have equal likelihood of being occupied

Consider N_i particles in any of the g_i quantum states associated with an energy ϵ_i . Any one particle has g_i choices for different states in this energy (and all of them equally likely)

If the particles were *distinguishable*, the total number of ways in which N_i distinguishable particles could be distributed among g_i quantum states would, therefore, be $g_i^{N_i}$

For *Indistinguishable* particles (as we have), any interchange of particles still results in the same state, so

The number of ways that N_i indistinguishable quasi independent particles can be distributed among g_i quantum states (that have energy ϵ_i) is:

$$\frac{g_i^{N_i}}{N_i!}$$

So long as the number g_i of states is much greater than N_i , if not, the truly correct number of ways I believe is $\frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}$

Equilibrium Distribution:

In the case of an ideal gas, there are many quantum states corresponding to the same energy level and the degeneracy g_i of each level is much larger than N_i number of particles in this state.

At any moment, we have:

$$\begin{aligned} & N_1 \text{ particles in energy } \epsilon_1 \text{ with degeneracy } g_1 \\ & N_2 \text{ particles in energy level } \epsilon_2 \text{ with degeneracy } g_2 \\ & \vdots \\ & N_i \text{ particles in energy level } \epsilon_i \text{ with degeneracy } g_i \end{aligned}$$

This is the **macrostate** of the gas (which let's say has N particles).

The number of ways in which this macrostate can be achieved is:

$$\Omega = \frac{g_1^{N_1} g_2^{N_2}}{N_1! N_2!} \dots$$

Where $g_1^{N_1}$ corresponds to the different ways we can put the N_1 particles in the g_1 boxes, and we divide by $N_1!$ because they are indistinguishable.

Remember that here many particles can have the same state but we suppose $g_i \gg N_i$

Then, we can take the logarithm of this:

$$\begin{aligned}\log \Omega &= \sum N_i \log g_i - \log N_i! \\ &= \sum [N_i \log g_i - N_i \log N_i + N_i] \\ &= \sum N_i \log \frac{g_i}{N_i} + N\end{aligned}$$

To know the correct numbers N_i , our problem is to make Ω maximum subject to the conditions:

$$\begin{aligned}\sum N_i &= N = cte \\ \sum N_i \epsilon_i &= U = cte\end{aligned}$$

Ω is the number of ways we can have a configuration (N_1, N_2, \dots) with N_i particles in each energy ϵ_i . It depends on the numbers g_i

All these sub configurations are equally likely, so the most probable superconfiguration (N_1, \dots) will be the one with the highest Ω .

To maximize omega, we differentiate:

$$\begin{aligned}d \log \Omega &= \sum d(N_i \log \frac{g_i}{N_i}) = \sum \log \frac{g_i}{N_i} dN_i + \sum \frac{N_i^2}{g_i} \left(-\frac{g_i}{N_i^2} \right) dN_i \\ &= \sum \log \frac{g_i}{N_i} dN_i - d \sum N_i \\ &= \sum \log \frac{g_i}{N_i} dN_i\end{aligned}$$

Now we set it equal to zero and add on the conditions:

$$\begin{aligned}\log \frac{g_1}{N_1} dN_1 + \log \frac{g_2}{N_2} dN_2 + \dots &= 0 \\ dN_1 + dN_2 + \dots &= 0 \\ \epsilon_1 dN_1 + \epsilon_2 dN_2 + \dots &= 0\end{aligned}$$

We multiply the second equation by $\log \lambda$ and the third by $-\beta$ (Lagrangian multipliers), we get:

$$\begin{aligned}\log \frac{g_1}{N_1} dN_1 + \log \frac{g_2}{N_2} dN_2 + \dots &= 0 \\ \log \lambda dN_1 + \log \lambda dN_2 + \dots &= 0 \\ -\beta \epsilon_1 dN_1 - \beta \epsilon_2 dN_2 - \dots &= 0\end{aligned}$$

We add this equations and the coefficient of each dN_i must be zero, so:

$$N_i = \lambda g_i e^{-\beta \epsilon_i}$$

That is, the most probable population N_i of particles in energy level ϵ_i is $N_i \lambda g_i e^{-\beta \epsilon_i}$

Significance of the Lagrangian Multipliers λ, β

The population N_i in the i th energy level ϵ_i is:

$$N_i = \lambda g_i e^{-\beta \epsilon_i}$$

Summing over all energy levels we get:

$$\begin{aligned} N &= \sum N_i = \lambda \sum g_i e^{-\beta \epsilon_i} \\ \Rightarrow \quad \lambda &= \frac{N}{\sum g_i e^{-\beta \epsilon_i}} \end{aligned}$$

We define:

$$Z := \sum g_i e^{-\beta \epsilon_i}$$

So that:

$$\lambda = \frac{N}{Z}$$

Substituting this value of λ , the actual configuration is:

$$N_i = N \frac{g_i e^{-\beta \epsilon_i}}{Z}$$

Now β must have something to do with temperature.

Let us consider a thermally insulated composite system consisting of two samples of ideal monatomic gas separated by a diathermic wall



FIGURE 12-3

An isolated composite system of two samples of ideal monatomic gas separated by a diathermic wall. The total internal energy is constant.

The number of ways we can get this configuration is the product of the number of ways of the first chamber times that of the second. Using logs, we get:

$$\log \Omega = \sum N_i \log \frac{g_i}{N_i} + N + \sum \tilde{N}_j \log \frac{\tilde{g}_j}{\tilde{N}_j} + \tilde{N}$$

We have the conditions:

$$\begin{aligned}\sum N_i &= N = \text{cte} \\ \sum \tilde{N}_j &= \tilde{N} = \text{cte} \\ \sum N_i \epsilon_i + \sum \tilde{N}_j \tilde{\epsilon}_j &= U = \text{cte}\end{aligned}$$

We want to find the maximum of Ω subject to these constraints. After using the Lagrange method, we get:

$$\begin{aligned}N_i &= \lambda g_i e^{-\beta \epsilon_i} \\ \tilde{N}_j &= \tilde{\lambda} \tilde{g}_j e^{-\beta \tilde{\epsilon}_j}\end{aligned}$$

All quantities are different, except for β , since β is related to temperature and the systems are at equilibrium.

We know that entropy in an isolated system increases when the system undergoes a spontaneous, irreversible process.

The thermodynamic probability also increases and approaches a maximum as equilibrium is approached.

Therefore we look for a correlation between S and Ω

Consider two similar systems A, B in thermal contact - One with entropy S_A and thermodynamic probability Ω_A and the other with S_B and Ω_B .

The total entropy and total thermodynamic probabilities are:

$$\begin{aligned}S &= S_A + S_B \\ \Omega &= \Omega_A \cdot \Omega_B\end{aligned}$$

If we let entropy be a function of thermodynamic probability, that is $S = f(\Omega)$.

WE must have that products are separated into sums, that is $f(\Omega_A \Omega_B) = f(\Omega_A) + f(\Omega_B)$

Therefore, we use the logarithm to relate them:

$S = k' \log \Omega$

The first law says that $d'Q = dU + PdV$

And if it takes place between two neighboring equilibrium states, it may be performed reversibly, in which case $d'Q = TdS$, so that: $dU = -PdV + TdS$

If it takes place at *constant V*, we then have:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V$$

This is the way in which the macroscopic concept of temperature is introduced into statistical mechanics.

