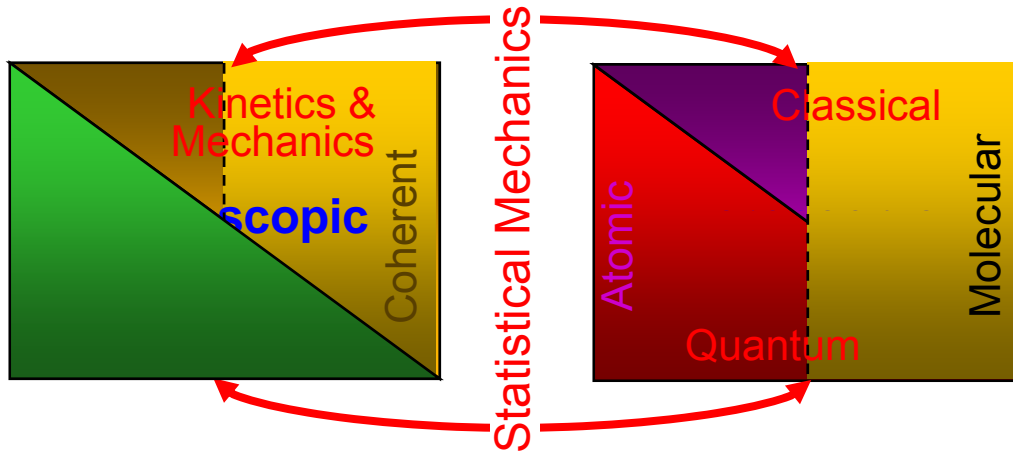


What is Thermo, Stat Mech, etc.?

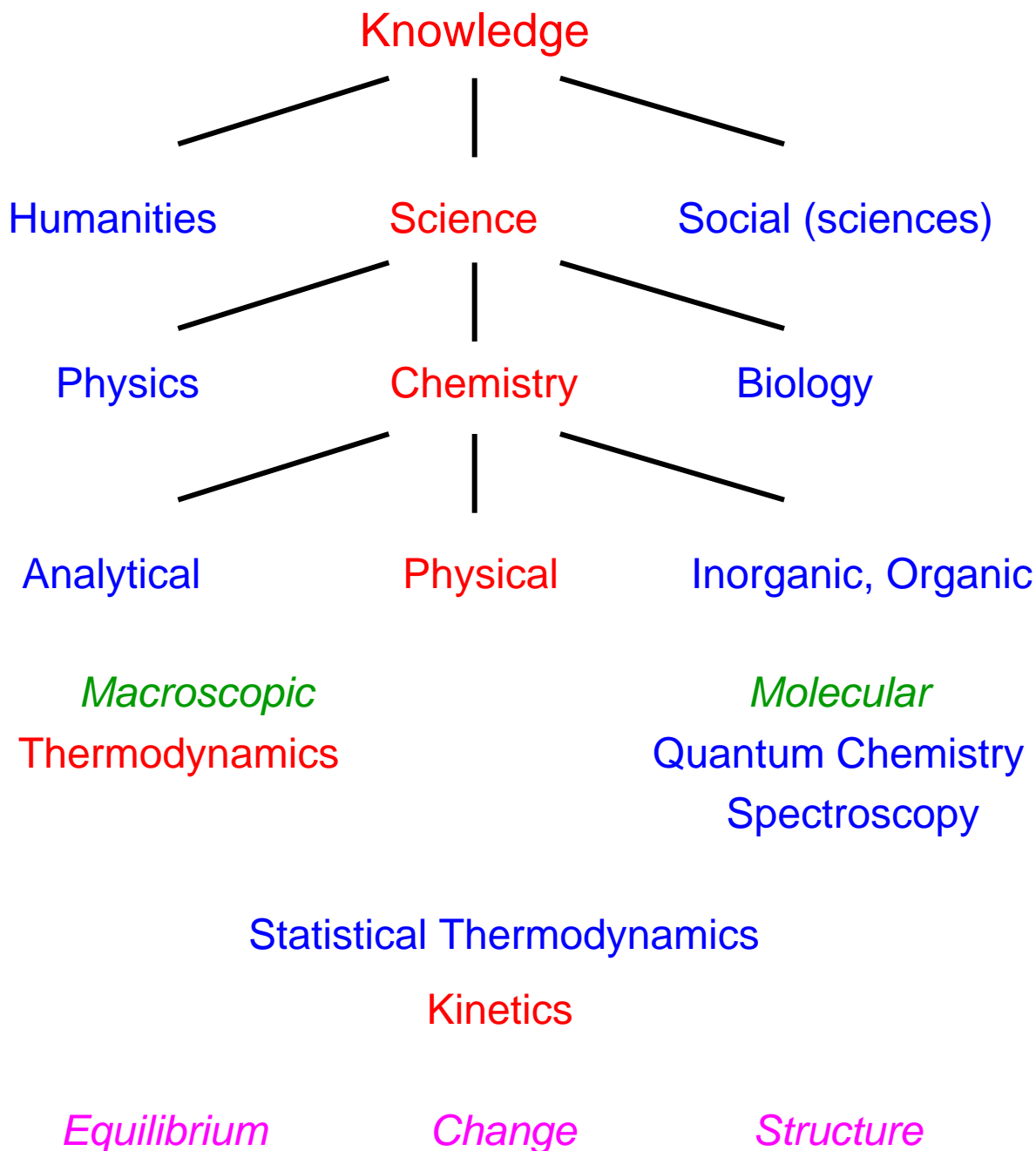


Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by then you are so used to it, it doesn't bother you any more. -- Arnold Sommerfield

Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics. Perhaps it will be wise to approach the subject cautiously. -- David L. Goodstein

Our approach will be to focus on the macroscopic, thermodynamic picture with occasional insight from the microscopic picture via statistical mechanics.

What is Thermodynamics?



Energy, Work and Heat

Energy is the capacity to do work.

Its classification into:

	kinetic	potential
	(by motion)	(by position)
e.g.	thermal	chemical, electrical

Is purely arbitrary!

Heat and **work** are *not* “types” of energy, but are processes involving *transfer* of energy. They appear and disappear at the system boundary. They are **path variables**.

Heat is the transfer of energy from one body to another of lower temperature.

Convention: if heat flows **into** the system, $q > 0$.

Work is the transfer of energy by some mechanism other than temperature difference.

Convention: if work is done **on** the system, $w > 0$.

Heat stimulates random motion.

Work stimulates organized motion.

Work “degrades” into heat.

- qualitative observations by Count Rumford (Ben Thompson)
- quantitative measurements by James Joule

Terminology 1

A **system** is a particular sample of matter or region of space.

An **isolated system** does not interact with its **surroundings**.

$$\text{system} + \text{surroundings} = \text{universe}$$

A **closed system** does not allow passage of mass over its boundaries, in contrast to...

An **open system**.

An **adiabatic system** has boundaries which permit no flow of heat. **It is insulated.**

A system is in a definite **state** when all its properties have definite values.

