2.1 Definitions

system — A thermodynamic system is that part of the physical universe the properties of which are under investigation. The system is confined to a definite place in space by the ***boundary*** which separates it from the rest of the universe, the ***surroundings***.

isolated system — A system is isolated when the boundary prevents any interaction with the surroundings. An isolated system produces no observable effect or disturbance in its surroundings.

open system — A system is open when mass passes across the boundary.

closed system — A system is closed when no mass passes across the boundary.

properties — The properties of a system are those physical attributes that are perceived by the senses, or are made perceptible by certain experimental methods of investigation.

state of a system — A system is in a definite state when each of its properties has a definite value.

change in state — A change in state is completely defined when the initial and final states are specified.

path — The path of a change in state is defined by giving the initial state, the sequence of intermediate states arranged in the order traversed by the system, and the final state.

process — the method of operation by means of which a change in state is effected. The description of a process consists in stating some or all of the following: (1) boundary, (2) the change in state, the path, or the effects produced in the system during each stage of the process, (3) the effects produced in the surroundings during each stage of the process.

cycle — the path of a transformation in which a system having undergone a change of state returns to its initial state. The process by means of which the transformation is effected is called a ***cyclical process***.

state variable — a variable that has a definite value when the state of a system is specified (also called a ***state function***).

Δ — Difference between the values of a state function in the final and initial states is denoted by Δ, for example

$\Delta V \equiv (V_f - V_i)$

The symbol Δ always signifies a difference of two values, which is always taken in this order:

final value minus initial value.

Each time you have a problem to solve in thermodynamics, you should pose the following questions to yourself:

- What is the system?
- Where is the boundary?
- What is the initial state?
- What is the final state?
- What is the path of the transformation?

Doing this is absolutely indispensable before beginning to work any problem.

2.2 Work and Heat

work — Any quantity that flows across the boundary of a system during a change in its state and is completely convertible into the lifting of a weight in the surroundings.

Note that in this thermodynamic definition of work:

1. Work appears only at the boundary of a system.
2. Work appears only *during* a change in state.
3. Work is manifested by an effect in the *surroundings*.
4. The quantity of work is $\boldsymbol{W = -mgh}$.
5. Work is an algebraic quantity. Work is *positive* if the weight is lowered (h is -), in which case we say that work has been destroyed in the surroundings or has flowed from the surroundings *to the system*. Work is *negative* if the weight is lifted (h is +), in which case we say that work has flowed *from the system* to the surroundings.

heat — A quantity that flows across the boundary of a system during a change in state by virtue of a difference in temperature between the system and its surroundings, and flows from a point of higher to a point of lower temperature.

Note that in this thermodynamic definition of heat:

1. Heat appears only at the boundary of a system.
2. Heat appears only *during* a change in state.
3. Heat is manifested by an effect in the *surroundings*.
4. The quantity of heat is equal to the number of grams of water in the surroundings which are increased by one degree in temperature starting at a specified temperature under a specified pressure.
5. Heat is an algebraic quantity. Heat is *positive* if a mass of water in the surroundings is cooled, in which case we say that heat has flowed from the surroundings *to the system*. Heat is *negative* if a mass of water in the surroundings is warmed, in which case we say that heat has flowed *from the system* to the surroundings.

The judgement as to how much heat flow or work flow has occurred in a transformation is based on *observation of effects produced in the surroundings*, not based upon what happens within the system. Observing the system before and after a change in state does not permit deducing anything about the heat or work flow.

The quantities of heat and work which flow depend upon the process and therefore on the *path* connecting the initial and final states. Heat and work are called *path functions*.

EXAMPLE: A system alters its volume against an opposing external pressure.

2.3 Work of expansion and compression, maximum and minimum work

Consider a system: a quantity of gas confined in a cylinder at a constant temperature T.

Initial conditions ($p_{gas,i}$, V_i , T)

Final conditions: ($p_{gas,f}$, V_f , T)

$\text{đ}W = -p_{op}dV$ or $-p_{ext}dV$ in the notation of your textbook

$$W = \int_{Vi}^{Vf} \text{đ}W = -\int_{Vi}^{Vf} p_{op}dV$$

a) suppose the path is described by
p_{op} = a constant = P_{ext}

$$W = \int_{Vi}^{Vf} \text{đ}W = -P_{ext}\int_{Vi}^{Vf} dV$$

b) suppose the path is described by $p_{op} = a\exp[-bV]$

$$W = \int_{Vi}^{Vf} \delta W \quad = -a \int_{Vi}^{Vf} \exp[-bV]dV$$

$$= +(a/b)\{ \exp[-bV_f] - \exp[-bV_i] \}$$

c) suppose the path is described by $p_{op} = a/V$

$$W = \int_{Vi}^{Vf} \delta W \quad = -a \int_{Vi}^{Vf} [1/V]\, dV$$

$$= \quad -a\{ [\ln V_f] - [\ln V_i] \} = -a \ln(V_f/V_i)$$

d) suppose the path is described by $p_{op} = p_{gas}(V)$.

$$W = \int_{Vi}^{Vf} \delta W \quad = - \int_{Vi}^{Vf} [p_{gas}(V)]\, dV$$

The function $p_{gas}(V)$ is given by the equation of state of the gas, which when substituted into the integral permits the integration to be carried out.

Note that δW does not integrate in the ordinary way, that is,

$$\int_{Vi}^{Vf} dV = V_f - V_i = \Delta V$$

$$\int_{Vi}^{Vf} \delta W = W \neq W_f - W_i$$

δW is an infinitesimal, not an exact differential
dV is an *exact differential* (MORE on this LATER).

EXAMPLE: A gas system alters its volume against an opposing external pressure in the following process:

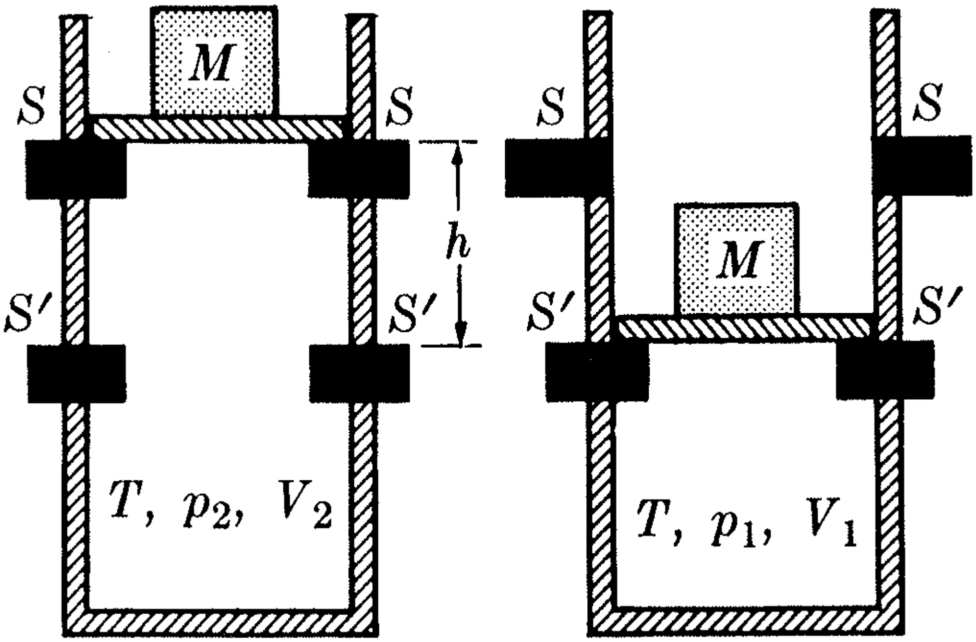
a single-stage compression from V_2 toV_1

p_{op} = a constant = P_{op}

The quantity of work is

$W = -Mgh$.

the weight is lowered (h is -), Work is *positive* in which case we say that work has flowed from the surroundings *to the system*.