In employing the method of Lagrangian multipliers, we found that:

$$d \log \Omega = \sum \log \frac{g_i}{N_i} dN_i$$

$$\log \frac{g_i}{N_i} = \beta \epsilon_i - \log \lambda$$

Therefore:

$$d \log \Omega = \sum \beta \epsilon_i dN_i - \log \lambda \sum dN_i$$

$$= \beta d \sum \epsilon_i N_i - \log \lambda d \sum N_i$$

For a closed system $d \sum N_i = 0$ and $\sum N_i \epsilon_i = U$, yielding:

$$d \log \Omega = \beta dU$$

Therefore:

$$\beta = \frac{d \log \Omega}{dU}_V = \frac{1}{k'} \frac{d}{dU} (\log \Omega)_V = \frac{1}{k'} \left(\frac{\partial S}{\partial U} \right)_V$$

The thing in parenthesis is $1/T$, so we have that:

$$\boxed{\beta = \frac{1}{k'T}}$$

Partition function for Canonical Ensemble

We have seen that the population N_i for the i th energy level is:

$$N_i = \lambda g_i e^{-\beta \epsilon_i}$$

substituting β and λ , we have:

$$\boxed{N_i = \frac{N}{Z} g_i e^{-\epsilon_i/k'T}}$$

$$\boxed{Z(V, T) = \sum g_i e^{-\epsilon_i/k'T}}$$

The partition function Z is an explicit function of temperature T and an implicit function of volume V .

Z is the statistical mechanical analog of the Helmholtz function $A(V, T)$. If we differentiate Z with respect to T we get:

$$\begin{aligned}\left(\frac{\partial Z}{\partial T}\right)_V &= \sum g_i \left(\frac{\epsilon_i}{k'T^2}\right) e^{-\epsilon_i/k'T} \\ &= \frac{1}{k'T^2} \sum \epsilon_i g_i e^{-\epsilon_i/k'T} \\ &= \frac{Z}{Nk'T^2} \sum \epsilon_i N_i \\ &= \frac{ZU}{Nk'T^2}\end{aligned}$$

It follows that:

$$U = Nk'T^2 \left(\frac{\partial \log Z}{\partial T}\right)_V$$

Also, $S = k' \log \Omega$, where $\log \Omega = \sum N_i \log \frac{g_i}{N_i} + N$.

Hence $S = -k' \sum N_i \log \frac{N_i}{g_i} + k'N$.

Substituting for N_i/g_i by using $N_i = \frac{Z}{U} g_i e^{-\epsilon_i/k'T}$, we get that:

$$S = NK' \log \frac{Z}{N} + \frac{U}{T} + Nk'$$

So we can calculate S once we know $\log Z$.

The Helmholtz function A can also be evaluated in terms of Z using:

$$\begin{aligned}A &= U - TS \\ &= U - T \left(NK' \log \frac{Z}{N} + \frac{U}{T} + Nk' \right) \\ &= -k'T(N \log Z - N \log N + N)\end{aligned}$$

Therefore:

$$A = -k'T(N \log Z - \log N!)$$

Then, since $dA = -PdV - SdT$, it follows that $P = -\left(\frac{\partial A}{\partial V}\right)_T$

Therefore, using the definition of A , we get:

$$P = Nk'T \left(\frac{\partial \log Z}{\partial V}\right)_T$$

So statistical mechanics provides a simple way of calculating things:

- Use quantum mechanics to find the ϵ values of the quantum states
- Find the partition function Z in terms of T and V
- Calculate the internal energy by differentiation $\log Z$ with respect to T
- Calculate the pressure by the formula (differentiate $\log Z$ respect to V)
- Calculate the entropy by using Z, U
- Calculate the Helmholtz function directly from $\log z$

Partition function of an ideal monoatomic Gas

The partition function was defined as:

$$Z = \sum_{\text{levels}} g_i e^{-\epsilon_i/k'T}$$

Or we can sum:

$$Z = \sum_{\text{states}} e^{-\epsilon_j/k'T}$$

Where we are summing over states instead of levels (here, each level will be summed g_i times and we will return to the original expression).

The energy of a quantum state j is:

$$\epsilon_j = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

With n_x, n_y, n_z the quantum numbers and a, b, c the dimensions of the box.

Therefore:

$$Z = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-(h^2/8mk'T)(n_x^2/a^2 + n_y^2/b^2 + n_z^2/c^2)}$$

$$\text{Or } Z = \sum_{n_x=1}^{\infty} e^{-(h^2/8mk'T)(n_x^2/a^2)} \sum_{n_y=1}^{\infty} e^{-(h^2/8mk'T)(n_y^2/b^2)} \sum_{n_z=1}^{\infty} e^{-(h^2/8mk'T)(n_z^2/c^2)}$$

Since n_x, n_y, n_z are very large to give rise to an appreciable level of energy, we replace by integrals:

$$Z = \left[\int_0^{\infty} e^{-(h^2/8mk'T)(n_x^2/a^2)} dn_x \right] \left[\int_0^{\infty} e^{-(h^2/8mk'T)(n_y^2/b^2)} dn_y \right] \left[\int_0^{\infty} e^{-(h^2/8mk'T)(n_z^2/c^2)} dn_z \right]$$

Solving the integrals using $\int_0^\infty e^{-ax^2} = \frac{1}{2}\sqrt{\frac{\pi}{a}}$, we get:

$$Z = \left(\frac{a}{2} \sqrt{\frac{8\pi mk'T}{h^2}} \right) \left(\frac{b}{2} \sqrt{\frac{8\pi mk'T}{h^2}} \right) \left(\frac{c}{2} \sqrt{\frac{8\pi mk'T}{h^2}} \right)$$

And since $abc = V$, we get:

$$\boxed{Z(V, T) = V \left(\frac{2\pi mk'T}{h^2} \right)^{3/2}}$$

$$\boxed{\log Z(V, T) = \log V + \frac{3}{2} \log T + \frac{3}{2} \log \left(\frac{2\pi mk'}{h^2} \right)}$$

Then, we can calculate all kinds of stuff:

- **Pressure:**

$$\begin{aligned} P &= Nk'T \left(\frac{\partial \log Z}{\partial V} \right)_T \\ &= Nk'T \frac{1}{V} \\ &= \frac{N}{V} k'T \end{aligned}$$

Comparing with the result that $P = NkT/V$, we see that $k' = k = R/N_A$ is the Boltzmann constant.

- **Internal Energy:**

$$\begin{aligned} U &= NkT^2 \left(\frac{\partial \log Z}{\partial T} \right)_V \\ &= NkT^2 \frac{3}{2T} \\ &= \frac{3}{2} NkT \end{aligned}$$

Which is exactly what we got before.