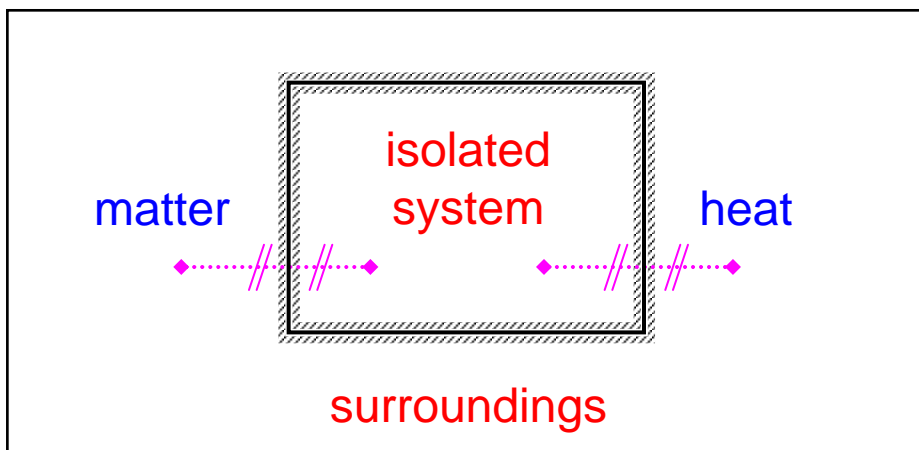
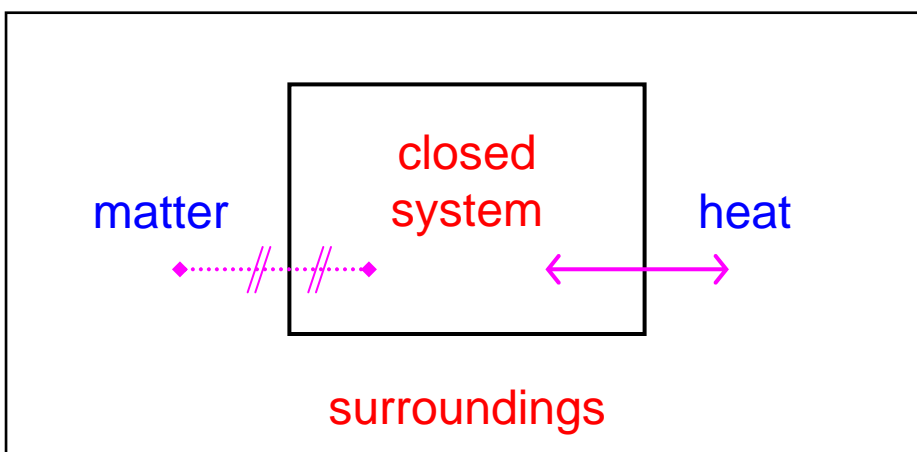
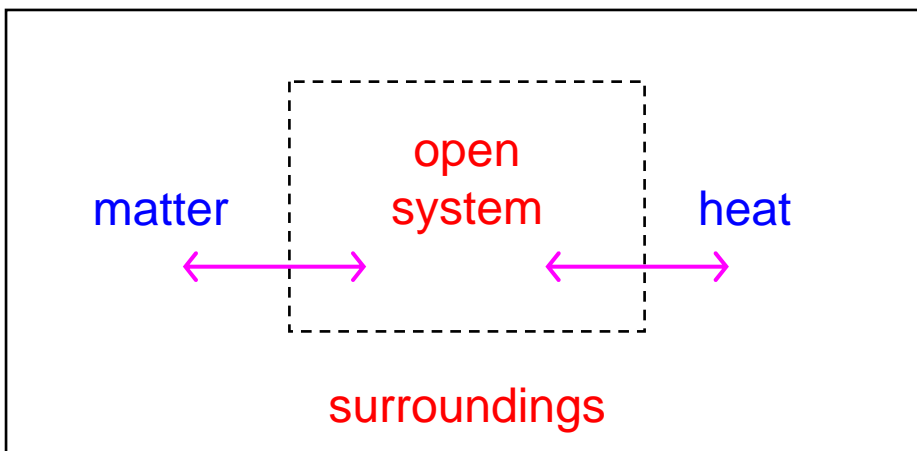
A system at **equilibrium** is time independent; it is not affected by the history of the system.

Extensive properties depend on the amount of substance in the system, e.g. n , V .

$$\text{Total Property} = \sum \text{property}(\text{part})$$

Intensive properties are independent of amount, e.g. P , T .

$$\text{Total Property} = \text{property of part}$$



Terminology 2

State variables (state functions) uniquely determine the state of a system at equilibrium. **Two samples of a substance with the same state variables are in the same state.**

The change in a state variable depends only on the initial and final states, *independent of path*.

Path functions depend on the **process** and therefore vary with **path**.

A **cyclic process** is one in which the initial and final states are the same, *i.e. no change in the state variables*.

In contrast, path functions generally have non-zero values for cyclic processes, dependent on the path.

A **reversible** process is one that can be reversed by an infinitesimal modification of a variable. The system is in equilibrium with the surroundings at all times. **This is an idealized situation, useful as a theoretical limit, but...**

All real processes are irreversible. It is possible to restore the system or the surroundings to their original states but not both.

An **equation of state** is the functional relationship between the properties of a system, *e.g, the ideal gas law*.

Ideal Gases -- Review

Ideal gases obey the ideal gas law:

$$PV = nRT$$

Pressure Pa $\equiv 1 \text{ N m}^{-2} \equiv 1 \text{ J m}^{-3} \equiv 1 \text{ kg m}^{-1} \text{ s}^{-2}$

Volume m^3 $\equiv 10^3 \text{ dm}^3 \equiv 10^3 \text{ litres}$

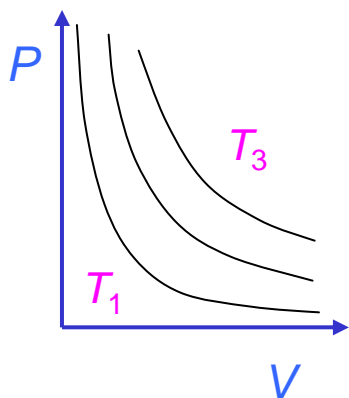
Temperature K

number of moles $n = \frac{w}{M} = \frac{N}{L}$ $L = 6.022 \times 10^{23}$ no. of atoms in 12 g ^{12}C

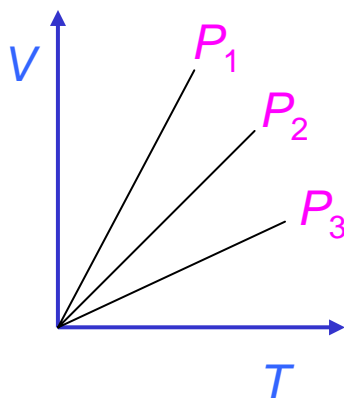
gas constant $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$

but if P is in atm ($\equiv 1.01325 \times 10^5 \text{ Pa}$) and V in litres,

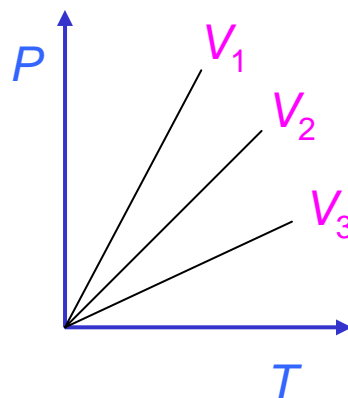
$$R = 0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$



isotherms



isobars



isochors

Mixtures of Ideal Gases

If the ideal gas law applies
to each component, i

$$P_i V = n_i RT$$

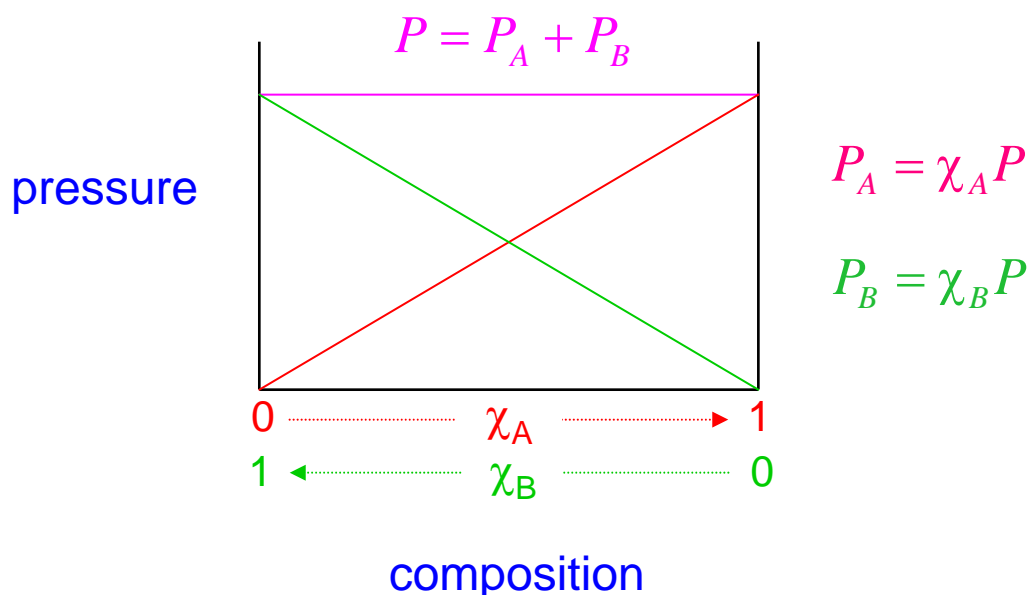
partial pressure

$$P_i = \frac{n_i RT}{V} = \frac{n_i P_{\text{tot}}}{n_{\text{tot}}} = \chi_i P_{\text{tot}}$$

Dalton's Law of
Partial Pressures

$$\sum_i P_i = \frac{P_{\text{tot}}}{n_{\text{tot}}} \sum_i n_i = P_{\text{tot}}$$

e.g. for two components:



Real gases are ideal only at the low density limit. Why?