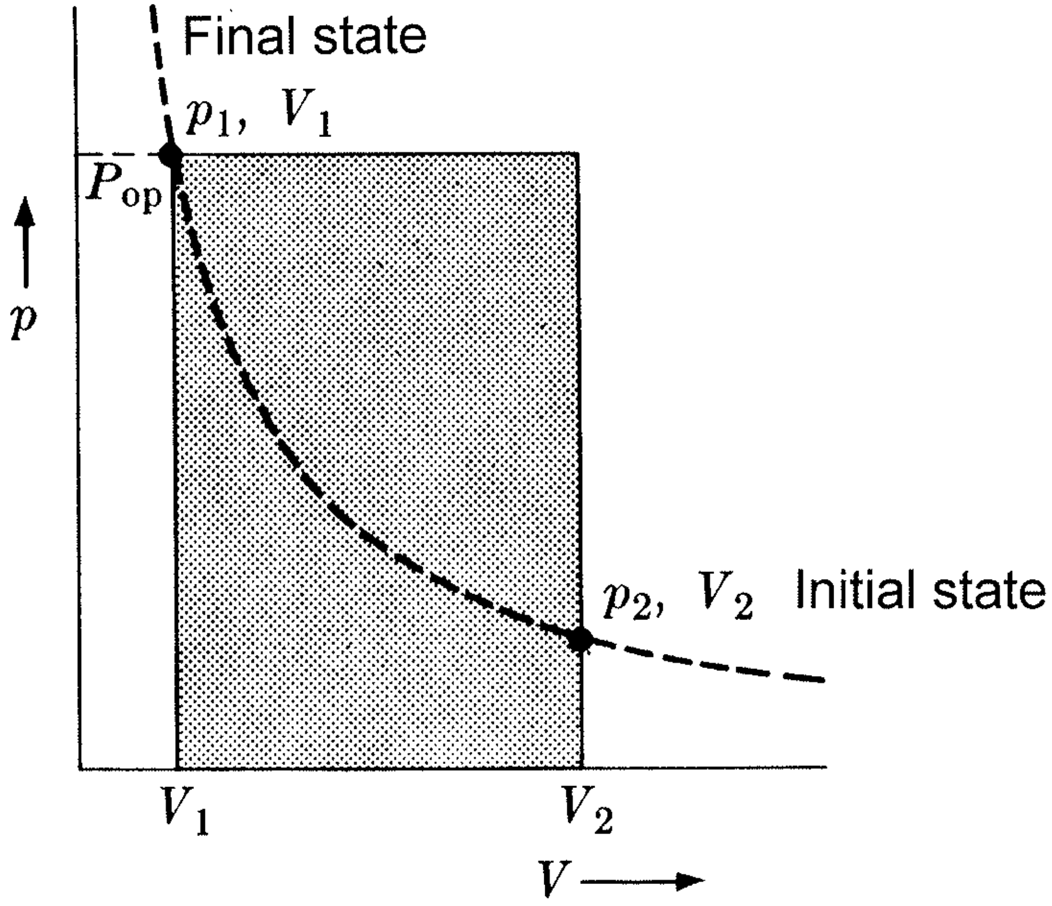


(a) Initial state (b) Final state

$$W = \int_{Vi}^{Vf} \delta W = - P_{op} \int_{V2}^{V1} dV$$

$$= P_{op}(V_2 - V_1) > 0.$$

compression



$$W = \int_{V_i}^{V_f} đW \quad = -P_{op} \int_{V_2}^{V_1} dV$$

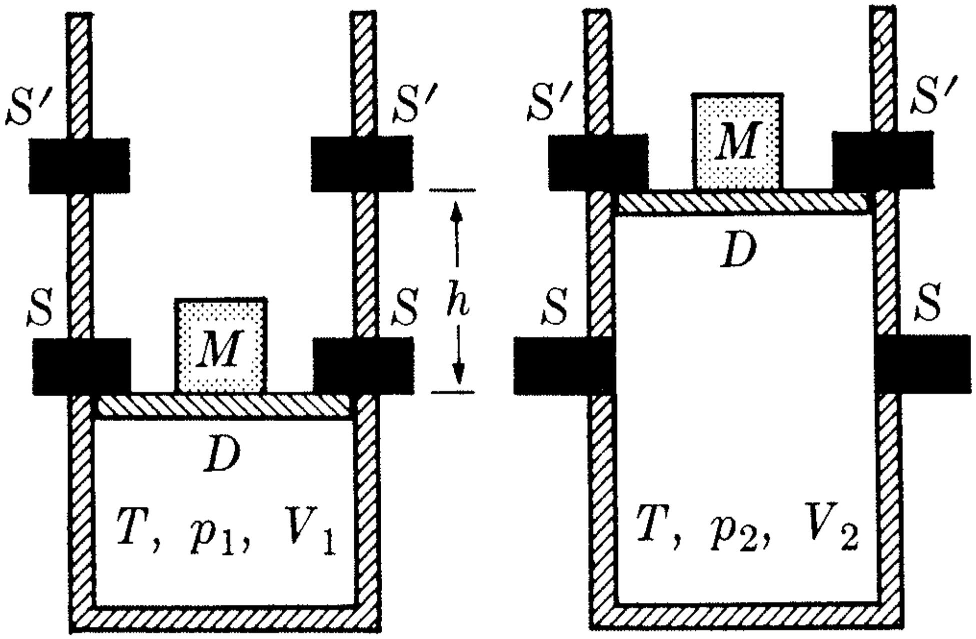
$$= P_{op}(V_2 - V_1) > 0.$$

EXAMPLE: A gas system alters its volume against an opposing external pressure in the following process:

a single-stage expansion from V_1 to V_2

p_{op} = a constant = P_{op}

The quantity of work is ***W* = −*Mgh***. the weight is raised (*h* is +), Work is *negative* in which case we say that work has flowed to the surroundings *from the system*.

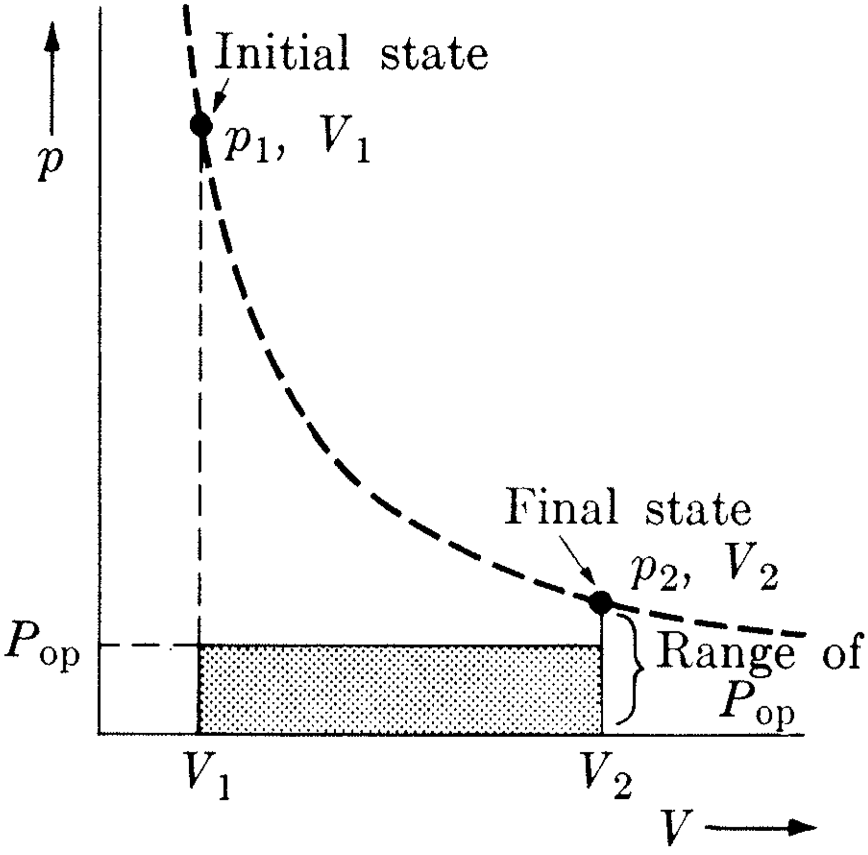


(a) Initial state (b) Final state

$$W = \int_{V_i}^{V_f} đW = -P_{op}\int_{V1}^{V2} dV$$

$$= -P_{op}(V_2 - V_1) < 0.$$

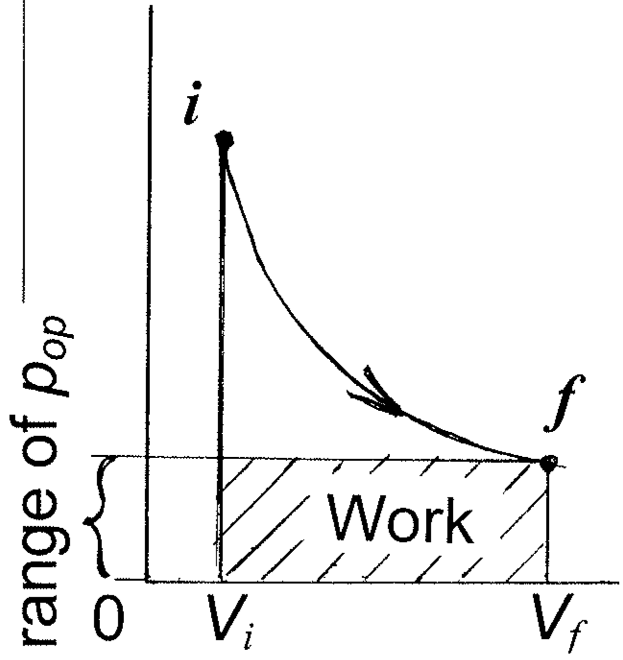
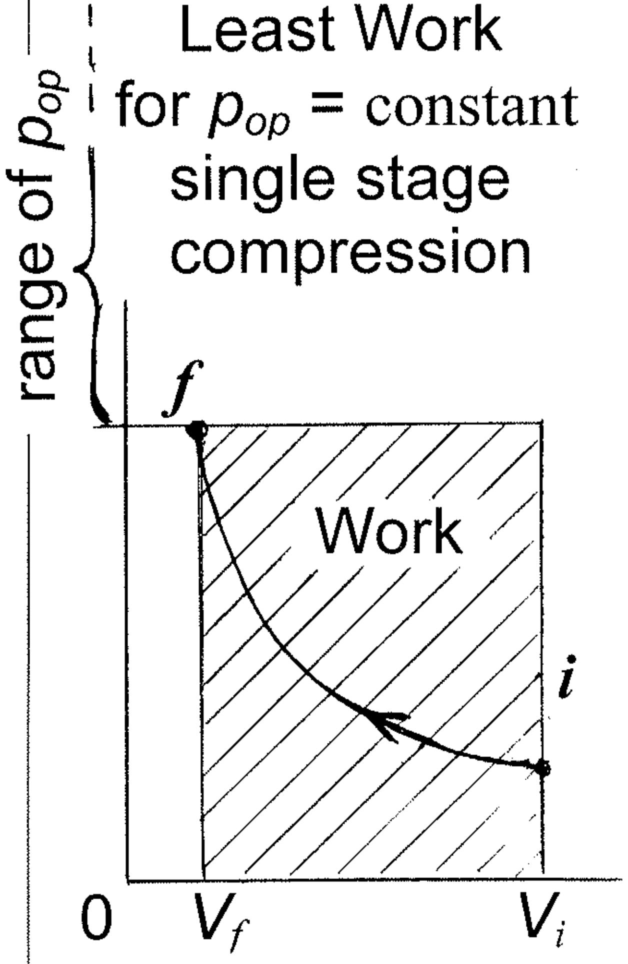
expansion



$$W = \int_{Vi}^{Vf} \eth W \quad = - P_{op} \int_{V1}^{V2} dV$$

$$= -P_{op}(V_2 - V_1) < 0.$$

Constraints for the p_{op} = constant

Expansion:	***Compression:***
$p_{op} \le p_{gas,\ final} < p_{gas,\ initial}$	$p_{op} \ge p_{gas,\ final} > p_{gas,\ initial}$
Best Work for p_{op} = constant single stage expansion  	Least Work for p_{op} = constant single stage compression 

$$\text{Work} = -\int p_{op}\,\mathrm{d}V = -p_{op}[V_f - V_i]$$

EXAMPLE: A gas system alters its volume against an opposing external pressure in the following process:

a two-stage expansion from V_1 to V_2

First stage: p_{op} = a constant = P''_{op}

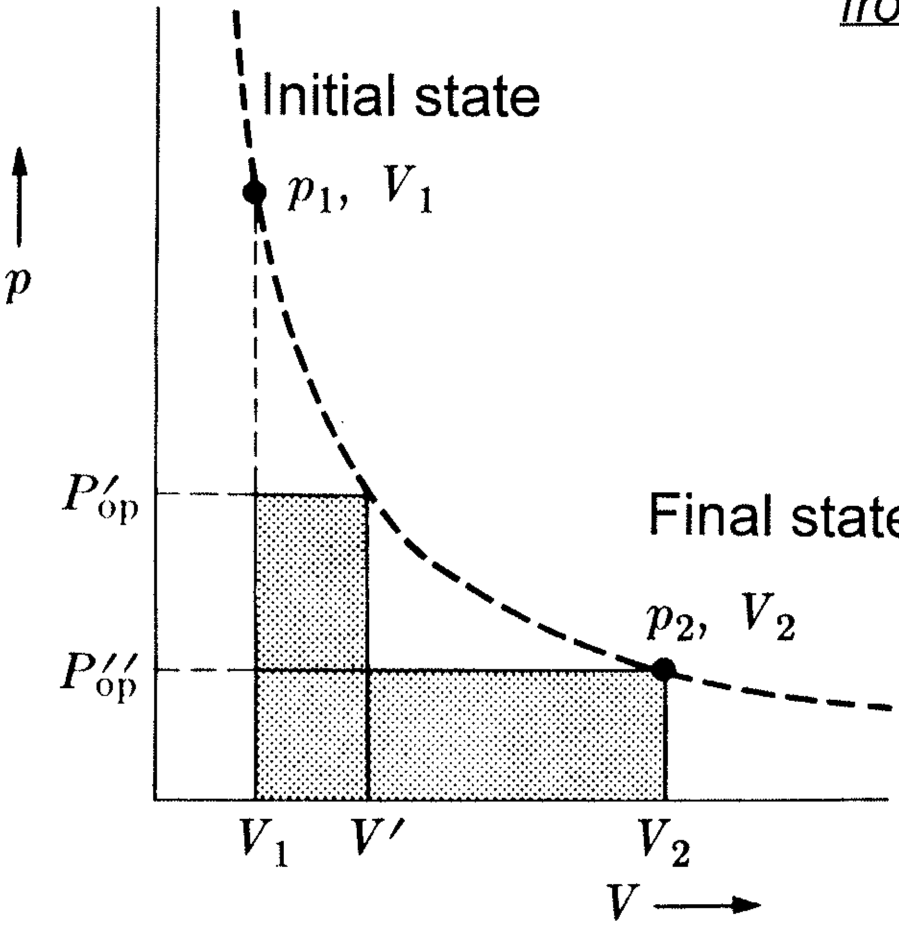
Second stage: p_{op} = a constant = P'_{op}

$$W = \int_{Vi}^{Vf} đW = -P''_{op}\int_{V1}^{V'} dV - P'_{op}\int_{V'}^{V2} dV$$

$$= -P''_{op}(V'-V_1) - P'_{op}(V_2-V') < 0.$$

work has flowed to the surroundings

<u>*from the system*</u>.



compare this with one-stage expansion. This produces more |work| from the system to the surroundings, for the same change in state of the system.