- **Entropy of ideal monoatomic gas:**

$$\begin{aligned} S &= Nk \log \frac{Z}{N} + \frac{U}{T} + Nk \\ &= \dots = Nk \left[\frac{3}{2} \log T + \log \frac{V}{N} + \log \left(\frac{2\pi mk}{h^2} \right)^{3/2} + \frac{5}{2} \right] \end{aligned}$$

If we take a mole of gas, $N = N_A$ and $N_A k = R$ so:

$$s = c_V \log T + R \log v + R \log \frac{(2\pi mk/h^2)^{3/2}}{N_A} + \frac{5}{2}R$$

Equipartition of Energy

Both kinetic theory and statistical mechanics when applied to an ideal gas yield the result that in equilibrium, the energy per particle associated with each degree of freedom is $\frac{1}{2}kT$

The property of the partition function which makes it useful is that, if we write the energy of a particle as a sum of terms, then Z takes the form:

$$\epsilon = \epsilon' + \epsilon'' + \epsilon''' + \dots$$

Then:

$$\begin{aligned} Z &= \sum e^{-\epsilon/kT} \\ &= \sum e^{-(\epsilon' + \epsilon'' + \epsilon''' + \dots)/kT} \\ &= \sum e^{-\epsilon'/kT} \sum e^{-\epsilon''/kT} \sum e^{-\epsilon'''/kT} \dots \\ &= Z' Z'' Z''' \dots \end{aligned}$$

If the various types of energies are calculated with classical physics, we can derive the classical principle of equipartition of energy.

We know that:

$$U = NkT^2 \left(\frac{\partial \log Z}{\partial T} \right)_V$$

Thus:

$$\langle \epsilon \rangle = \frac{U}{N} = - \left(\frac{\partial \log Z}{\partial (1/kT)} \right)_V = - \left(\frac{\partial \log Z}{\partial \beta} \right)_V$$

Suppose ϵ to consist of terms representing translational energy $1/2mv^2$, those representing rotational $1/2I\omega^2$, vibrational $1/2m\xi^2$, $1/2m\dot{\xi}^2$, etc.

All these forms of energy are of the form $b_i p_i^2$.

Therefore:

$$\epsilon = b_1 p_1^2 + \dots + b_f p_f^2$$

Then, since the partition function is the product of the separate partition functions, we have that:

$$\begin{aligned} Z &= \int_0^\infty e^{-\beta b_1 p_1^2} dp_1 \int_0^\infty e^{-\beta b_2 p_2^2} dp_2 \dots \int_0^\infty e^{-\beta b_f p_f^2} dp_f \\ &= (\beta^{-1/2} K_1)(\beta^{-1/2} K_2) \dots (\beta^{-1/2} K_f) \end{aligned}$$

Where $K_i = \int_0^\infty e^{-b_i\beta p_i^2} dy_i$. Then:

$$Z = \beta^{-f/2} K_1 K_2 \cdots K_f$$

Then, since $\langle \epsilon \rangle = -\partial[\log Z / \partial \beta]_V$ (and the K_i don't contain β after doing the integral), we have that:

$$\langle \epsilon \rangle = \frac{f}{2\beta}$$

And since $\beta = 1/kT$, we have:

$$\boxed{\langle \epsilon \rangle = \frac{f}{2} kT}$$

So, Principle of equipartition: When a large number of indistinguishable quasi-independent particles whose energy is expressed as the sum of squared terms come to equilibrium, the average internal energy per particle is f times $1/2kT$

That is why a monoatomic gas has energy $U = N(3/2kT) = \frac{3}{2}nRT$

And for diatomic, $U = \frac{5}{2}nRT$

Distribution of Speeds in an ideal monoatomic Gas

We consider an ideal monatomic gas. If w denoted the speed of an atom in an ideal gas consisting of N atoms, we want the average or the average square:

$$\begin{aligned}\langle w \rangle &= \frac{1}{N} \int_0^\infty w dN_w \\ \langle w^2 \rangle &= \frac{1}{N} \int_0^\infty w^2 dN_w\end{aligned}$$

And dN_w is the number of atoms with speeds between w and $w + dw$.

To do these, we must know dN_w in terms of w , a relation known as the Maxwell's law of distribution of speeds for particles in a gas.

We derive it

We start with the equation expressing the equilibrium value of the number of atoms N_ϵ with energy ϵ :

$$N_\epsilon = \frac{N}{Z} g_\epsilon e^{-\epsilon/kT}$$

Where g_ϵ is the number of quantum states available for atoms of energy ϵ .

These states correspond to positive integer values for each n_x, n_y, n_z such that:

$$n_x^2 + n_y^2 + n_z^2 = \frac{L^2}{h^2} 8me = r^2$$

To count how many of these states are possible, we consider a phase space with variables n_x, n_y, n_z .

We want to count the amount dg_ϵ of states between the (one octant) sphere of radius $r = (L/h)(8m\epsilon)^{1/2}$ and the sphere of radius $r + dr$

The volume of this region is:

$$\begin{aligned} dg_\epsilon &= \frac{1}{8}(4\pi r^2 dr) \\ &= \frac{1}{8}(4\pi) \left(\frac{L^2}{h^2} 8m\epsilon \right) d \left(\frac{L}{h} (8m\epsilon)^{1/2} \right) \end{aligned}$$

Simplifying and setting $V = L^3$, we get:

$$dg_\epsilon = \frac{2\pi V (2m)^{3/2}}{h^3} \epsilon^{1/2} d\epsilon$$

The number of atoms dN_ϵ in the energy range between ϵ and $\epsilon + d\epsilon$ is then clearly:

$$dN_\epsilon = N \frac{dg_\epsilon}{Z} e^{-\epsilon/kT}$$

We have shown before that $Z = V \left(\frac{2\pi m k T}{h^2} \right)^{3/2}$. Hence:

$$dN_\epsilon = N \frac{dg_\epsilon}{Z} e^{-\epsilon/kT} = \frac{2N}{\pi^{1/2} (kT)^{3/2}} \epsilon^{1/2} e^{-\epsilon/kT} d\epsilon$$

If the speed of an atom is w , then $\epsilon = \frac{1}{2}mw^2$, and:

$$dN_w = \frac{2N}{\pi^{1/2} (kT)^{3/2}} \left(\left(\frac{1}{2} mw^2 \right)^{1/2} m w dw (e^{-\epsilon/(2mw^2/kT)}) \right)$$

And finally:

$$\frac{dN_w}{dw} = \frac{2N}{\sqrt{2\pi}} \left(\frac{m}{kT} \right)^{3/2} w^2 e^{-(1/2)mw^2/kT}$$

This is the **Maxwells Speed distribution function**

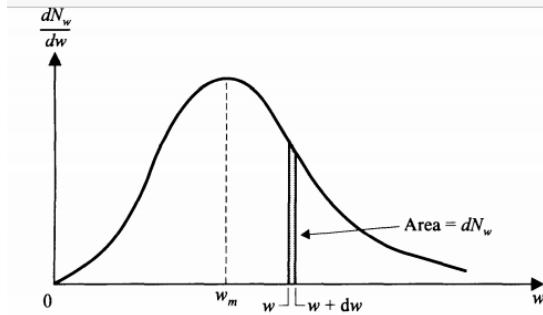


FIGURE 12-5
Graph of Maxwell's speed-distribution function, where the speed w_m is the most probable speed.

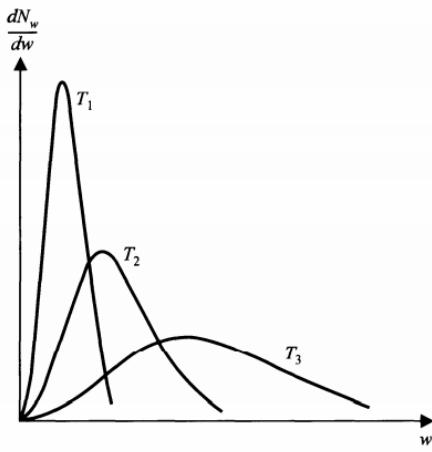


FIGURE 12-6
Maxwell's speed-distribution function at various temperatures; $T_3 > T_2 > T_1$.