Real Gases

- have non-zero volume at low T and high P
- have repulsive and attractive forces between molecules

↑
short range,
important at high P

↘
longer range,
important at moderate P

At low pressure, molecular volume and intermolecular forces can often be neglected, i.e. properties \rightarrow ideal.

Virial Equations

$$P\bar{V} = RT \left[1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \dots \right] \quad \bar{V} = V_m = \frac{V}{n}$$

$$P\bar{V} = RT \left[1 + B'P + C'P^2 + \dots \right]$$

B is the second virial coefficient.

C is the third virial coefficients.

They are temperature dependent.

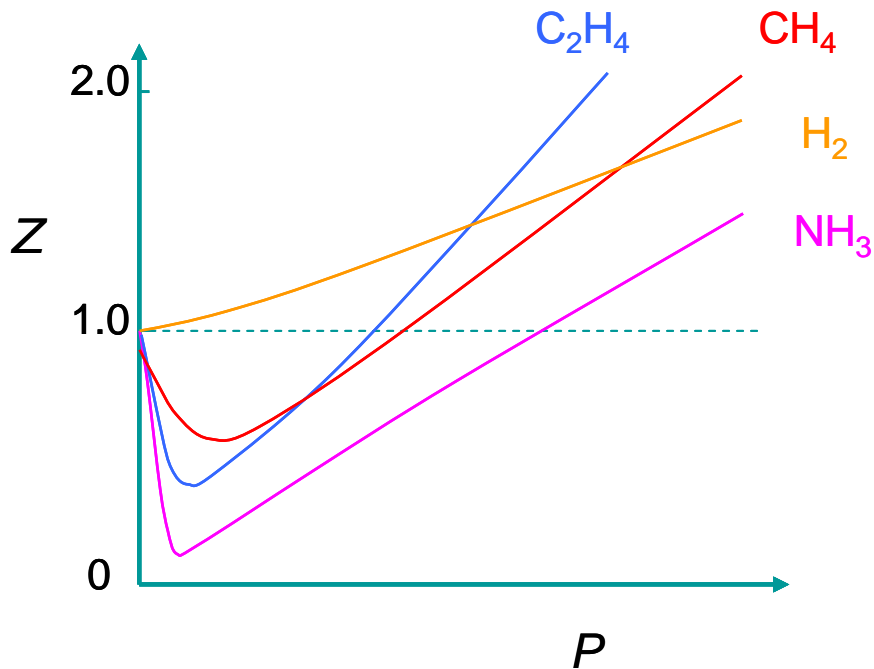
Van der Waals Equation

$$\left(P + \frac{a}{\bar{V}^2} \right) (\bar{V} - b) = RT$$

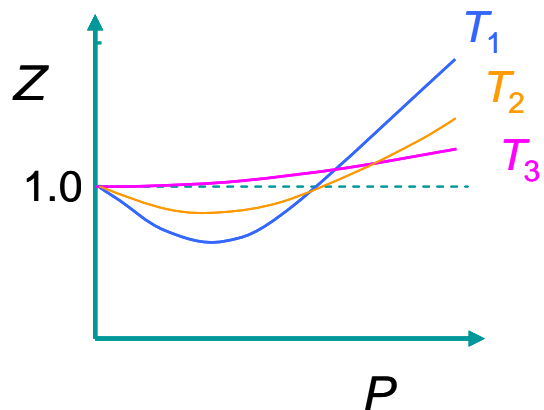
Compressibility Factor

also known as compression factor

$$Z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V}_{\text{ideal}}}$$



The curve for each gas becomes more ideal as $T \rightarrow \infty$



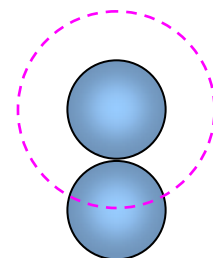
The van der Waals Equation 1

$$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$$

Intermolecular attraction
= "internal pressure"

"molecular volume"
≈ excluded volume

$$\frac{4}{3}\pi(2r)^3 / 2 = \frac{2}{3}\pi\sigma^3$$



$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

$$Z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V} - b} - \frac{a}{RT\bar{V}}$$

$$= 1 + \frac{1}{RT} \left(b - \frac{a}{RT}\right) P + \frac{a}{(RT)^3} \left(2b - \frac{a}{RT}\right) P^2 + \dots \quad (\text{boring algebra})$$

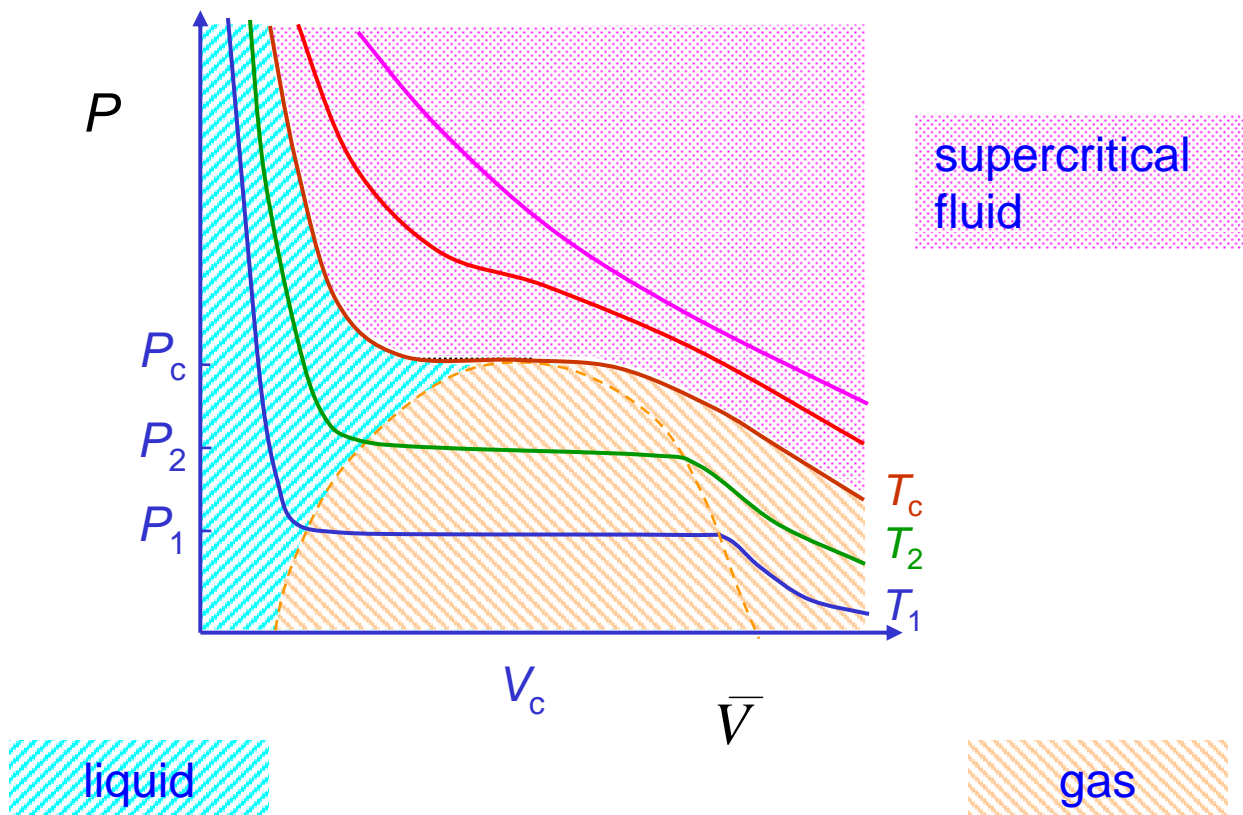
$$\Rightarrow \left(\frac{\partial Z}{\partial P}\right)_T = \frac{1}{RT} \left(b - \frac{a}{RT}\right) + \dots$$