EXAMPLE: A gas system alters its volume against an opposing external pressure in the following process:

a two-stage compression from V_2 to V_1

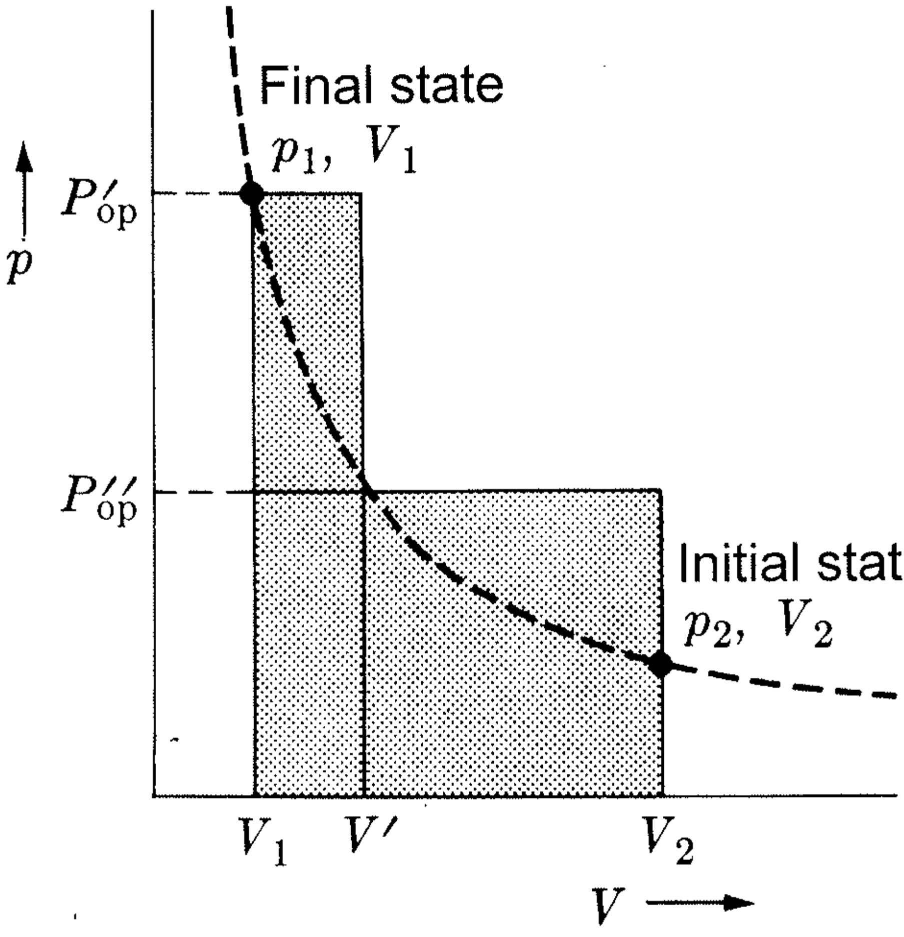
First stage: p_{op} = a constant = P''_{op}

Second stage: p_{op} = a constant = P'_{op}

$$W = \int_{V_i}^{V_f} đW \quad = - P''_{op} \int_{V_2}^{V'} dV - P'_{op} \int_{V'}^{V_1} dV$$

$$= P''_{op} (V_2 - V') + P'_{op} (V' - V_1) > 0.$$

work has flowed from the surroundings <u>*to the system*</u>.



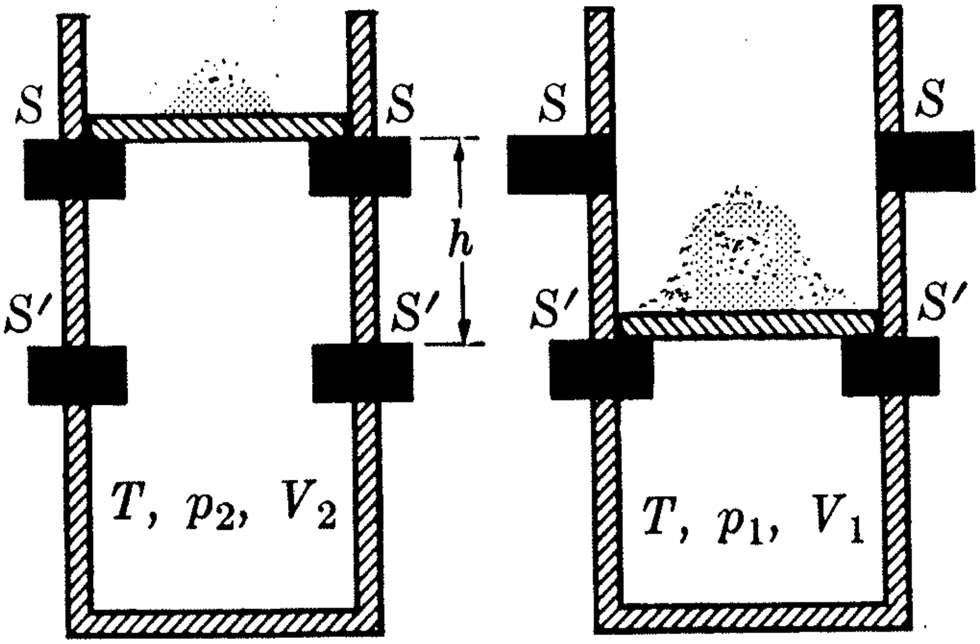
compare this with one-stage compression. This requires less $|\text{work}|$ from the surroundings to the system, for the same change in state of the system.

EXAMPLE: A gas system alters its volume against an opposing external pressure in the following process:

a reversible compression from V_2 to V_1 along the path described by $p_{op} = p_{gas}(V)$

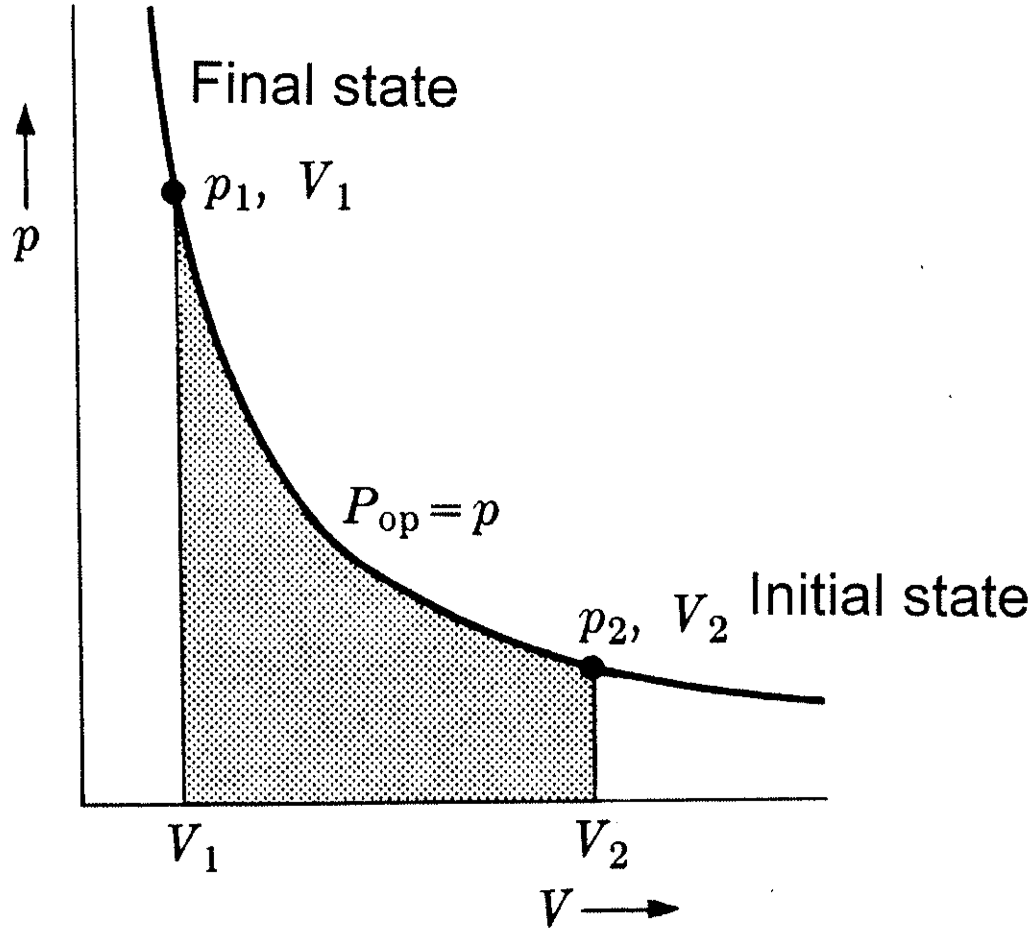
$$W = \int_{V_i}^{V_f} \delta W \quad = - \int_{V_2}^{V_1} [p_{gas}(V)]\, dV$$

Work is *positive*. The minimum amount of work has flowed from the surroundings *to the system*.



(a) Initial state (b) Final state

reversible compression



Compare this with 1-stage and 2-stage compression.
This requires minimum $|\text{work}|$
from the surroundings to the system,
for the same change in state of the system.