Statistical Interpretation of work and heat

We have considered a large number N of indistinguishable quasi independent particles in a cubic container V . The energy levels ϵ_i of individual particles undergoing translational motion are given by:

$$\epsilon_i = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

Let $B_i = n_x^2 + n_y^2 + n_z^2$, so that we get:

$$\epsilon_i = \frac{h}{8m} B_i V^{-2/3}$$

Taking the log we get:

$$\log \epsilon_i = \log \frac{h^2}{2m} + \log B_i - \frac{2}{3} \log V$$

The effect of a small change of V on ϵ is given by taking the differential:

$$\frac{d\epsilon_i}{\epsilon_i} = -\frac{2}{3} \frac{dV}{V}$$

Therefore:

$$\begin{aligned} d\epsilon_i &= -\frac{2}{3} \frac{\epsilon_i}{V} dV \\ \Rightarrow N_i d\epsilon_i &= -\frac{2}{3} \frac{N\epsilon_i}{V} dV \\ \Rightarrow \sum N_i d\epsilon_i &= -\frac{2}{3} \frac{U}{V} dV \end{aligned}$$

We can see that

$$P = \frac{NkT}{V} = \frac{2^3 N k T}{3V} = \frac{2U}{3V}$$

Substituting this result, we get:

$$\sum N_i d\epsilon_i = -P dV$$

Therefore, a change in volume, causes changes in the energy values of the energy levels without producing changes in the populations of the levels.

If the populations change but the ϵ_i remain constant, we have from $d \log \Omega = \beta d \sum \epsilon_i N_i - \log \lambda d \sum N_i$, that $d \log \Omega = \beta \sum \epsilon_i dN_i$

Since $k d \log \Omega = dS$, $k \beta \sum \epsilon_i dN_i = dS$, and setting $k \beta$ equal to $1/T$, we get:

$$\sum \epsilon_i dN_i = T dS$$

So that a reversible heat transfer changes the populations of the energy levels without changing the energy values themselves.

TdS Gibbs Duhem Equations

If in a system σ we make an infinitesimal and reversible process in which there is a heat exchange of $d'Q$ with a temperature with source dT , then the entropy is:

$$dS = \frac{d'Q_{rev}}{T}$$

And the variation of internal energy will be given by an equation of the form:

$$\begin{aligned} dU &= dQ + \sum_{i=1}^n X_i dY_i \\ &= TdS + \sum_{i=1}^n X_i dY_i \end{aligned}$$

This equation is only valid for reversible processes.

We can see that:

$$dU = \left(\frac{\partial U}{\partial S} \right)_{Y_i} dS + \sum_{i=1}^n \left(\frac{\partial U}{\partial Y_i} \right)_{SY_j \neq i} dY_i$$

So we have that:

$$\begin{aligned} T &= \left(\frac{\partial U}{\partial S} \right)_{Y_j} \\ X_i &= \left(\frac{\partial U}{\partial Y_i} \right)_{SY_j \neq i} \end{aligned}$$

We then conclude that:

$$U = TS + \sum_{i=1}^n X_i Y_i$$

In particular, for a simple thermodynamic system we have:

$$U = TS - pV + \mu n$$

And differentiating we have:

$$dU = TdS + SdT + \sum_{i=1}^n X_i dY_i + \sum_{i=1}^n Y_i dX_i$$

And using the first equation, we have that:

$$SdT + \sum_{i=1}^n Y_i dX_i = 0$$

This is the **Gibbs Duhem equation**

TdS equations

We consider a thermodynamic system σ . If we make an infinitesimal reversible process, the change in energy is:

$$\begin{aligned} dU &= TdS - pdV \\ \Rightarrow TdS &= dU + pdV \end{aligned}$$

Example:

For a monoatomic ideal gas, $U = \frac{3}{2}nRT$, $P = \frac{nRT}{V}$, therefore:

$$\begin{aligned} dS &= \frac{3}{2}nR \frac{dT}{T} + nR \frac{dV}{V} \\ \Rightarrow S_f - S_i &= \frac{3}{2}nR \log \frac{T_f}{T_i} + nR \log \frac{V_f}{V_i} \end{aligned}$$

Therefore:

$$S = \frac{3}{2}nR \log T + nR \log V + S_0$$

Let's take T, V as independent variables, then:

$$\begin{aligned} U &= U(T, V) \\ S &= S(T, V) \\ dU &= \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \\ dS &= \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \end{aligned}$$

Then, substituting into $dU = TdS - pdV$ we get:

$$\left[\left(\frac{\partial U}{\partial T} \right)_V - T \left(\frac{\partial S}{\partial T} \right)_V \right] dT = \left[T \left(\frac{\partial S}{\partial V} \right)_T - \left(\frac{\partial U}{\partial V} \right)_T - P \right] dV$$

- For a process at constant V :

$$\begin{aligned} \left(\frac{\partial U}{\partial T} \right)_V &:= C_V = T \left(\frac{\partial S}{\partial T} \right)_V \\ \Rightarrow \left(\frac{\partial S}{\partial T} \right)_V &= \frac{C_V}{T} \end{aligned}$$

- Process at constant T :

$$T \left(\frac{\partial S}{\partial V} \right)_T = p + \left(\frac{\partial U}{\partial V} \right)_T$$

Because S is a state function (exact differential), then:

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 S}{\partial V \partial T}$$

Then, using the results we had:

$$\begin{aligned}\frac{\partial^2 S}{\partial T \partial V} &= \frac{1}{T} \left(\frac{\partial C_V}{\partial V} \right)_T = \frac{1}{T} \frac{\partial^2 U}{\partial T \partial V} \\ \frac{\partial^2 S}{\partial V \partial T} &= -\frac{1}{T_2} \left(p + \left(\frac{\partial U}{\partial V} \right)_T \right) + \frac{1}{T} \left(\left(\frac{\partial p}{\partial T} \right)_V + \frac{\partial^2 U}{\partial V \partial T} \right)\end{aligned}$$

We equal both things and get:

$$\begin{aligned}p + \left(\frac{\partial U}{\partial V} \right)_T &= T \left(\frac{\partial p}{\partial T} \right)_V \\ \Rightarrow \left(\frac{\partial U}{\partial V} \right)_T &= T \left(\frac{\partial P}{\partial T} \right)_V - P \\ \Rightarrow \left(\frac{\partial S}{\partial V} \right)_T &= \left(\frac{\partial P}{\partial T} \right)_V = \frac{\beta}{k}\end{aligned}$$

So, we get that:

$$TdS = C_v dT + \frac{\beta}{k} T dV$$

For a finite process:

$$\int_i^f dS = S_f - S_i = \int_{T_1}^{T_2} C_V \frac{dT}{T} + \int_{V_1}^{V_f} \frac{\beta}{k} dV$$

After doing some modifications, we can get:

$$C_p - C_V = \frac{\beta^2 TV}{k}$$

Potenciales Termodinamicos

Suppose we have a simple system (two variables), then it has the equation:

$$TdS = dU + pdV$$

This equation involves 5 variables, but only 2 are independent (ie. totally necessary to describe the system).