The initial slope depends on a , b and T :

- positive for $b > a/RT$ molecular size dominant
- negative for $b < a/RT$ forces dominant
- zero at $T = a/Rb$ **Boyle Temperature**
~ ideal behaviour over wide range of P

Condensation of Gases

Real gases condense... don't they?



T_c , P_c and V_c are the critical constants of the gas.

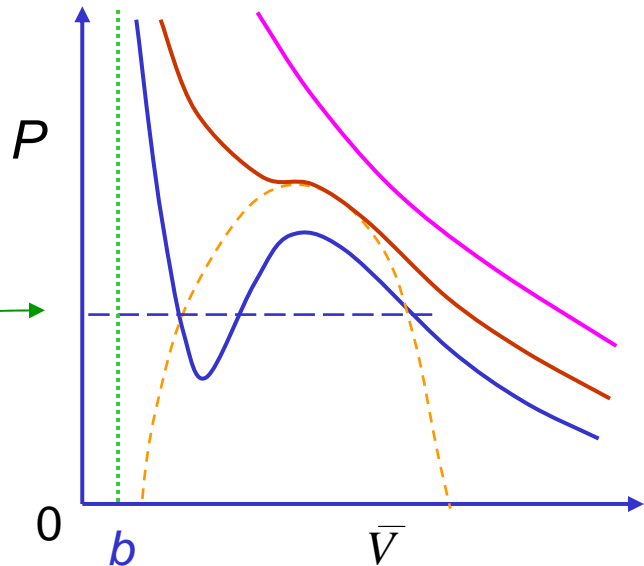
Above the critical temperature the gas and liquid phases are continuous, i.e. there is no interface.

The van der Waals Equation 2

The van der Waals Equation is not exact, only a model.
 a and b are empirical constant.

$$\bar{V}^3 - \left(b + \frac{RT}{P}\right)\bar{V}^2 + \frac{a}{P}\bar{V} - \frac{ab}{P} = 0$$

The cubic form of the equation predicts 3 solutions



There is a point of inflection at the critical point, so...

slope:
$$\left(\frac{\partial P}{\partial \bar{V}}\right)_T = -\frac{RT}{(\bar{V} - b)^2} + \frac{2a}{\bar{V}^3} = 0$$

curvature:
$$\left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T = \frac{2RT}{(\bar{V} - b)^3} - \frac{6a}{\bar{V}^4} = 0$$

$$\Rightarrow P_c = \frac{a}{27b^2} \quad \bar{V}_c = 3b \quad T_c = \frac{8a}{27Rb}$$

$$Z_c = \frac{P_c \bar{V}_c}{RT_c} = \frac{3}{8} \quad T_B = \frac{a}{Rb} = \frac{27}{8} T_c$$

The Principle of Corresponding States

Reduced variables are dimensionless variables expressed as fractions of the critical constants:

$$P_r = \frac{P}{P_c} \quad \bar{V}_r = \frac{\bar{V}}{\bar{V}_c} \quad T_r = \frac{T}{T_c}$$

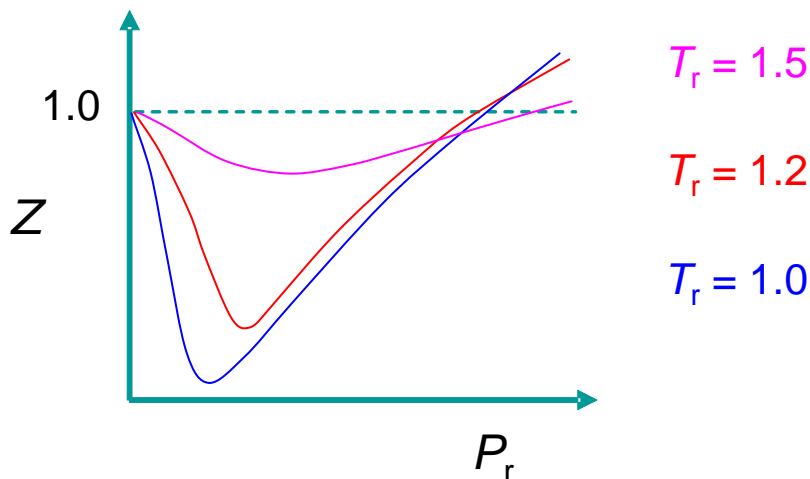
Real gases in the same state of reduced volume and reduced temperature exert approximately the same reduced pressure.

They are in **corresponding states**.

If the van der Waals Equation is written in reduced variables,

$$\left(P_r + \frac{3}{\bar{V}_r^2} \right) (3\bar{V}_r - 1) = 8T_r$$

Since this is independent of a and b , all gases follow the same curve (approximately).



Properties of Real Gases as $P \rightarrow 0$

Real gases have interactions between molecules. These change when the gas is compressed, but ...

...they need not go to zero as $P \rightarrow 0$.

e.g. consider

$$\left(\frac{\partial Z}{\partial P}\right)_T$$

For an ideal gas: $\left(\frac{\partial Z}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\frac{P\bar{V}}{RT}\right) = \frac{\partial}{\partial P}(1) = 0$

For a real gas: $Z = \frac{P\bar{V}}{RT} = 1 + B'P + C'P^2 + \dots$

$$\left(\frac{\partial Z}{\partial P}\right)_T = B' + 2C'P + \dots$$

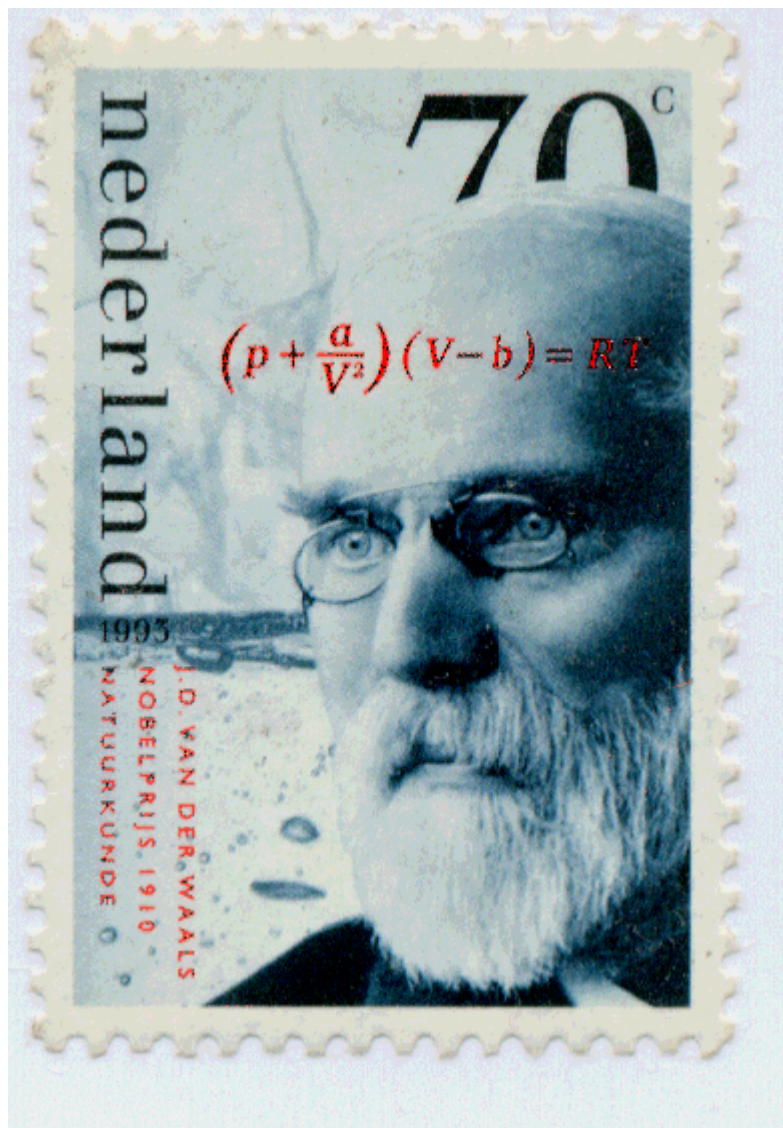
and in the limit: $\lim_{P \rightarrow 0} \left(\frac{\partial Z}{\partial P}\right)_T = B' \neq 0$