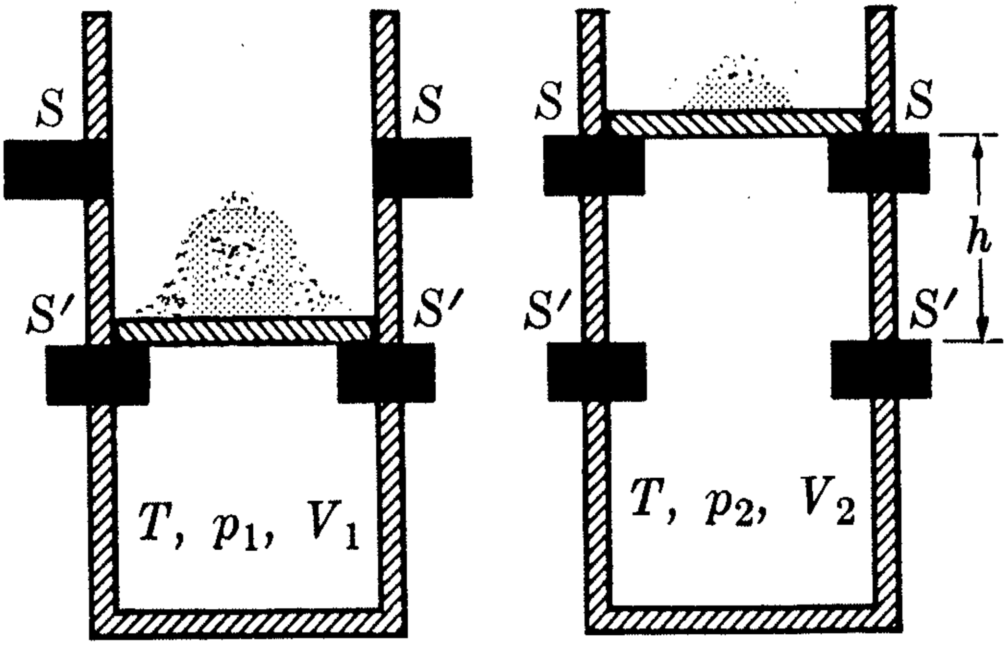
EXAMPLE: A gas system alters its volume against an opposing external pressure in the following process:

a reversible expansion from V_1 to V_2

along the path described by $p_{op} = p_{gas}(V)$

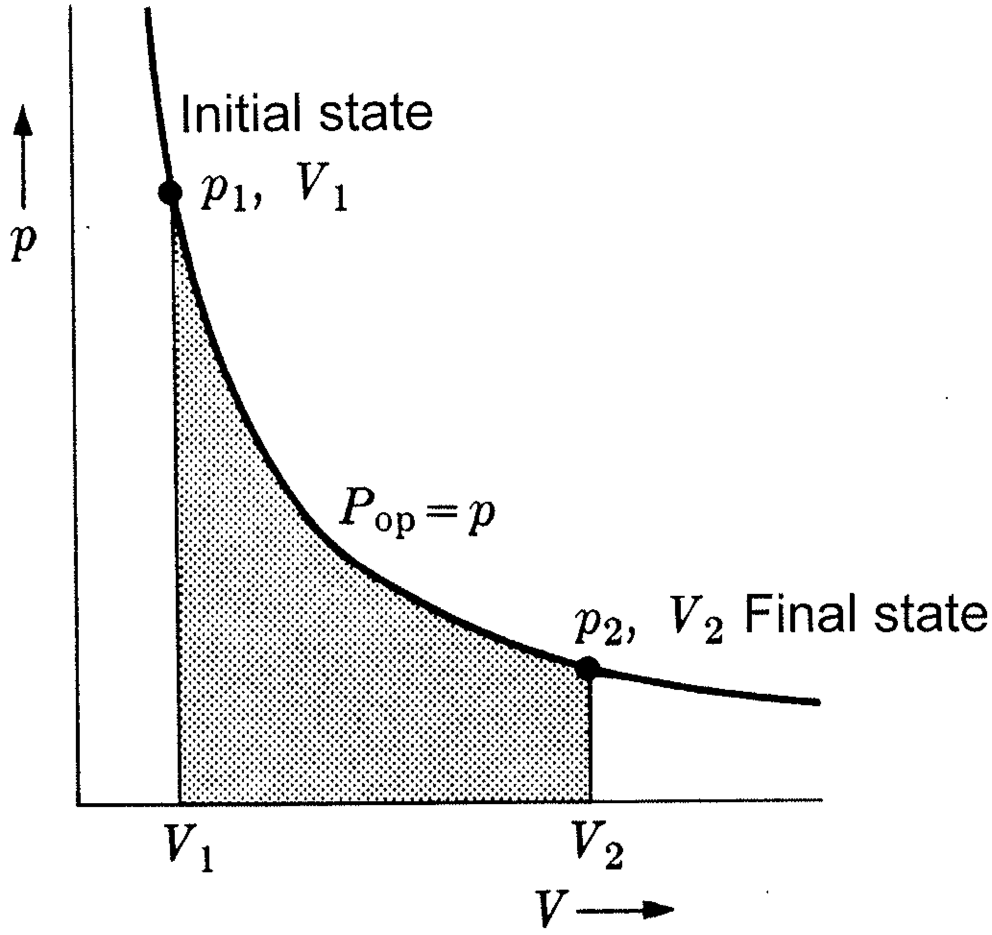
$$W = \int_{Vi}^{Vf} \delta W \quad = - \int_{V1}^{V2} [p_{gas}(V)]\, dV$$

Work is _negative_ . The maximum amount of work has flowed to the surroundings _from the system_.



(a) Initial state (b) Final state

reversible expansion



Compare this with 1-stage and 2-stage expansion.
This produces <u>maximum</u> $|\text{work}|$
from the system to the surroundings,
for the same change in state of the system.

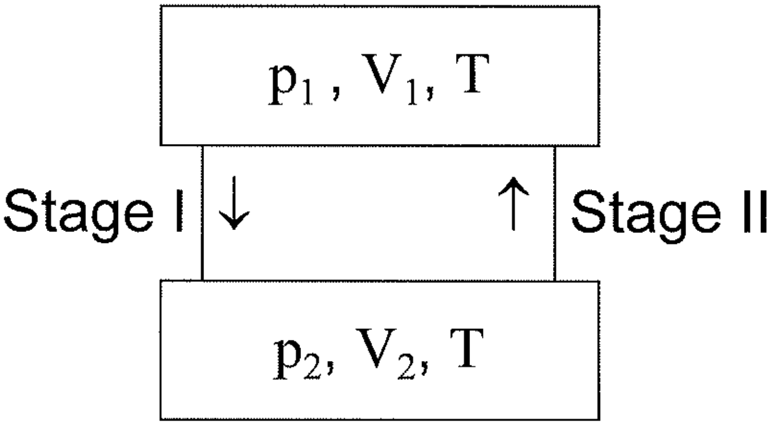
Note that whether $V_f < V_i$ (gas undergoes the process of compression) or $V_f > V_i$, (gas undergoes the process of expansion) the integration is the same. The only difference is that the opposing external pressure has to be greater than or at least as great as $p_{gas,f}$ in order to have compression, while the opposing external pressure has to be no larger than $p_{gas,i}$ in order to have expansion.

For a gaseous system in an isothermal process (T= constant throughout the path), the *maximum work produced* in the surroundings during the expansion of a gas (that is, the maximum amount of work that can be removed from a system) is also the *minimum amount of work that is required* to flow from the surroundings to the system to carry out the compression of a gas:

$$W_{max\ or\ min} = -\int_{Vi}^{Vf} [p_{gas}(V)]\, dV, \quad T = constant$$

2.4 Reversible and irreversible transformations, cyclic transformations

Consider a system: a quantity of gas confined in a cylinder at a constant temperature T. Stage I process: Initial conditions ($p_{gas,i} = p_1$, $V_i = V_1$, T), final conditions ($p_{gas,f} = p_2$, $V_f = V_2$, T) with $V_2 > V_1$, followed by Stage II process: Initial conditions ($p_{gas,i} = p_2$, $V_i = V_2$, T), final conditions ($p_{gas,f} = p_1$, $V_f = V_1$, T). This is a 2-stage cycle. The system has returned to its original state (p_1 , V_1, T).



p_1 , V_1, T

Stage I ↓

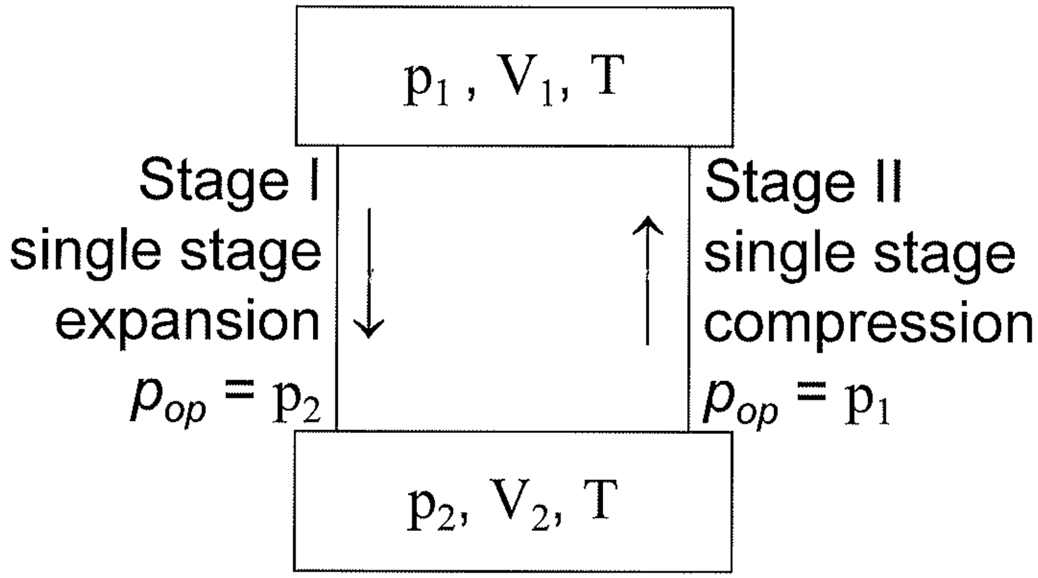
↑ Stage II

p_2, V_2, T

Question: Calculate the work for this cycle, W_{cycle}.

Answer: Can't do it, didn't describe the path!

Suppose we perform this cycle by **PROCESS A**: Stage I is a single stage expansion with $p_{op} = p_2$ followed by Stage II, a single stage compression with $p_{op} = p_1$.



p_1, V_1, T

Stage I
single stage
expansion
$p_{op} = p_2$

Stage II
single stage
compression
$p_{op} = p_1$

p_2, V_2, T

$W_{exp} = -p_2(V_2 - V_1) \qquad W_{comp} = p_1(V_2 - V_1)$

$$W_{cycle} = W_{exp} + W_{comp} = -p_2(V_2 - V_1) + p_1(V_2 - V_1)$$
$$= (p_1 - p_2)(V_2 - V_1) > 0$$

Net work has been destroyed in the surroundings; work passed across the boundary from the surroundings to the system. The system was restored to its initial conditions but *the surroundings have not been restored*: weights are lower in the surroundings after the cycle! This is an ***irreversible process***.

Suppose we perform this cycle by **PROCESS B**: infinitely slowly do a multistage expansion with $p_{op} = p_{gas} - \delta$, where δ is infinitesimally small at each stage, then infinitely slowly do a multistage compression with $p_{op} = p_{gas} + \delta$ at each stage.

$$W_{exp} = -\int_{V1}^{V2} p_{gas}\, dV \qquad W_{comp} = -\int_{V2}^{V1} p_{gas}\, dV.$$

$$W_{cycle} = W_{exp} + W_{comp} = 0$$

The system was restored to its initial conditions and <u>the surroundings are also restored to their initial conditions, since no net work is produced.</u> This is a ***reversible process***.

In a reversible process the internal equilibrium of the gas is disturbed only infinitesimally and in the limit, not at all. At any stage in a reversible transformation the system does not depart from equilibrium by more than an infinitesimal amount.

The goal of reversibility can be very closely approached, but not attained.

$$W_{\text{cycle}} = \int đW \neq 0 \qquad q_{\text{cycle}} = \int đq \neq 0$$

Since the quantity of work that appears in the surroundings depends upon the way in which the change in state is brought about, the integral representing work is said to be a <u>line integral</u> whose value depends upon the <u>path</u>.