If we select two of these variables, we will need in general two equations to get the other three.

Nevertheless, if we know V, S , then only one equation is necessary to obtain the other two. That equation is:

$$U = U(S, V)$$

In this case:

$$\begin{aligned} T &= \left(\frac{\partial U}{\partial S} \right)_V \\ P &= - \left(\frac{\partial U}{\partial V} \right)_S \end{aligned}$$

Buy as we have already seen: $C_V = T \left(\frac{\partial S}{\partial T} \right)_V$ and also, $\left(\frac{\partial T}{\partial S} \right)_V = \left(\frac{\partial^2 U}{\partial S^2} \right)_V$. So:

$$C_V = \frac{T}{\left(\frac{\partial^2 U}{\partial S^2} \right)_V}$$

We see that the derivatives of U give us the intensive variables, and the second derivatives the caloric properties. For this reason, we call U a **thermodynamical potential**.

Finally, because U is an exact differential, we have that:

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$$

Which is the **First Maxwell relation**.

The problem with U as a temrodynamical potential is that S is not a simple thing to measure (and we need to know S, V)

So we look for a form to define a potential that only requires V, T . For this, we begin with $TdS = dU + pdV$ and add a zero:

$$\begin{aligned} TdS + SdT - SdT &= dU + pdV \\ \Rightarrow -SdT &= d(U - TS) + pdV \end{aligned}$$

Therefore, we define the **Helmholtz or Free energy function** A as:

$$F = U - TS$$

And we get that:

$$-SdT = dF + PdV$$

Therefore, knowing:

$$F = F(T, V)$$

We have that:

$$dF = \left(\frac{\partial F}{\partial T} \right)_V dT + \left(\frac{\partial F}{\partial V} \right)_T dV$$

And therefore:

$$\begin{aligned} -P &= \left(\frac{\partial F}{\partial V} \right)_T \\ -S &= \left(\frac{\partial F}{\partial T} \right)_V \\ C_V &= T \left(\frac{\partial S}{\partial T} \right)_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V \end{aligned}$$

So knowing F as function of V, T allows us to calculate P, S and C_V

Because F is a state function (because it is $U - TS$), it is an exact differential, so:

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

Theorem: If a system σ has a reversible process between two points A, B (at equilibrium) with the temperature of these states being equal to the room temperature. And the system only interchanges heat with the surroundings. Then the work done by the system is equal to the change in F . This is why it is called **free energy**.

- **Proof:** We know from second law that in any process:

$$\int_A^B \frac{d'Q}{T} \leq S(B) - S(A)$$

Because the surroundings are like a temperature source, we have that:

$$Q_T \leq T[S(B) - S(A)]$$

On the other hand:

$$U(B) - U(A) = Q_T - W_{A \rightarrow B}$$

Then, we have that:

$$\begin{aligned} W_{A \rightarrow B} &\leq -U(B) + U(A) + T[S(B) - S(A)] \\ &= -[U(B) - TS(B)] + [U(A) - TS(A)] \\ &= -[F(B) - F(A)] \end{aligned}$$

Where at the end we used that $T = T(A) = T(B)$.

So that gives us an upper limit to the amount of work. In a reversible process:

$$(W_{A \rightarrow B})_{rev} = -\Delta F$$

Note: The theorem is not restricted to isothermal processes between A, B , the only restriction is that the end states have equal temperature (but the middle ones can have other).

Corollary: For isochoric processes ($W = 0$), F doesn't change.

This is clear from the theorem.

So this means that in a isochoric transformation, the most stable state is that for which F is minimum.

We can define another Legendre transform. We define:

$$G = U + PV - TS = F + PV$$

$$dG = -SdT + VdP$$

The **Gibbs function**. Then, knowing P, T , we can get:

$$G = G(P, T)$$

And:

$$dG = \left(\frac{\partial G}{\partial P} \right)_T dP + \left(\frac{\partial G}{\partial T} \right)_P dT$$

Therefore, we can get:

$$\begin{aligned} -S &= \left(\frac{\partial G}{\partial T} \right)_P \\ V &= \left(\frac{\partial G}{\partial P} \right)_T \end{aligned}$$

So we can get S, V from T, P . Also:

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_P$$

And because G is a state function, it is exact, and we get the **third Maxwell relation**:

$$-\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$$

Theorem: In a transformation isobaric and isothermic between two equilibrium states, the function G stays the same.

- **Proof:**

Let $V(A), V(B)$ be the volumes, then:

$$W_{A \rightarrow B} = P[V(B) - V(A)]$$

Because the transformation is isothermal, the system exchanges heat only with its surroundings, and at T . The theorem from F (that therefore applies) says that:

$$W_{A \rightarrow B} \leq -F(B) + F(A)$$

Then:

$$\begin{aligned} p[V(B) - V(A)] + F[B] - F[A] &\leq 0 \\ \Rightarrow P[V(B) - V(A)] + U(B) - TS(B) - U(A) + TS(A) &\leq 0 \\ \Rightarrow [pV(B) + U(B) - TS(B)] - [PV(A) + U(A) - TS(A)] &\leq 0 \end{aligned}$$

Therefore:

$$\boxed{G(B) \leq G(A)}$$

And if the process is reversible, we have the equality.

So, the most stable state for a system that might undergo spontaneous isothermal isobaric process is that for which G is minimum.

Lastly, we introduce:

$$H = U + PV$$

That is the **enthalpy** of the system.

$$dH = TdS + VdP$$

If we know P, S , and $H(P, S)$, then:

$$dH = \left(\frac{\partial H}{\partial P}\right)_S dP + \left(\frac{\partial H}{\partial S}\right)_P dS$$

Then, we can calculate:

$$T = \left(\frac{\partial H}{\partial S}\right)_P$$

$$V = \left(\frac{\partial H}{\partial P}\right)_S$$

And also:

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P$$

$$= \left(\frac{\partial H}{\partial T}\right)_P$$

AS H is a state function, the **Fourth Maxwell relation says**:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

Summary

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dF = -PdV - SdT$$

$$dG = -SdT + VdP$$

De (8.10):

$$T = \left(\frac{\partial U}{\partial S} \right)_V \quad p = - \left(\frac{\partial U}{\partial V} \right)_S$$

$$\therefore \boxed{\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V} \quad (\text{M.1})$$

De (9.32):

$$T = \left(\frac{\partial H}{\partial S} \right)_p \quad V = \left(\frac{\partial H}{\partial p} \right)_S$$

$$\therefore \boxed{\left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p} \quad (\text{M.2})$$

De (9.13):

$$p = - \left(\frac{\partial F}{\partial V} \right)_T \quad S = - \left(\frac{\partial F}{\partial T} \right)_V$$

$$\therefore \boxed{\left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T} \quad (\text{M.3})$$

De (9.22):

$$S = - \left(\frac{\partial G}{\partial T} \right)_p \quad V = \left(\frac{\partial G}{\partial p} \right)_T$$

$$\therefore \boxed{\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p} \quad (\text{M.4})$$

Third Law

Calculating the absolute value of S or of any potential like F requires knowing constants. For example, for an ideal gas:

$$S(T, V) = nR\left(\frac{3}{2} \log T + \log V\right) + S_0$$

Of Helmholtz:

$$F(T, V) = \frac{3}{2}nR(T - T \log T) - nRT \log V - TS_0 + F_0$$

Law: For all substances in their condensed phase, ΔS tends to 0 when $T \rightarrow 0$:

$$\lim_{T \rightarrow 0} \Delta S == \lim_{T \rightarrow 0} \frac{\partial(\Delta G)}{\partial T} = 0$$

Remember that $S = -\frac{\partial G}{\partial T}$

Therefore, for any isothermal process that occurs at 0K, entropy remains constant.