Not all properties of real gases tend to ideal values as $P \rightarrow 0$.

van der Waals

Johannes Diderik van der Waals, 1837 - 1923

Nobel Prize in Physics 1910



<http://www.s-ohe.com/stamp.html>

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The First Law of Thermodynamics

$q > 0$ for heat flow into the system
 $w > 0$ for work done on the system

- ❖ For finite changes of state: $\Delta U = q + w$
- ❖ For infinitesimal changes: $dU = \delta q + \delta w$

U is the internal energy of the system.

- ❖ When a system changes from one state to another along an adiabatic path, the amount of work done is the same, whatever the means employed.

$$\text{For } q = 0, \quad w_{\text{ad}} = U_{\text{final}} - U_{\text{initial}} = \Delta U$$

$$\text{For } q \neq 0, \quad q = \Delta U - w = w_{\text{ad}} - w$$

- ❖ The energy of an isolated system is constant.

$$\text{For } q = 0, w = 0 \quad \Delta U = 0$$

\Rightarrow *No perpetual motion machines!*

- ❖ In any cyclic transformation the work done by a system on its surroundings is equal to the heat withdrawn from the surroundings.

$$-\oint \delta w = \oint \delta q \quad \Leftrightarrow \quad \oint dU = 0$$

- ❖ The energy of the universe is constant.

$$\Delta U_{\text{system}} = -\Delta U_{\text{surroundings}}$$

Temperature

Two systems in thermal equilibrium are at the same temperature.

If system A is in thermal equilibrium with system B,
and A is in thermal equilibrium with C,
then B must be in thermal equilibrium with C.

This is a statement of the **zeroth law of thermodynamics**.

Ideal gas temperature: $T = \lim_{P \rightarrow 0} \left(\frac{PV}{nR} \right)$

Unit of temperature: $1 \text{ Kelvin} = \frac{T(\text{triple point of water})}{273.16}$

The freezing point of water at 1 atm is 273.15 K.

The boiling point of water at 1 atm is 373.12 K.

The Celsius scale is defined as $t / ^\circ\text{C} = T / \text{K} - 273.15$

It is possible to define an **absolute temperature scale** (**Kelvin scale**) by considering the work done in an isothermal reversible expansion/compression.

$$w = nRT \ln \frac{V_1}{V_2}$$

Pressure–Volume Work 1

Expansion

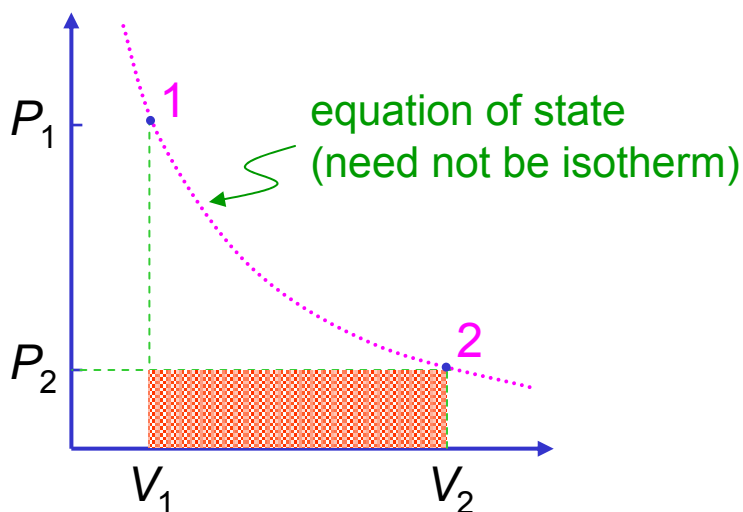
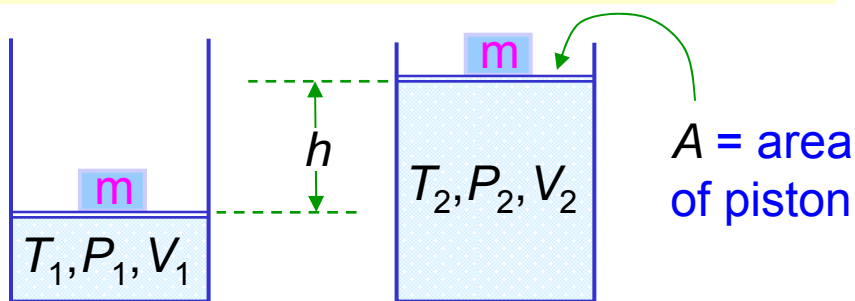
$$P_1 > mg / A$$