In contrast,

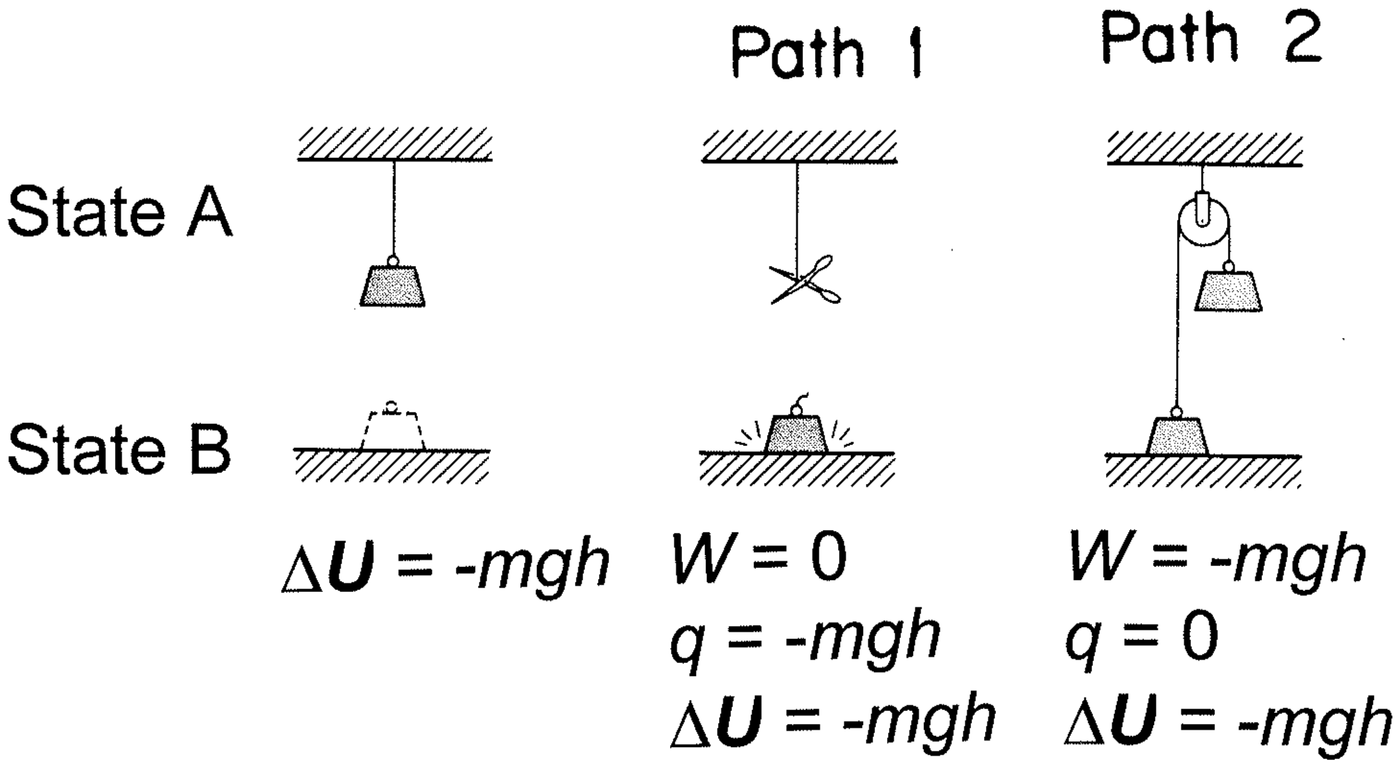
$$\int \mathrm{d}y = 0 \quad \text{for } y = \text{any state function}$$

If we sum the differential of any state function of the system over any cycle, the total difference, the cyclic integral, must be zero.

Conversely, if we find a differential quantity dy such that

$$\int \mathrm{d}y = 0 \qquad \text{for all cycles}$$

then dy is the differential of some state function or state property y.


Path 1
Path 2
State A
State B
$\Delta \boldsymbol{U} = -mgh$
$W = 0$
$q = -mgh$
$\Delta \boldsymbol{U} = -mgh$
$W = -mgh$
$q = 0$
$\Delta \boldsymbol{U} = -mgh$

2.5 The energy *U*, the First Law of Thermodynamics

The ***first law of thermodynamics*** is a statement of the following universal experience: If a system is subjected to any cyclic transformation, the work produced in the surroundings is equal to the heat withdrawn from the surroundings.

The first law is also a statement of the conservation of energy ***U***:

$$\mathrm{d}U = \text{đ}q + \text{đ}W \quad \text{or} \quad \Delta U = q + W$$

(system + surroundings) includes everything.

If the system is returned to its original state, then the work produced in the surroundings must equal to the heat withdrawn from the surroundings.

In the system's accounting, the change in internal energy of the system must be accounted for by the net heat + work appearing at the surroundings.

In other words, for any change of state of the system,

$$\Delta U_{system} + \Delta U_{surr.} = 0$$

Clausius stated this as: “The energy of the universe is a constant.”

Choosing a system of fixed mass, we can describe the state of the system by specifying T and V. Then we can write the energy $\boldsymbol{U}$ as a function of T and V:

$\boldsymbol{U} = \boldsymbol{U}(T, V)$ and the change in $\boldsymbol{U}$, $\mathrm{d}U$ is related to the changes in temperature $\mathrm{d}T$ and the changes in volume $\mathrm{d}V$ through the total differential expression

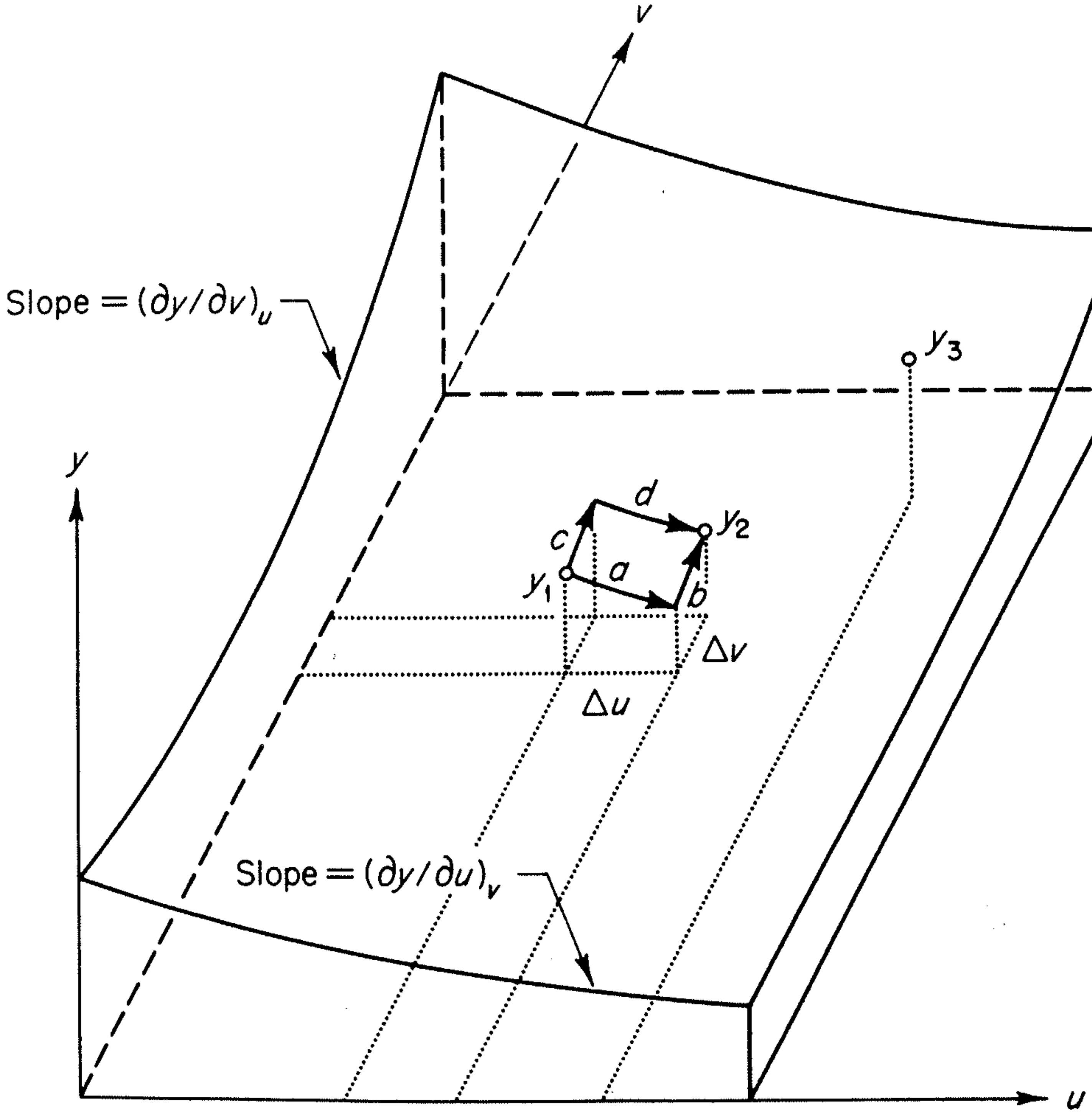
$$\mathrm{d}\boldsymbol{U} = (\partial \boldsymbol{U}/\partial \mathrm{T})_V \mathrm{d}T + (\partial \boldsymbol{U}/\partial V)_T \mathrm{d}V$$

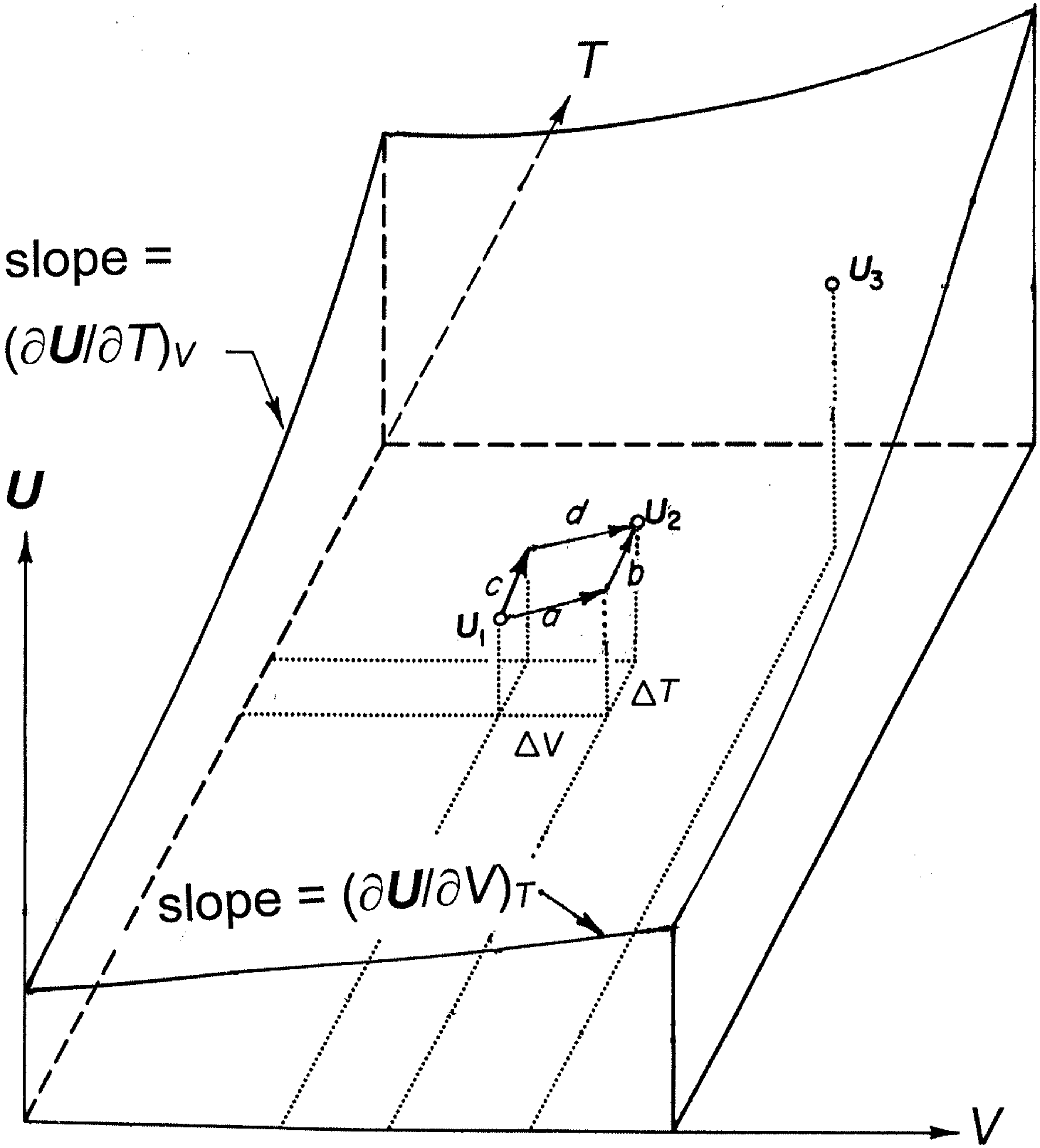
The subscript “$_V$ “ means “at constant V”.