Corollary: This means that at 0K, S cannot depend on the variables of the system, that is:

$$\lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial P} \right)_T = \lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial V} \right)_T = 0$$

Consequences of Nernst Postulate

As we saw before, because S doesn't change in 0K, we have that:

$$\lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial P} \right)_T = 0$$

And using Maxwell Law 4, we get that:

$$\lim_{T \rightarrow 0} \left(\frac{\partial V}{\partial T} \right)_P = 0$$

Also, using That $\partial S/\partial V \rightarrow 0$, we can also find that:

$$\lim_{T \rightarrow 0} \left(\frac{\partial P}{\partial T} \right)_V = 0$$

Therefore, the behavior of P, V as functions of T is identical near 0K, this implies that:

$$\lim_{T \rightarrow 0} C_p = \lim_{T \rightarrow 0} C_V = C$$

And we can also conclude that:

$$\lim_{T \rightarrow 0} C_p = \lim_{T \rightarrow 0} C_V = C = 0$$

Statements

- **Statement 1:** The limit of change in entropy for a thermodynamic system in a reversible and isothermic process between equilibrium states, tends to 0 when $T \rightarrow 0K$
- **Statement 2:** It is impossible to reduce the temperature of a system to 0K in a finite number of operations

Theorem: Statement 1 and statement 2 are equivalent

Phase Transition

It is a well known experimental fact that phase changes happen at constant temperature and pressure.

In this conditions, it is most appropriate to use the Gibbs function $G(T, P)$ and that two or more phases of the system coexist in their equilibrium states if they have the same Gibbs function value.

Let's consider a simple substance such that it has 3 coexisting phases. If we vary temperature and pressure reversibly, the change of Gibbs function per mass unit is:

$$dg = -sdT + vdP$$

Where:

$$\begin{aligned} -s &= \left(\frac{\partial g}{\partial T} \right)_P \\ v &= \left(\frac{\partial g}{\partial p} \right)_T \end{aligned}$$

So, we can characterize phase transitions by the following conditions:

- a) There are changes in v and s
- b) The first derivatives of the Gibbs function are discontinuous in the transition

The changes in phase that satisfy a) or b) are called **First order transitions of phase**

For 2 any phases that we will designate as i, f , the condition for them to coexist at equilibrium is:

$$g_i(T, P) = g_f(T, P)$$

If we vary T, P without perturbing equilibrium, we have:

$$\left(\frac{\partial g_i}{\partial T} \right)_P \delta T + \left(\frac{\partial g_i}{\partial P} \right)_T \delta P = \left(\frac{\partial g_f}{\partial T} \right)_P \delta T + \left(\frac{\partial g_f}{\partial P} \right)_T \delta P$$

Which then implies the **Clapeyron equation**:

$$\frac{dP}{dT} = \frac{s_f - s_i}{v_f - v_i} = \frac{\Delta H_{fi}}{T(v_f - v_i)}$$

In the special case of the curve of vapor pressure (curve that separates liquid and vapor in a hydrostatic system), then we have that $v_g \gg v_l$ and the equation says:

$$\frac{dp}{dT} = \frac{H_{gl}}{Tv_g}$$

And if $v_g = \frac{RT}{P}$ has the ideal gas law, then:

$$\frac{dP}{dT} = -\frac{\Delta H_{gl} P}{RT^2}$$

And integrating:

$$\log P = -\frac{\Delta H_{gl}}{RT} + cte$$

And this is the approximate form of the evaporation curve.

Second type transformation

It is a phase transition such that entropies change in continuous form (that is, the derivatives of g are continuous), but that any other quantity associated to the second derivative of g (for example: k, C_P, β) be discontinuous.

We can remember that:

$$\begin{aligned} C_P &= -T \left(\frac{\partial^2 G}{\partial T^2} \right)_P \\ k &= \frac{1}{V} \left(\frac{\partial^2 G}{\partial P^2} \right)_T \\ \beta &= \frac{1}{V} \frac{\partial^2 G}{\partial P \partial T} \end{aligned}$$

Now, as s, v are continuous functions for the transition, we have that:

$$s_i(T, P) = s_f(T, P)$$

For a virtual change $\delta T, \delta P$, that doesn't affect the equilibrium state, we have:

$$\left(\frac{\partial s_i}{\partial P} \right)_T \delta P + \left(\frac{\partial s_i}{\partial T} \right)_P \delta T = \left(\frac{\partial s_f}{\partial P} \right)_T \delta P + \left(\frac{\partial s_f}{\partial T} \right)_P \delta T$$

And using some equations, we have that:

$$-\beta_i v \delta P + \frac{C_p}{T} dT = -\beta_f v \delta P + \frac{C_p}{T} \delta T$$

Then, calculating $\frac{\delta P}{\delta T}$ and taking the limit for $\delta T \rightarrow 0$, we get:

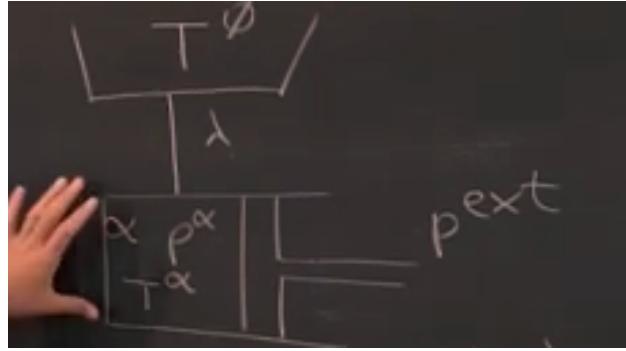
$$\frac{dP}{dT} = \frac{C_p^{(f)} - C_p^{(i)}}{Tv(\beta_f - \beta_i)}$$

Analogously, from the equation $v_i(T, P) = v_f(T, P)$ takes us to:

$$\frac{dP}{dT} = \frac{\beta_f - \beta_i}{k_f - k_i}$$

Combination of First and Second Law (B) (For Closed Systems)

We begin studying a system α with Pressure P_α , Temperature T_α that is in contact with a heat source T_ϕ connected through a conductor λ and it can be pushed by a piston at pressure P^{ext}



- System $\alpha + \lambda$

We write the first law:

$$dU^{\alpha+\lambda} = -dQ^\phi - p^{ext}dV^\alpha$$

Consider that the heat is given just at the point of contact of the source with λ .

The second law:

$$\begin{aligned} dS^{\alpha+\lambda} &= d_e S^{\alpha+\lambda} + d_i S^{\alpha+\lambda} \\ &= -\frac{dQ^\phi}{T^\phi} + d_i S^{\alpha+\lambda} \end{aligned}$$

We now eliminate dQ^ϕ from the second law using the first and get:

$$dS^{\alpha+\lambda} = \frac{1}{T} dU^{\alpha+\lambda} + \frac{p^{ext}}{T^\phi} dV^\alpha + d_i S^{\alpha+\lambda}$$

The problem with this expression is that we have a mix of quantities of the system $\alpha + \lambda$ together with quantities of the source.