$$P_2 = P_{\text{ex}} = mg / A$$

$$w = -(mg)h$$

$$= -(P_{\text{ex}} A)h$$

$$= -P_{\text{ex}} (V_2 - V_1)$$



Expansion into a vacuum

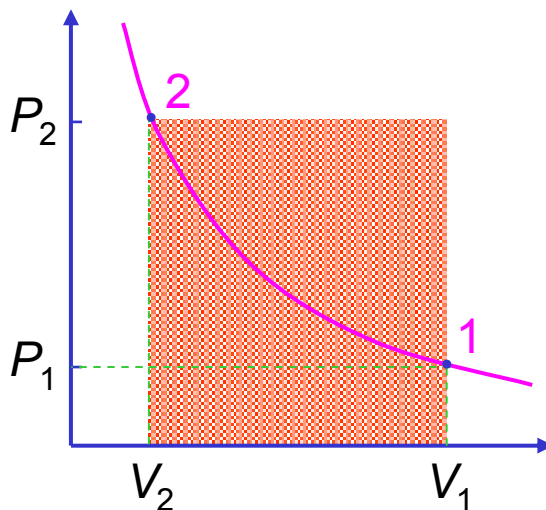
$$P_{\text{ex}} = 0 \Rightarrow w = 0$$

Compression

$$P_1 < P_{\text{ex}}$$

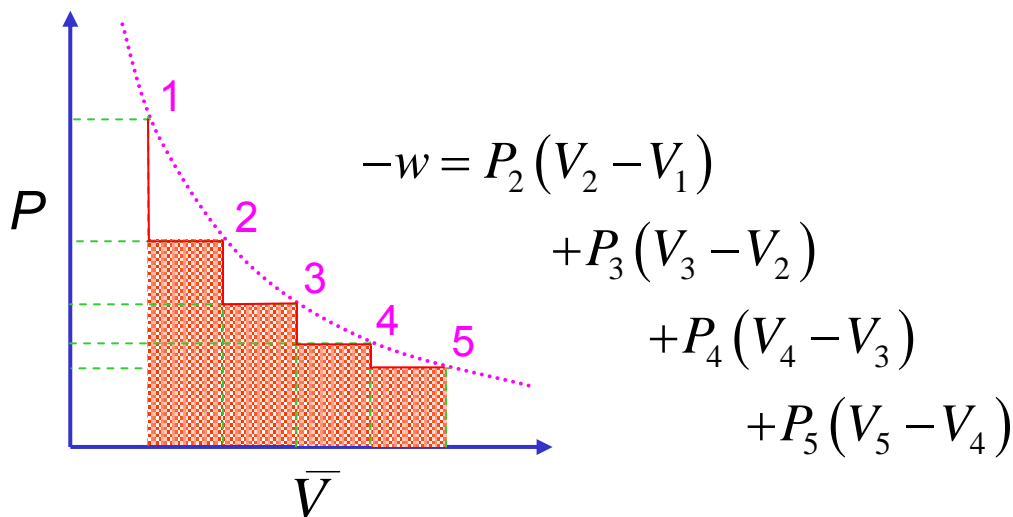
$$P_2 = P_{\text{ex}}$$

$$w = -P_{\text{ex}} (V_2 - V_1)$$



Pressure–Volume Work 2

Multi-stage Expansion



Reversible Expansion

Make steps so small that

$$dP \rightarrow 0, dV \rightarrow 0$$

Then $-\delta w = P_{\text{ex}} dV$

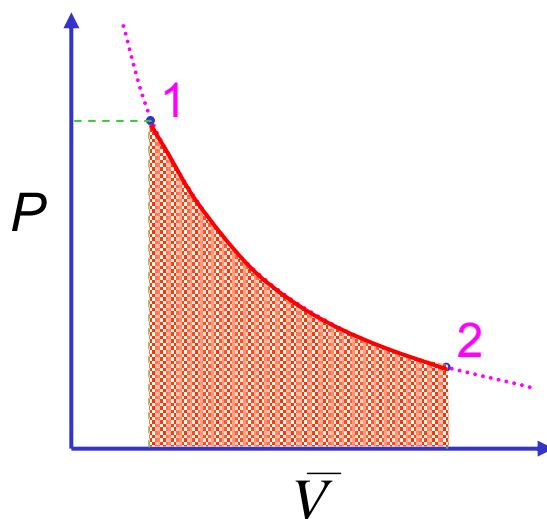
$$= (P_{\text{int}} + dP) dV$$

$$\rightarrow P_{\text{int}} dV$$

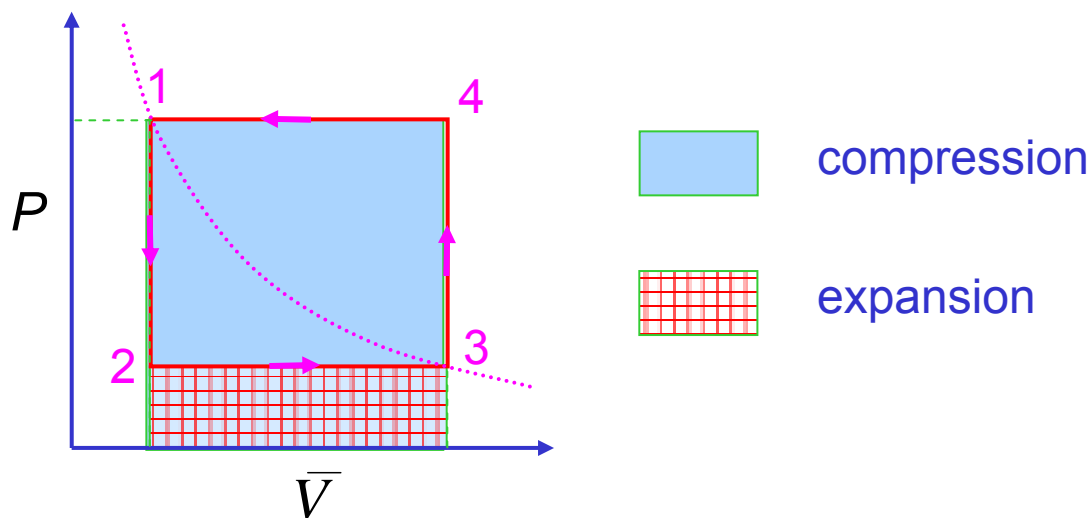
$$w = \int_{\text{path}} dw = - \int_1^2 P_{\text{int}} dV$$

For ideal gases $P_{\text{int}} = nRT/V$

and at fixed temperature $w_{\text{rev}} = -nRT \ln \left(\frac{V_2}{V_1} \right) = nRT \ln \left(\frac{P_2}{P_1} \right)$



Pressure–Volume Work 3



Consider the cyclic path $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$

$$\begin{aligned} -w &= 0 + P_3(V_3 - V_1) + 0 + P_1(V_1 - V_3) \\ &= (P_3 - P_1)(V_3 - V_1) \end{aligned}$$

Consider the cyclic reversible path $1 \rightarrow 3 \rightarrow 1$

$$\begin{aligned} -w &= \int_{V_1}^{V_3} P dV + \int_{V_3}^{V_1} P dV \\ &= \int_{V_1}^{V_3} P dV - \int_{V_1}^{V_3} P dV = 0 \end{aligned}$$

Even for a cyclic process w depends on path

$$\oint dU = 0 \quad \Leftrightarrow \quad -\oint \delta w = \oint \delta q$$

Energy vs. Enthalpy

For a change in state at constant volume, no expansion work is done, so $\Delta U = q_V$, $dU = \delta q_V$

However, for a change in state at constant pressure,

$$\Delta U = q_P + w, \quad dU = \delta q_P - PdV$$

$$\Delta U = \int_1^2 dU = \int_1^2 \delta q_P - \int_{V_1}^{V_2} PdV$$

$$U_2 - U_1 = q_P - P(V_2 - V_1) \quad P \text{ constant}$$

$$(U_2 + PV_2) - (U_1 + PV_1) = q_P$$

$$(U_2 + P_2V_2) - (U_1 + P_1V_1) = q_P \quad P = P_1 = P_2$$

Enthalpy

$$H = U + PV$$

$$\Delta H = q_P, \quad dH = \delta q_P$$

H , being a function of state variables only, is also a state variable.

For a general change of state (P and V may both change),

$$\begin{aligned} \Delta H &= \Delta U + \Delta(PV) \\ &= \Delta U + P\Delta V + V\Delta P + \Delta P\Delta V \\ dH &= dU + PdV + VdP \end{aligned}$$

Heat Capacity

Transfer of heat to a system *may* result in a rise in T .

$$\delta q = C dT$$

↖ path function, so C depends on conditions.

Define: $\delta q_V = C_V dT$ at constant volume, *no work*

$\delta q_P = C_P dT$ at constant pressure, *only PV work*

From 1st Law, $dU = \delta q + \delta w = \delta q - P_{\text{ex}} dV$

assume no
other work

$$dU = \delta q_V \quad \text{for } dV = 0$$

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

Similarly

$$dH = dU + PdV - VdP$$

$$= (\delta q - PdV) + PdV - VdP$$

$$= \delta q_P \quad \text{for } dP = 0$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

For ideal gases $dH = dU + d(PV) = dU + nRdT$

$$C_P dT = C_V dT + nRdT$$

$$\bar{C}_P = \bar{C}_V + R$$

The Relation Between C_P and C_V

$$C_P - C_V = \left(\frac{\partial H}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V$$

$$= \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V$$

$H = U + PV$

But since

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

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

$$\Rightarrow C_P - C_V = \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

work needed to overcome intermolecular forces expansion per degree

$$\left(\frac{\partial U}{\partial V} \right)_T = \text{“internal pressure”}$$

For ideal gases

$$\left(\frac{\partial U}{\partial V} \right)_T = 0, \quad \left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P} \quad \Rightarrow \quad C_P - C_V = nR$$

For liquids and solids

$$\left(\frac{\partial V}{\partial T} \right)_P \text{ is so small that } C_P \approx C_V$$

Adiabatic Expansion 1

adiabatic = insulated: $q = 0, \quad \delta q = 0$
 $\Delta U = w \quad dU = \delta w$

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

$$w = \int_1^2 dU = \int_{T_1}^{T_2} C_V dT + \dots \quad (0 \text{ for ideal gases})$$
$$= C_V \Delta T \quad \text{if } C_V \text{ is independent of } T$$

For adiabatic expansion $w \leq 0, \quad \Delta U \leq 0 \Rightarrow T_2 \leq T_1$

Free expansion: $P_{\text{ex}} = 0 \Rightarrow w = 0, \quad \Delta T = 0$

Fixed pressure: $w = -P_{\text{ex}} \Delta V$
 $w = \Delta U = C_V \Delta T$
 $\Rightarrow \Delta T = -\frac{P_{\text{ex}} \Delta V}{C_V}$

Reversible expansion: $P = P_{\text{ex}}$
 $w = -\int_{V_1}^{V_2} P(V, T) dV$

Substitute appropriate equation of state. 