What does this say?

If the temperature of the system increases by an amount $\mathrm{d}T$ and the volume increases by an amount $\mathrm{d}V$, then the total increase in energy is the sum of two contributions.

$(\partial \boldsymbol{U}/\partial \mathrm{T})_V \mathrm{d}T$ is the increase in energy resulting from the temperature increase alone.


v
y
Slope = $(\partial y/\partial v)_u$
y_3
d
y_2
c
y_1
a
b
Δv
Δu
Slope = $(\partial y/\partial u)_v$
u


T
slope =
$(\partial \boldsymbol{U}/\partial T)_V$
U_3
$\boldsymbol{U}$
d
U_2
c
b
U_1
a
ΔT
ΔV
slope = $(\partial \boldsymbol{U}/\partial V)_T$
V

2.6 Exact and inexact differentials

What is an ***exact differential*** ?
An exact differential integrates to a finite difference.

$$\int_{\mathrm{yi}}^{\mathrm{yf}} \mathrm{d}y = y_f - y_i$$

which is *independent of the path of integration*.

In contrast, "$p\mathrm{d}V$" is the kind of expression that cannot be regarded as the differential of any function of the state of the system; it is an ***inexact differential***.

Since p is in general, a function of two variables, say T and V, it is evident that the integral of $p\mathrm{d}V$ is meaningless unless some functional relationship between T and V is specified (the path); only in that case can the line integral

$$W = \int_{\mathrm{Vi}}^{\mathrm{Vf}} \text{đ}W = -\int_{\mathrm{Vi}}^{\mathrm{Vf}} p_{op}\mathrm{dV}$$

be evaluated.

2.7 Examples of Changes in State (at Constant Volume, at Constant Pressure); Definition of *H*

2.7.1 Changes in State at Constant Volume

$$dU = (\partial U/\partial T)_V dT + (\partial U/\partial V)_T dV$$

If the volume of the system is constant as the system undergoes a change in state, then $dV=0$

$$dU = (\partial U/\partial T)_V dT \qquad \text{when } dV=0$$

and

$$\Delta U = \int_{T_i}^{T_f} (\partial U/\partial T)_V dT \qquad \text{when } dV=0$$

Also, since $dV = 0$, $V_i = V_f$ and the integral

$$W = - \int_{V_i}^{V_f} p_{op} dV$$

is zero, of course.

The first law says $\Delta U = q + W$, leading to

$$\Delta U = q_V$$

The subscript "$_V$" means "at constant V".

$\Delta U = q_V$, constant volume change of any system

leads us to write

$$\mathrm{d}\boldsymbol{U} = \text{đ}q_V$$

or $\mathrm{d}\boldsymbol{U} = (\partial \boldsymbol{U}/\partial T)_V \mathrm{d}T = \text{đ}\boldsymbol{q}_V$

which relates the heat withdrawn from the surroundings to the increase in temperature $\mathrm{d}T$ of the system at constant volume.

The ratio $(\text{đ}\boldsymbol{q}_V/\mathrm{d}T)$ of the heat withdrawn from the surroundings to the temperature increase of the system is called the ***heat capacity of the system at constant volume***, $\boldsymbol{C}_V$.

$$\boldsymbol{C}_V \equiv (\text{đ}\boldsymbol{q}_V/\mathrm{d}T) = (\partial \boldsymbol{U}/\partial T)_V$$

This identifies the partial derivative $(\partial \boldsymbol{U}/\partial T)_V$ with an easily measurable quantity $\boldsymbol{C}_V$.

For an infinitesimal change

$$\mathrm{d}\boldsymbol{U} = \boldsymbol{C}_V \mathrm{d}T$$

which can be integrated to

$$\Delta \boldsymbol{U} = \int_{\mathrm{Ti}}^{\mathrm{Tf}} \boldsymbol{C}_V \mathrm{d}T$$ constant volume change of any system

2.7.2 Changes in State at Constant Pressure

Define $\boldsymbol{H} \equiv \boldsymbol{U} + pV$

$\mathrm{d}\boldsymbol{H} \equiv \mathrm{d}\boldsymbol{U} + p\mathrm{d}V + V\mathrm{d}p$

Since $\boldsymbol{H}$ is a state function, $\mathrm{d}\boldsymbol{H}$ is an exact differential. $\boldsymbol{H}$ is called the ***enthalpy***.

Choosing a system of fixed mass, we can describe the state of the system by specifying T and p. Then we can write the energy $\boldsymbol{H}$ as a function of T and p:

$\boldsymbol{H} = \boldsymbol{H}(T, p)$ and the change in $\boldsymbol{H}$, $\mathrm{d}\boldsymbol{H}$ is related to the changes in temperature $\mathrm{d}T$ and the changes in pressure $\mathrm{d}p$ through the total differential expression

$$\mathrm{d}\boldsymbol{H} = (\partial \boldsymbol{H}/\partial \mathrm{T})_p \mathrm{d}T + (\partial \boldsymbol{H}/\partial p)_T \mathrm{d}p$$

At constant pressure, $\mathrm{d}p=0$

$\Delta \boldsymbol{H}_p = \int \mathrm{d}\boldsymbol{H} = \int (\partial \boldsymbol{H}/\partial T)_p \, \mathrm{d}T$

The subscript "$_p$" means "at constant pressure".

At constant pressure P, the first law

$\mathrm{d}\boldsymbol{U} = \text{đ}q + \text{đ}W$ leads to $\Delta \boldsymbol{U} = q_p - \mathrm{P}\Delta V$

and the definition

$\boldsymbol{H} \equiv \boldsymbol{U} + pV$ leads to $\Delta \boldsymbol{H} = \Delta \boldsymbol{U} + \mathrm{P}\Delta V$

Therefore,

$\Delta \boldsymbol{H}_p = q_p$ or $\int (\partial \boldsymbol{H}/\partial T)_p \,\mathrm{d}T = q_p$

The ratio of the heat withdrawn from the surroundings to the temperature increase of the system is called the ***heat capacity of the system at constant pressure***, $\boldsymbol{C_p}$**.**

$\boldsymbol{C_p} \equiv (\eth \boldsymbol{q_p} /\mathrm{d}T)$ so that $q_p = \int C_p \mathrm{d}T$

which relates the heat withdrawn from the surroundings to the increase in temperature $\mathrm{d}T$ of the system at constant pressure.

Thus, $(\partial \boldsymbol{H}/\partial T)_p$ can be identified with the heat capacity at constant pressure.

$$(\partial \boldsymbol{H}/\partial T)_p = C_p ,$$

This identifies the partial derivative $(\partial \boldsymbol{H}/\partial T)_p$ with an easily measurable quantity $C_{\boldsymbol{p}}$.

$$\Delta \boldsymbol{H}_p = \int_{\mathrm{Ti}}^{\mathrm{Tf}} C_p \,\mathrm{d}T$$

constant pressure

<u>any system</u>

2.8 Relation between C_p and C_V

The heat capacity of any system may have any value from $-\infty$ to $+\infty$, depending on the path since the heat withdrawn from the surroundings may have different values. Only two values C_p and C_V have major importance.

How are they related?

$$\text{đ}q + \text{đ}W = \mathrm{d}U = (\partial U/\partial T)_V \mathrm{d}T + (\partial U/\partial V)_T \mathrm{d}V$$

$$\text{đ}q - p_{op}\mathrm{d}V \qquad = C_V\mathrm{d}T + (\partial U/\partial V)_T \mathrm{d}V$$

At a constant pressure, $p_{op} = \mathrm{p}$

$$\text{đ}q_p - \mathrm{p}\mathrm{d}V \qquad = C_V\mathrm{d}T + (\partial U/\partial V)_T \mathrm{d}V$$

$$\text{đ}q_p = C_V\mathrm{d}T + \{\, \mathrm{p} + (\partial U/\partial V)_T \}\mathrm{d}V$$

Differentiate with respect to T at constant p,

$$(\text{đ}q_p /\partial T)_p = C_V + \{\, \mathrm{p} + (\partial U/\partial V)_T \}(\partial V/\partial T)_p$$

$$C_p - C_V = \{\mathrm{p} + (\partial U/\partial V)_T \}(\partial V/\partial T)_p \quad \textit{general}$$

In a ***constant volume process***, no work is produced, the average distance between molecules remains the same. Heat capacity is small, all of the heat withdrawn goes into the chaotic motion of the molecules and is reflected by a temperature increase.

In a ***constant pressure process***, the system expands against the opposing pressure and produces work in the surroundings; the heat withdrawn from the surroundings is divided into 3 portions:

- produces work in the surroundings
- provides energy necessary to separate the molecules to larger distances
- increases the energy of the chaotic motion (reflects a temperature increase)

To produce a temperature increment of one degree, more heat must be withdrawn in the constant pressure process than is withdrawn in the constant volume process, thus $C_p > C_V$.

heat capacity ratio = $\gamma \equiv (C_p \,/\, C_V) > 1$

For an ideal gas:

$C_p - C_V = [p + (\partial U/\partial V)_T]\,(\partial V/\partial T)_p$ (general)

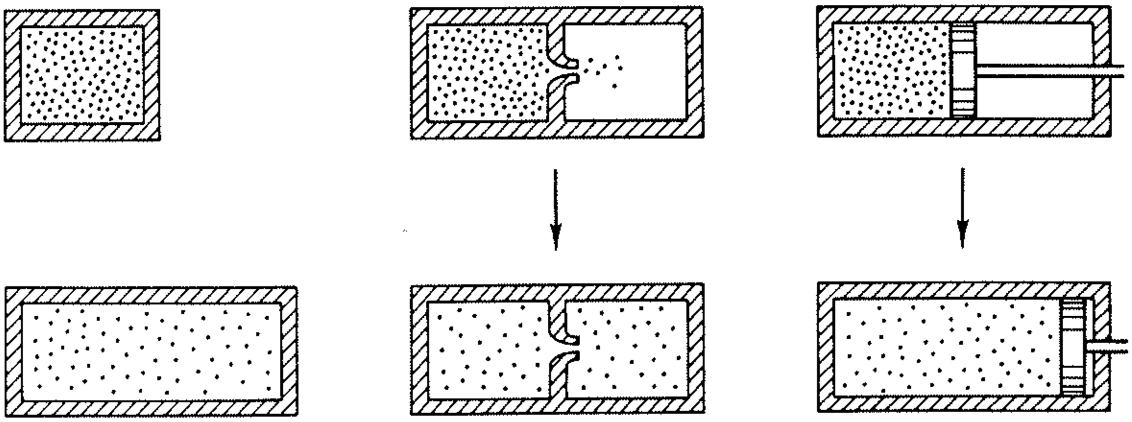
Substituting the following:

$(\partial U/\partial V)_T = 0$, (as we shall see in the Joule expt.)