Now, in the production of heat we have

$$d_i S^{\alpha+\lambda} = dQ^\phi \left(\frac{1}{T^\phi} - \frac{1}{T^\alpha} \right) - \frac{p^{ext} - p^\alpha}{T^\alpha} dV^\alpha + d_i S^\alpha$$

The first term is the production of entropy due to the exchange of heat with a finite difference of temperature.

The second term is the production of entropy due to a difference in pressure.

And the third is any internal production of entropy that we haven't accounted for.

We put this into our last equation (and substituting dQ^ϕ again using the first law) and after some algebra, we get:

And we also use that S and U are extensive, so $dS^{\alpha+\lambda} = dS^\alpha + dS^\lambda$ and similarly for dU and also use that $dS^\alpha = \frac{dU^\lambda}{T^\alpha}$. Now we get:

$$dS^\alpha = \frac{1}{T}dU + \frac{P}{T}dV + d_i S^\alpha$$

From the second law, we know that $d_i S \geq 0$, so we conclude that:

$$dS \geq \frac{1}{T}dU + \frac{P}{T}dV$$

So, if U, V are constants, we have that $dS \geq 0$, which is again the law of increase in entropy.

For an isolated system (in this case, this means that $dV = dU = 0$), entropy can only increase (or stay the same).

so we reached the same conclusion as we did a long time ago but without talking about heat.

This means that equilibrium states for closed isolated systems are those with maximum entropy.

For a **reversible process**, the inequality converts into an equality, so that:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

Which means also that (because S is a state variable):

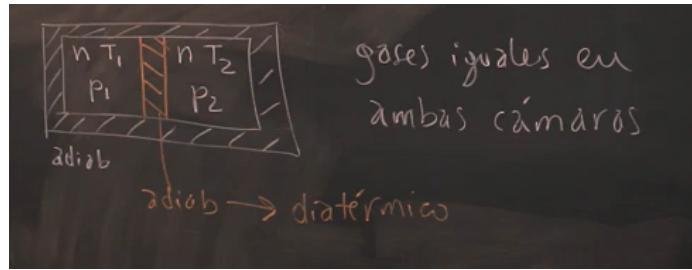
$$\begin{aligned}\frac{1}{T} &= \frac{\partial S}{\partial U}_V \\ \frac{P}{T} &= \frac{\partial S}{\partial V}_U\end{aligned}$$

This makes U, V the *natural variables* of entropy. Which means that if we know S as a function of U, V , we can get all the variables of the system (we can differentiate as seen above to get T, P as functions of U and V).

That is, if we know $S(U, V)$, we can get all the information of the system (this wouldn't work for S as the function of other variables, for which there would be some unknown constants).

Example of equilibrium as the maximum of S :

We have the next system of two gasses separated



When we change the inner wall to diathermic, the gasses will exchange heat and they will reach some equilibrium (we know that happens when they get the same T).

We can see that U and V are constants for the whole system (it is an isolated system), So, **the equilibrium point is a maximum of S** .

First, we write an expression for the entropy (supposing the gasses are ideal):

$$\Delta S = \Delta S_1 + \Delta S_2 = nC_v \log \frac{T_{1f}}{T_1} + nC_V \log \frac{T_{2f}}{T_2}$$

Considering both volumes stay the same. Also, the change in internal energy is 0:

$$\Delta U = \Delta U_1 + \Delta U_2 = nC_V(T_{1f} - T_1) + nC_V(T_{2f} - T_2) = 0$$

Then we can use the second equation to relate T_{2f} to the other temperatures and use some properties to get:

$$\Delta S = nC_V \log \frac{T_{1f}(T_1 + T_2 - T_{1f})}{T_1 T_2}$$

And now S is a function of only T_{1f} , so we look for a maximum of this by differentiating and equaling to 0. We will get the expected result:

$$T_{1f} = \frac{T_1 + T_2}{2}$$

And substituting for the expression for T_{2f} , we get the same result, as expected.

Since this is the state of maximum entropy, the system will go to this state and this will be the equilibrium state for this isolated system.

Notice that in this system the entropy is produced by the system itself, the only source of entropy is $d_i S$

Energetic Representation

- **Internal Energy:**

We can rewrite the expression we had earlier in terms of internal energy:

$$dU^{\alpha+\lambda} = T^\phi dS^{\alpha+\lambda} - p^{ext} dV^\alpha - T^\phi d_i S^{\alpha+\lambda}$$

And with only the variables of the system:

$$dU = TdS - PdV - Td_iS$$

And because $d_iS \geq 0$, we have that in general:

$$dU \leq TdS - PdV$$

So that, for a process in S, V constants, we will have that $dU \leq 0$.

So the equilibrium of a state with constant S, V will tend to a minimum in U .

If the **process is reversible**, we take the equal sign:

$$dU = TdS - PdV$$

And therefore:

$$\begin{aligned} T &= \frac{\partial U}{\partial S})_V \\ P &= -\frac{\partial U}{\partial V})_S \end{aligned}$$

So the natural variables of U are S, V .

Knowing $U(S, V)$, we have all the thermodynamic information of a system by only differentiation.

Also, at constant S, V , we have that U looks for minimization.

Also, because U is a exact differential, crossed derivatives are constant, so, using what we had earlier, we get a **Maxwell relation**:

$$\frac{\partial T}{\partial V})_S = -\frac{\partial P}{\partial S})_V$$

- **Enthalpy**

We define:

$$H = U + PV = U - V \frac{\partial U}{\partial V})_S$$

So:

$$\begin{aligned} dH &= dU + pdV + VdP \\ &= TdS - pdV - Td_iS + pdV + VdP \\ &= TdS + VdP - Td_iS \end{aligned}$$

And using $dS = d_eS + d_iS$, we get $dH = Td_eS + VdP$
 So at constant P , $dH = Td_eS = dQ$

So, **Difference in enthalpy is the heat exchanged at constant pressure**

Now, because $d_iS \geq 0$, we have that, at S, P constant: $dH \leq 0$
 So, at constant S, P , the system will evolve until finding a minimum value of H

In a **Reversible process**:

$$dH = TdS + VdP$$

So we conclude that:

$$\begin{aligned} T &= \frac{\partial H}{\partial S}_P \\ V &= \frac{\partial H}{\partial P}_S \end{aligned}$$

And using the equality of crossed derivatives, we get another **Maxwell expression**:

$$\frac{\partial T}{\partial P}_S = \frac{\partial V}{\partial S}_P$$

- **Helmholtz**

$$F = U - TS$$

$$F = F(T, V)$$

So that:

$$dF = -PdV - SdT - Td_iS$$

Theorem of maximum work: For any isothermal reversible process, the maximum work is the change in F .

In a T, V constant process, we have that $dF \leq 0$, so it seeks a minimum

In a **Reversible process**:

$$dF = -SdT - pdV$$

And therefore:

$$S = -\frac{\partial F}{\partial T}_V$$

$$P = -\frac{\partial F}{\partial V}_T$$

And Maxwell law:

$$\frac{\partial S}{\partial V}_T = \frac{\partial P}{\partial T}_V$$

- **Gibbs:**

$$G = U + PV - TS$$

$$G = G(T, P)$$

Differential:

$$dG = -SdT + VdP + dW_{noexpansivo} - Td_iS$$

So at P, T constant, the maximum non expansive work we can get is the difference of G .