Not useful if T changes.

Adiabatic Expansion 2

Reversible adiabatic expansion of ideal gases:

$$dU = \delta w$$

$$\delta q = 0$$

$$C_V dT = -PdV = -\frac{nRT}{V} dV$$

ideal gases only

$$\bar{C}_V \int_1^2 \frac{1}{T} dT = -R \int_1^2 \frac{1}{V} dV$$

$$\begin{aligned} \bar{C}_V \ln(T_2/T_1) &= -R \ln(V_2/V_1) \\ &= -(\bar{C}_P - \bar{C}_V) \ln(V_2/V_1) \end{aligned}$$

$$\ln(T_2/T_1) = -(\gamma - 1) \ln(V_2/V_1)$$

$$\gamma = \frac{\bar{C}_P}{\bar{C}_V}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

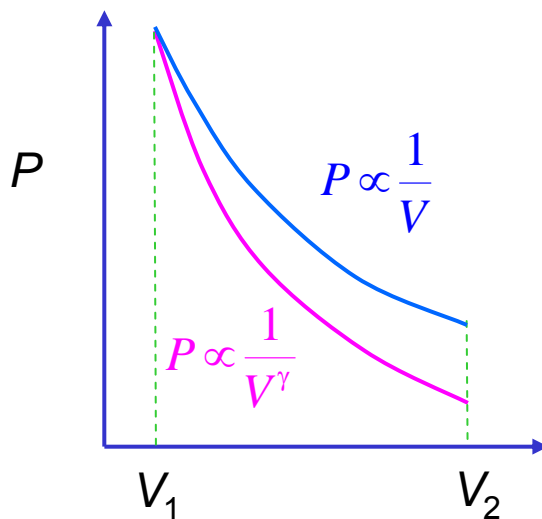
Also, since

$$\frac{P_2 V_2}{P_1 V_1} = \frac{T_2}{T_1}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^\gamma$$

or $P_1 V_1^\gamma = P_2 V_2^\gamma$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma}$$



Types of Expansion Work — Summary

For **all types** of expansion $\delta w = -P_{\text{ex}} dV$

For **reversible** changes $P_{\text{ex}} = P = P(V, T)$ in general

In an **irreversible** expansion $P_{\text{ex}} < P$, $(-w) < (-w_{\text{rev}})$

For **isothermal** expansions T is held constant by leakage of heat into the system from the surroundings.

For an ideal gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$, $\Delta U = 0$, $q = w$

In an **adiabatic** expansion $q = 0$

so the internal energy must provide for the work: $w = \Delta U$

For **reversible expansion of an ideal gas** through a given volume change from the same initial state,

$$(-w_{\text{isothermal}}) > (-w_{\text{adiabatic}})$$

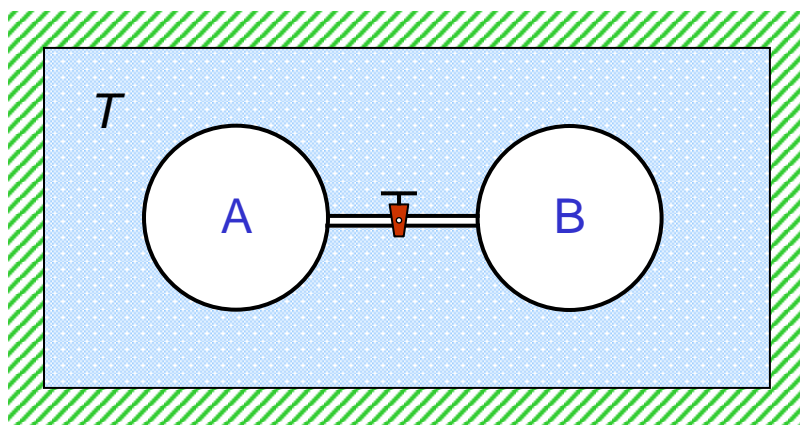
since U is continuously replenished by heat intake to keep the temperature constant.

The Joule Expansion Experiment

For a closed system, the state function U is determined by T and V alone:

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

Joule tried to measure this partial derivative.



1. Gas in A, vacuum in B.
2. Open valve.
3. Any change in T ?

He found no change in temperature when the gas expanded from V_A to $V_A + V_B$, i.e. $q = 0$. Also, no work was done (free expansion), so $w = 0$. Conclusion: $\Delta U = 0$ and hence

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 \quad \text{or} \quad U = U(T) \quad \text{only}$$

Strictly only true for ideal gases.

Not true for liquids and solids, but since $\Delta U \approx \left(\frac{\partial U}{\partial V} \right)_T \Delta V$ and ΔV is very small, the effect of ΔV on U is usually ignored.

Pressure Dependence of Enthalpy

For a closed system, the state function H is determined by T and P alone:

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$
$$= C_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

For ideal gases $H = U + PV = U + nRT$

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

Not true for real gases, liquids and solids!

$$dH = dU + PdV + VdP$$
$$C_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV + PdV + VdP$$

At fixed temperature, $dT = 0$

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

small for liquids and solids

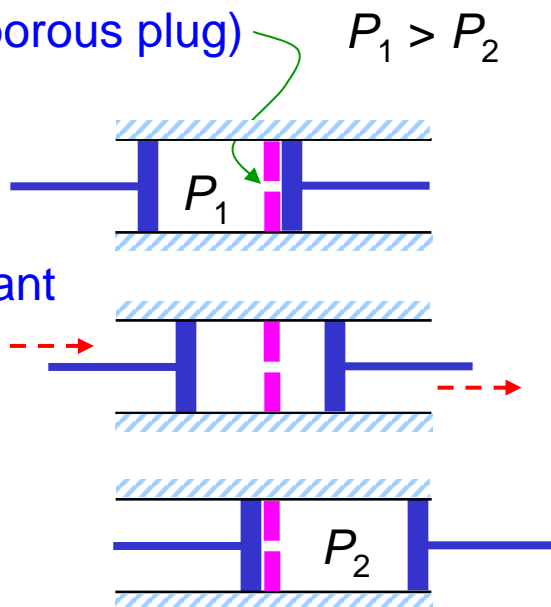
Investigate real gases at constant enthalpy, i.e. $dH = 0$

$$\Rightarrow \left(\frac{\partial H}{\partial P} \right)_T = -C_P \left(\frac{\partial T}{\partial P} \right)_H$$

The Joule-Thompson Experiment

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

Pump gas through throttle (hole or porous plug) $P_1 > P_2$



Keep pressures constant by moving pistons.