$p(\partial V/\partial T)_p = R$ (from the ideal gas equation of state)

leads to

$$C_p - C_V = R$$



gas at T_1, p_1, V_1

State A

State B

gas at T_1, p_2, V_2

Path 1

$W = 0$

$q = \Delta \boldsymbol{U}$

Path 2

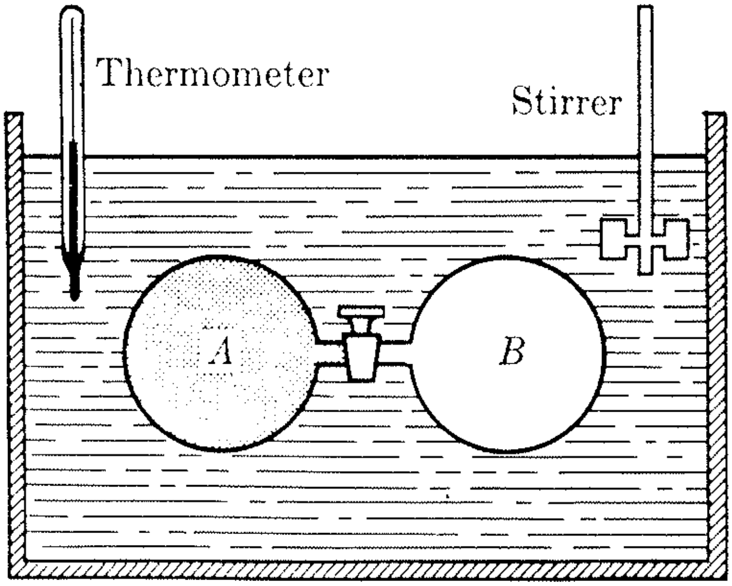
$W = -\int p_{op} \mathrm{d}V$

$q = \Delta \boldsymbol{U} - W$

$$\Delta \boldsymbol{U} = \int C_V \mathrm{d}T + \int (\partial \boldsymbol{U}/\partial V)_T \mathrm{d}V$$
$$= \int_{V1}^{V2} (\partial \boldsymbol{U}/\partial V)_T \mathrm{d}V \quad \textit{since } \mathrm{d}T = 0$$

2.9 The measurement of $(\partial U/\partial V)_T$ and $(\partial H/\partial p)_T$

2.9.1 Joule's experiment provides $(\partial U/\partial V)_T$



No observed temperature difference in the water before and after opening the stopcock.

$$\text{đ}q + \text{đ}W = \mathrm{d}U = (\partial U/\partial T)_V \mathrm{d}T + (\partial U/\partial V)_T \mathrm{d}V$$

Expansion against zero opposing pressure means $\text{đ}W = 0$.

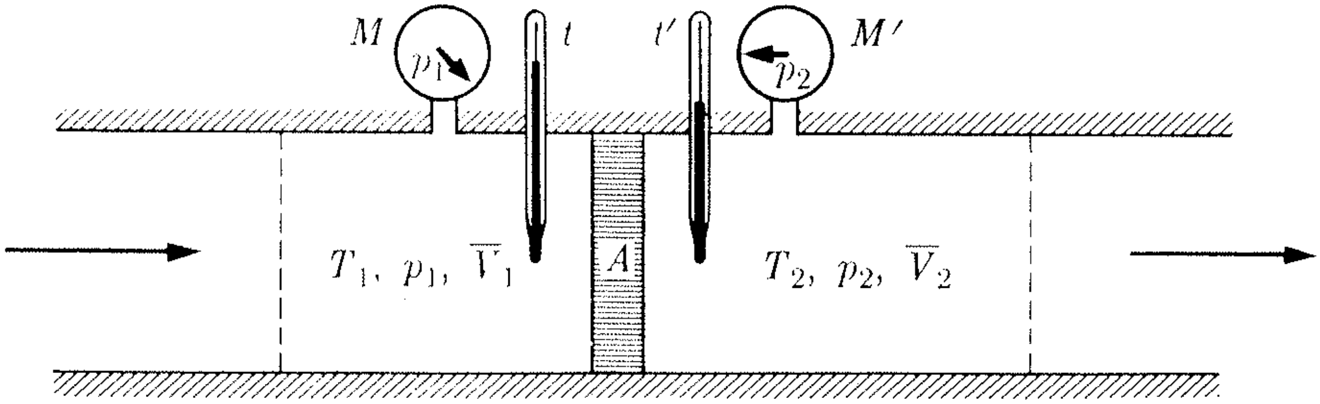
No observed temperature change in the surrounding water means $\text{đ}q = 0$.

Since the water and the system are in thermal equilibrium, then for the system also, $\mathrm{d}T = 0$.

$$\mathrm{d}U = 0 = 0 + (\partial U/\partial V)_T \mathrm{d}V$$

$\mathrm{d}V \neq 0$, therefore, $(\partial U/\partial V)_T = 0$

2.9.2 Joule-Thomson expt. provides $(\partial H/\partial p)_T$



Insulated so that $q = 0$.
RHS volume increases by $\overline{V}_2$
LHS volume decreases by $\overline{V}_1$

$\therefore \quad W = (-p_2\overline{V}_2)_{RHS} + (+p_1\overline{V}_1)_{LHS}$ for one mole of gas that passes through the plug.

$$q + W = U_2 - U_1 = -p_2\overline{V}_2 + p_1\overline{V}_1$$

$\therefore \quad H_2 = H_1$

Measure $\Delta T/\Delta p$ to obtain $\mu_{JT} = (\partial T/\partial p)_H$.

$$dH = C_p dT + (\partial H/\partial p)_T dp\ .$$

For $dH = 0$, and differentiate with respect to p

$$0 = C_p(\partial T/\partial p)_H + (\partial H/\partial p)_T$$

$$\boldsymbol{(\partial H/\partial p)_T = -C_p\,\mu_{JT}}$$

$$dH = C_p dT + (\partial H/\partial p)_T dp = dU + p dV + V dp$$

$$= C_V dT + (\partial U/\partial V)_T dV + p dV + V dp \, .$$

For $dT = 0$ and differentiate with respect to p,

$$(\partial H/\partial p)_T = (\partial U/\partial V)_T (\partial V/\partial \mathrm{p})_T + p(\partial V/\partial \mathrm{p})_T + V$$

$$(\partial H/\partial p)_T = [p + (\partial U/\partial V)_T](\partial V/\partial \mathrm{p})_T \quad + V$$

For the ideal gas,

$H = U + pV = U + RT$ for one mole.

Since we have already shown that U is only a function of T for an ideal gas (Joule expt.), then H is only a function of T for an ideal gas.

$$(\partial H/\partial p)_T = 0$$

For the general non-ideal gas:

We have already found the general relationships

$(\partial \mathbf{H}/\partial p)_T = [p + (\partial \mathbf{U}/\partial V)_T](\partial V/\partial p)_T + V$

and

$C_p - C_V = \{ p + (\partial \mathbf{U}/\partial V)_T\}(\partial V/\partial T)_p$

We shall prove later on that the quantities $(\partial \mathbf{U}/\partial V)_T$ and $(\partial \mathbf{H}/\partial p)_T$ can be related directly to the equation of state, as follows:

$(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p$

$(\partial \mathbf{H}/\partial p)_T = - T(\partial V/\partial T)_p + V$

Therefore, **for any gas**, ideal or not, we can find the derivatives $(\partial V/\partial T)_p$ and $(\partial p/\partial T)_V$ from the equation of state, and then we can find the functions:

$$\boxed{\begin{aligned} &(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p \\ &(\partial \mathbf{H}/\partial p)_T = - T(\partial V/\partial T)_p + V \\ &C_p - C_V = \{ p + (\partial \mathbf{U}/\partial V)_T\}(\partial V/\partial T)_p \end{aligned}}$$

The **special case** that the equation of state is

$$pV = RT$$

gives

$$(\partial p/\partial T)_V = R/V \quad \text{and } (\partial V/\partial T)_p = R/p$$

These lead to

$$(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p = 0$$

$$(\partial \mathbf{H}/\partial p)_T = - T(\partial V/\partial T)_p + V = 0$$

$$C_p - C_V = \{ p + (\partial \mathbf{U}/\partial V)_T\}(\partial V /\partial T)_p = R$$

$(\partial \mathbf{U}/\partial V)_T$ and $(\partial \mathbf{H}/\partial p)_T$ from the equation of state

Later on, we shall prove from the first and second laws of thermodynamics, that

$$(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p$$
$$(\partial \mathbf{H}/\partial p)_T = -T(\partial V/\partial T)_p + V$$

For the equation of state $pV = nRT$

We get $(\partial p/\partial T)_V = nR/V$

and $(\partial V/\partial T)_p = nR/p$

$$(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p = nRT/V - nRT/V$$
$$= 0$$

$$(\partial \mathbf{H}/\partial p)_T = -T(\partial V/\partial T)_p + V = -nRT/p + nRT/p$$
$$= 0$$

For the equation of state

$$pV = nRT + nap$$

where *a* is dependent on *T*

From $p = nRT/(V-na)$ we get

$$(\partial p/\partial T)_V = nR/(V-na)$$
$$+n^2RT(V-na)^{-2}(\mathrm{d}a/\mathrm{d}T)$$
$$(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p$$
$$= nRT/(V-na)$$
$$+n^2RT(V-na)^{-2}(\mathrm{d}a/\mathrm{d}T) - nRT/(V-na)$$
$$= n^2RT^2(V-na)^{-2}(\mathrm{d}a/\mathrm{d}T)$$

{=0 if *a* is independent of *T*}

From $V = nRT/p + na$ we get

$$(\partial V/\partial T)_p = nR/p + n(\mathrm{d}a/\mathrm{d}T)$$
$$(\partial \mathbf{H}/\partial p)_T = -T(\partial V/\partial T)_p + V$$
$$= -nRT/p - nT(\mathrm{d}a/\mathrm{d}T) + nRT/p + na$$
$$= na - nT(\mathrm{d}a/\mathrm{d}T)$$

{= *na* if *a* is independent of *T*}

For the equation of state

$$[p+(n/V)^2 a]V = nRT$$

where a is dependent on T

From $p = nRT/V - (n/V)^2 a$ we get

$(\partial p/\partial T)_V = nR/V - (n/V)^2(\mathrm{d}a/\mathrm{d}T)$

$(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p$

$= nRT/V - (n/V)^2 T(\mathrm{d}a/\mathrm{d}T) - nRT/V + (n/V)^2 a$

$(\partial \mathbf{U}/\partial V)_T = (n/V)^2 a - (n/V)^2 T(\mathrm{d}a/\mathrm{d}T)$

{$= (n/V)^2 a$ if a is independent of T}

Can not easily find $(\partial \mathbf{H}/\partial p)_T$ from $(\partial V/\partial T)_p$ because we have a cubic equation in V

For the equation of state

$$[p+(n/V)^2a][V-nb] = nRT$$

where a and b are dependent on T

From $p = -(n/V)^2a + nRT/(V-nb)$ we get

$$(\partial p/\partial T)_V = -(n/V)^2(\mathrm{d}a/\mathrm{d}T) + nR/(V-nb)$$
$$+n^2RT(V-nb)^{-2}(\mathrm{d}b/\mathrm{d}T)$$

$$(\partial \mathbf{U}/\partial V)_T = T(\partial p/\partial T)_V - p$$
$$= nRT/(V-nb) - (n/V)^2T(\mathrm{d}a/\mathrm{d}T)$$
$$-nRT/(V-nb) + (n/V)^2a$$
$$+n^2RT^2(V-nb)^{-2}(\mathrm{d}b/\mathrm{d}T)$$

$$(\partial \mathbf{U}/\partial V)_T = (n/V)^2a - (n/V)^2T(\mathrm{d}a/\mathrm{d}T)$$
$$+n^2RT^2(V-nb)^{-2}(\mathrm{d}b/\mathrm{d}T)$$

{= $(n/V)^2a$ if a,b are independent of T}

Can not easily find $(\partial \mathbf{H}/\partial p)_T$ from $(\partial V/\partial T)_p$ because we have a cubic equation in V

2.10 Adiabatic Changes in State

adiabatic change in state — A change in state during which no heat flows, $đq = 0$.