We also have that at T, P constants, $dG \leq 0$

So G seeks a minimum.

For a reversible process:

$$dG = -SdT + VdP$$

And therefore:

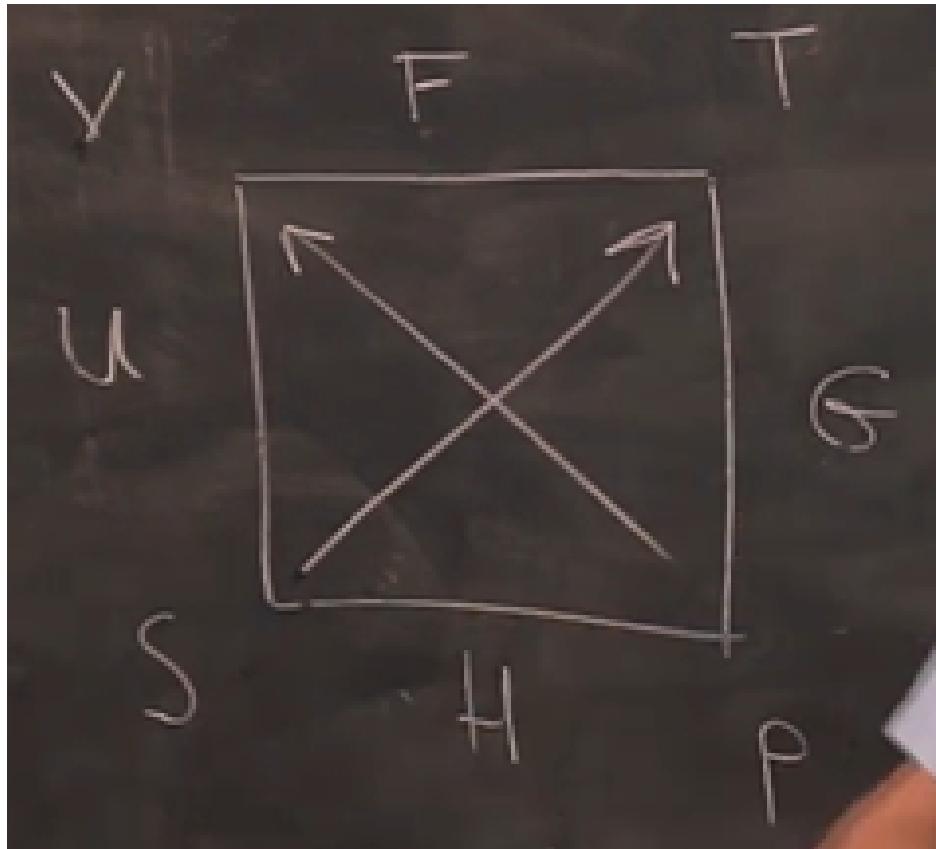
$$S = -\frac{\partial G}{\partial T}_P$$

$$V = \frac{\partial G}{\partial P}_T$$

And maxwell law is:

$$\frac{\partial S}{\partial P}_T = -\frac{\partial V}{\partial T}_P$$

So, leaving two variables fixed, there is always some potential that will seek minimizing or maximizing.



Summary

Resumen de fórmulas combinación 1^{ra} y 2^{da} ley (sistema cerrado)

Sistema (α) + conductor (λ) (procesos irreversibles, sólo trabajo expansivo)

$$dS^{\text{ext},\lambda} = \frac{1}{T^e} dU^{\alpha+\lambda} + \frac{p^{\text{ext}}}{T^e} dV^\alpha + d_i S^{\alpha+\lambda}$$

$$dU^{\alpha+\lambda} = T^e dS^{\text{ext},\lambda} - p^{\text{ext}} dV^\alpha - T^e d_i S^{\alpha+\lambda}$$

Cálculo de producción de entropía en el sistema α (procesos irreversibles, sólo trabajo expansivo)

$$Td_i S = TdS - pdV - dU$$

$$Td_i S = TdS + Vdp - dH \quad (H \equiv U + pV)$$

$$Td_i S = -SdT - pdV - dF \quad (F \equiv U - TS)$$

$$Td_i S = -SdT + Vdp - dG \quad (G \equiv U + pV - TS)$$

Evolución: el equilibrio corresponde a mínimos de cada potencial termodinámico o a un máximo de la entropía, en procesos en los que sus variables naturales son constantes.

Ecuaciones de Gibbs (sólo sistema α, procesos reversibles, sólo trabajo expansivo)			
$dU = TdS - pdV$	$T = \left. \frac{\partial U}{\partial S} \right _V$	$p = -\left. \frac{\partial U}{\partial V} \right _S$	
$dH = TdS + Vdp$	$T = \left. \frac{\partial H}{\partial S} \right _p$	$V = \left. \frac{\partial H}{\partial p} \right _S$	($\Delta H = Q$, proceso a p cte. rev o irrev.)
$dF = -SdT - pdV$	$S = -\left. \frac{\partial F}{\partial T} \right _V$	$p = -\left. \frac{\partial F}{\partial V} \right _T$	($\Delta F = W_{\text{total}}^{\text{max}}$, proceso a T cte.)
$dG = -SdT + Vdp$	$S = -\left. \frac{\partial G}{\partial T} \right _p$	$V = \left. \frac{\partial G}{\partial p} \right _T$	($\Delta G = W_{\text{no exp}}^{\text{max}}$, proceso a T y p ctes.)
Relaciones de Maxwell			
$\left. \frac{\partial T}{\partial V} \right _S = -\left. \frac{\partial p}{\partial S} \right _V$	$\left. \frac{\partial T}{\partial p} \right _S = \left. \frac{\partial V}{\partial S} \right _p$	$\left. \frac{\partial S}{\partial V} \right _T = \left. \frac{\partial p}{\partial T} \right _V$	$\left. \frac{\partial S}{\partial p} \right _T = -\left. \frac{\partial V}{\partial T} \right _p$

More things

The Thermodinamical state equation:

We begin with the expression for $F = U - TS$, we differentiate with respect to V at constant T and use Maxwell to get:

$$\frac{\partial U}{\partial V})_T = -P + T \frac{\partial P}{\partial T})_V$$

The other Thermodynamical state eq:

Now we start with $G = H - TS$ and differentiate with respect to P at constant T and use Maxwell to obtain:

$$\frac{\partial H}{\partial P})_T = V - T \frac{\partial V}{\partial T})_P$$

Following similar procedures, we can get a lot of similar expressions

Stability (Curvature of Thermodynamical Potentials)

Example:

We think of a system undergoing a process at S, V constant. Then, the equilibrium corresponds to a minimum of U .

We will use molar quantities for extensive variables $X_m := X/n$

Stability requires that:

$$\frac{\partial^2 U}{\partial V^2})_S > 0$$

We can do some calculations to conclude that this is equivalent to asking that $k > 0$

Second stability condition:

$$\frac{\partial^2 U}{\partial S^2})_V > 0$$

Which with some calculations, we obtain that this is equivalent to $C_V > 0$