For an adiabatic change in state,
since $đq = 0$, the first law leads to
$dU = đW, \qquad \Delta U = W,$
The work that crosses the boundary from the system to the surroundings is at the expense of a decrease in energy of the system.
A decrease in energy in a system is evidenced almost entirely by a decrease in temperature of the system: i.e., if work appears in the surroundings in an adiabatic change in state, the temperature of the system falls.

For an ideal gas:

$dU = C_V dT + (\partial U/\partial V)_T dV$ *general*

$\quad = C_V dT + 0$ *ideal gas*

For an adiabatic change,
$dU = đW = -p_{op} dV$ *adiabatic*

$\therefore\ -p_{op}\mathrm{d}V = C_V\,\mathrm{d}T$ *adiabatic, ideal gas*

$p = nRT/V$ *ideal gas*

If adiabatic change is carried out reversibly,

$p_{op} = p_{gas}$ *reversible*

$-(nRT/V)dV = C_V\,\mathrm{d}T$ *adiabatic, ideal gas,*
& reversible

for one mole

$-R(dV/\bar{V}) = \bar{C}_V(\mathrm{d}T/T)$ *adiabatic, ideal gas,*
& reversible

Integrating,

$-R\ln(V_f/V_i) = \bar{C}_V\ln(T_f/T_i)$ *adiabatic, ideal gas,*
& reversible

$R = \bar{C}_p - \bar{C}_V$ *ideal gas*

$R/C_V = (\bar{C}_p/\bar{C}_V) - 1 = \gamma - 1$ *ideal gas*

$$\left.\begin{array}{l} -(\gamma - 1)\ln(V_f/V_i) = \ln(T_f/T_i) \\ (V_i/V_f)^{(\gamma - 1)} = (T_f/T_i) \\ (V_1/V_2)^{(\gamma - 1)} = (T_2/T_1) \\ p_1V_1^{\gamma} = p_2V_2^{\gamma} \end{array}\right]$$

adiabatic,
ideal gas,
& reversible
only

$1\ \mathrm{J} = 1\ \mathrm{kg\ m^2\ s^{-2}}$

$k_B = 1.38066\times10^{-23}\ \mathrm{J\ K^{-1}}$

$R = N_{\mathrm{Avogadro}} k_B$

$$
\begin{aligned}
R &= 8.31441\ \mathrm{J\ mol^{-1}\ K^{-1}} \\
&= 1.98718\ \mathrm{cal\ mol^{-1}\ K^{-1}} \\
&= 0.082057\ \ell\ \mathrm{atm\ mol^{-1}\ K^{-1}}
\end{aligned}
$$

monatomic gas

molar heat capacity $C_V = (3/2)\ R$

2.11 Application of the First Law of Thermodynamics to Chemical Reactions,

the Standard Enthalpy Change, $\Delta H^{\ominus}(T)$

the standard state — The standard state of a substance at a specified temperature is its pure form at 1 bar

1 bar is 10^5 pascals, 1 atm = 1.01325 bar

1 bar = 0.987 atm

Examples:

the standard state of water at 300 K is pure liquid water at 300 K and 1 bar.

the standard state of methane at 300 K is pure CH_4 gas at 300 K and 1 bar.

standard enthalpy of transition —the enthalpy change that accompanies a change in physical state.

Examples of changes in physical state:

vaporization: liquid→gas

fusion: solid → liquid

sublimation: solid→gas

solid phase transition:

monoclinic →orthorhombic

$\mathbf{H}^{\ominus}$(liquid, 1 bar, 353.2 K) C_6H_6(liq)

$\mathbf{H}^{\ominus}$(gas, 1 bar, 353.2 K) C_6H_6(gas)

For the transition,

vaporization at the standard boiling point,

353.2 K: $C_6H_6(\text{liq}) \rightarrow C_6H_6(\text{gas})$

$$\Delta_{\mathbf{vap}}\mathbf{H}^{\ominus}\mathbf{(}353.2\text{ K}\mathbf{)} = \mathbf{H}^{\ominus}(C_6H_6\text{ gas, 1 bar,353.2 K}) - \mathbf{H}^{\ominus}(C_6H_6\text{ liquid,1 bar,353.2K}) = 30.8\text{ kJ mol}^{-1}$$

standard enthalpy of vaporization $\Delta_{\mathbf{vap}}\mathbf{H}^{\ominus}$

— the enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar

The normal boiling point is at 1 atm, the standard boiling point is at 1 bar.
For H_2O they are 100.00°C (normal) and 99.6°C (standard).

reference state of an element — the most stable state of the element at the specified temperature and 1 bar.

standard enthalpy of formation $\Delta_f H^{\ominus}(T)$ — the enthalpy change accompanying the formation of one mole of a pure substance at 1 bar from its elements in their reference state at 1 bar all at temperature (T), T chosen conventionally to be 298.15 K.

$$\text{elements} \rightarrow \text{compound}$$

standard enthalpy of combustion $\Delta_c H^{\ominus}$— the enthalpy change per mole of a pure substance at 1 bar reacting with O_2(gas) at 1 bar to form CO_2(gas) at 1 bar and H_2O(liquid or gas) at 1 bar at temperature (T), T chosen conventionally to be 298.15 K, in which case it involves H_2O(liquid).

(standard) ***reaction enthalpies*** can be obtained from a combination of various enthalpy changes. So long as the net reaction is the same, no matter how the net chemical equation s arrived at, the net enthalpy change is the same *because **H** is a state function.*

For example for the reaction at 1 bar

$$C_6H_6(\text{liq}, 298.15\ \text{K}) + (15/2)O_2\,(\text{g}, 298.15\ \text{K}) \rightarrow 3H_2O(\text{liq}, 298.15\ \text{K}) + 6CO_2\,(\text{g}, 298.15\ \text{K})$$

$\Delta_{rxn}\boldsymbol{H} = ?$

We could use the sum of the following reactions, all at 298.15 K and 1 bar and $\Delta_f \mathbf{H}^\ominus$ of each:

$$
\begin{aligned}
&- \{\, 6C(s) + 3H_2(g) &&\rightarrow C_6H_6\,(liq) \,\} \\
&+ 3 \{\, H_2(g) + (1/2)O_2\,(g) &&\rightarrow H_2O(liq\ ) \,\} \\
&+ 6 \{\, C(s) + O_2\,(g) &&\rightarrow CO_2\,(g) \,\}
\end{aligned}
$$

$$
\begin{aligned}
\Delta_{rxn}\mathbf{H} &= -\ \Delta_f \mathbf{H}^\ominus (C_6H_6\,(liq) \\
&\quad +3\ \Delta_f \mathbf{H}^\ominus (H_2O(liq)) \ \ + 6\ \Delta_f \mathbf{H}^\ominus (CO_2\,(g))
\end{aligned}
$$

or we could use the sum of the following reactions, all at 298.15 K and 1 bar and $\Delta_{at} \mathbf{H}^\ominus$ of each:

$$
\begin{aligned}
&C_6H_6\,(liq) &&\rightarrow\ 6C(g) + 6H(g) \\
&+ (15/2) \{\, O_2\,(g) &&\rightarrow 2O\,(g) \,\} \\
&- 3 \{\, H_2O(liq\ ) &&\rightarrow\ 2H(g) + O\,(g) \,\} \\
&- 6 \{\, CO_2\,(g) &&\rightarrow\ C(g) + 2O\,(g) \,\}
\end{aligned}
$$

$$
\begin{aligned}
\Delta_{rxn}\mathbf{H} &= \Delta_{at}\mathbf{H}^\ominus (C_6H_6\,(liq) +(15/2)\Delta_{at}\,\mathbf{H}^\ominus (O_2\,(g)) \\
&\quad -3\Delta_{at}\,\mathbf{H}^\ominus (H_2O(liq)) - 6\Delta_{at}\,\mathbf{H}^\ominus (CO_2\,(g))
\end{aligned}
$$

2.12 Temperature Dependence of Reaction Enthalpy Changes

Again, *because **H** is a state function*, we can make up a convenient process
to calculate $\Delta_{rxn}\boldsymbol{H}(T')$ from $\Delta_{rxn}\boldsymbol{H}(298.15K)$.

For example for the reaction
C_6H_6(g, 1 bar, 600 K)
+ $(15/2)O_2$ (g, 600 K)
$\rightarrow 3H_2O$(g, 600 K) + $6CO_2$ (g, 600 K)

If we already know $\Delta_{\mathbf{rxn}}\mathbf{H}^{\ominus}(298.15K)$,

what is $\Delta_{\mathbf{rxn}}\mathbf{H}^{\ominus}(600\ K)$ **= *?***

We can add to our previous equation at 298.15 K the following, all at 1 bar:

$$-\{a\} - \{b\} - \{c\} - (15/2)\{d\} + 3\{e\} + 3\{f\} + 3\{g\} + 6\{h\}$$

$C_6H_6(\text{liq}, 298\text{ K}) \rightarrow C_6H_6(\text{liq}, 353\text{ K})$ (a)
$C_6H_6(\text{liq}, 353\text{ K}) \rightarrow C_6H_6(\text{g}, 353\text{ K})$ (b)
$C_6H_6(\text{g}, 353\text{ K}) \rightarrow C_6H_6(\text{g}, 600\text{ K})$ (c)
$O_2(\text{g}, 298\text{ K}) \rightarrow O_2(\text{g}, 600\text{ K})$ (d)
$H_2O(\text{liq}, 298\text{ K}) \rightarrow H_2O(\text{liq}, 373\text{ K})$ (e)
$H_2O(\text{liq}, 373\text{ K}) \rightarrow H_2O(\text{g}, 373\text{ K})$ (f)
$H_2O(\text{g}, 373\text{ K}) \rightarrow H_2O(\text{g}, 600\text{ K})$ (g)
$CO_2(\text{g}, 298\text{ K}) \rightarrow CO_2(\text{g}, 600\text{ K})$ (h)

and the ΔH for each is easily calculated as

either $\Delta_{vap}\mathbf{H}^{\ominus}$ or from $\Delta H = \int C_p \mathrm{d}T$