Work done by system

$$-w = P_2V_2 - P_1V_1$$

Since $q = 0$

$$\Delta U = U_2 - U_1 = w = P_1V_1 - P_2V_2$$

$$\Rightarrow U_2 + P_2V_2 = U_1 + P_1V_1$$

$$H_2 = H_1 \quad \text{constant enthalpy}$$

Measure change in T of gas as it moves from side 1 to side 2.

$$\mu_{JT} = \left(\frac{\Delta T}{\Delta P} \right)_{\Delta P \rightarrow 0}$$

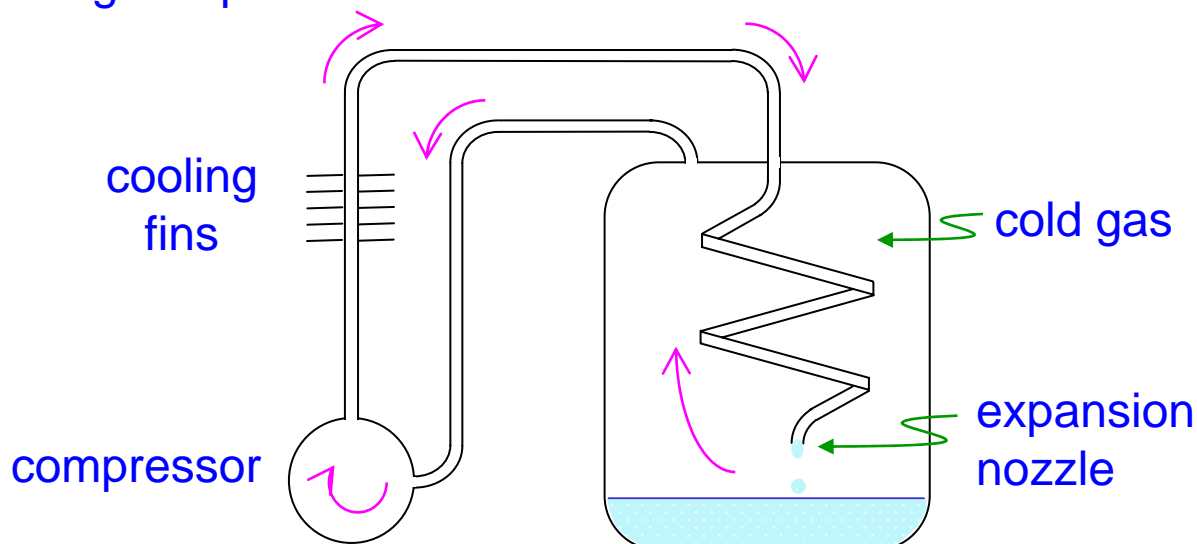
A modern, more direct experiment uses similar apparatus but with a heater to offset the temperature drop.

$$\left(\frac{\partial H}{\partial P} \right)_T = \lim_{\Delta P \rightarrow 0} \left(\frac{q}{\Delta P} \right)$$

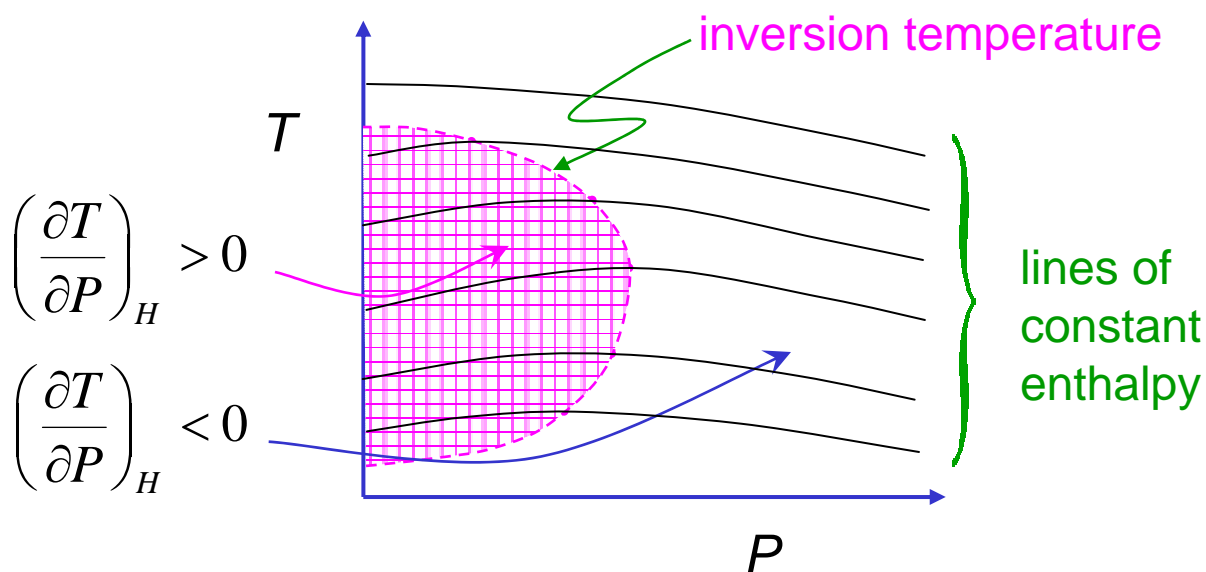
The Linde Refrigerator

For most gases at room temperature $\mu_{JT} > 0$ so sudden (adiabatic) expansion results in a drop in T .

This is the basis of operation of the **Linde refrigerator** and gas liquefaction.



In general, μ_{JT} depends on T and can even change sign.



The Molecular Interpretation of U

What is U ? ΔU can be related to thermochemical observables:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V, \quad \Delta U = \int_{T_1}^{T_2} C_V dT \quad \text{for ideal gases}$$

$$U(T) - U(0) = \int_0^T C_V dT$$

Can U be calculated from molecular properties?

$$U = \sum_{\text{molecules}} u = N \langle u \rangle \quad \text{ignoring intermolecular forces}$$

Classically, $\langle u \rangle$ is given by the **Equipartition Law**:

“The average energy of each different mode of motion of a molecule is $\frac{1}{2}kT$.”

$$k = \text{Boltzmann constant} = R/L \\ = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

Implicit in this “law” is the concept that there is no coupling between molecular modes of motion.

Total: $u = \epsilon_{\text{tr}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} (+\epsilon_{\text{el}})$

Translation: $\epsilon_{\text{tr}} = \frac{1}{2}mv^2 = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\dot{y}^2 + \frac{1}{2}m\dot{z}^2$

Rotation: $\epsilon_{\text{rot}} = \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2$

Vibration: $\epsilon_{\text{vib}} = T + V = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2$ per mode

$$\text{no. of vib. modes} = \begin{cases} 3n - 6 & \text{for non-linear molecules} \\ 3n - 5 & \text{for linear molecules} \end{cases}$$

The Molecular Interpretation of U (cont.)

When quantum effects can be ignored, the average energy of every quadratic term in the energy expression has the same value, $\frac{1}{2}kT$.

Monoatomic gases $\langle u \rangle = \frac{3}{2}kT$, $\bar{C}_V = \left(\frac{\partial \bar{U}}{\partial T} \right)_V = 1.5R$

Diatomic gases $\langle u \rangle = \left(\frac{3}{2} + 1 + 1 \right)kT$, $\bar{C}_V = 3.5R$

Linear polyatomics $\langle u \rangle = \left(\frac{3}{2} + 1 + 3n - 5 \right)kT$
e.g. for $n = 3$, $\bar{C}_V = 6.5R$

Non-linear molecules $\langle u \rangle = \left(\frac{3}{2} + \frac{3}{2} + 3n - 6 \right)kT$
e.g. for $n = 3$, $\bar{C}_V = 6.0R$

Experimental observations do *not* agree with these predictions, except for monoatomic gases. In particular:

- The predicted values are too high.
- Experimental values are temperature-dependent.

Accurate calculations are provided by **statistical mechanics**, where it can be shown that the equipartition principle only holds in the limit of high temperature, specifically for the condition $kT \gg \Delta E$, where ΔE is the appropriate spacing of energy levels.

Equipartition \equiv free transfer of energy between modes

Temperature Dependence of C_V

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V, \quad \text{where } U - U_0 = N(\langle \varepsilon_{\text{tr}} \rangle + \langle \varepsilon_{\text{rot}} \rangle + \dots)$$

$$= C_V^{\text{tr}} + C_V^{\text{rot}} + C_V^{\text{vib}} + C_V^{\text{el}}$$

$$\bar{C}_V^{\text{tr}} = 1.5R \quad \text{for all } T$$

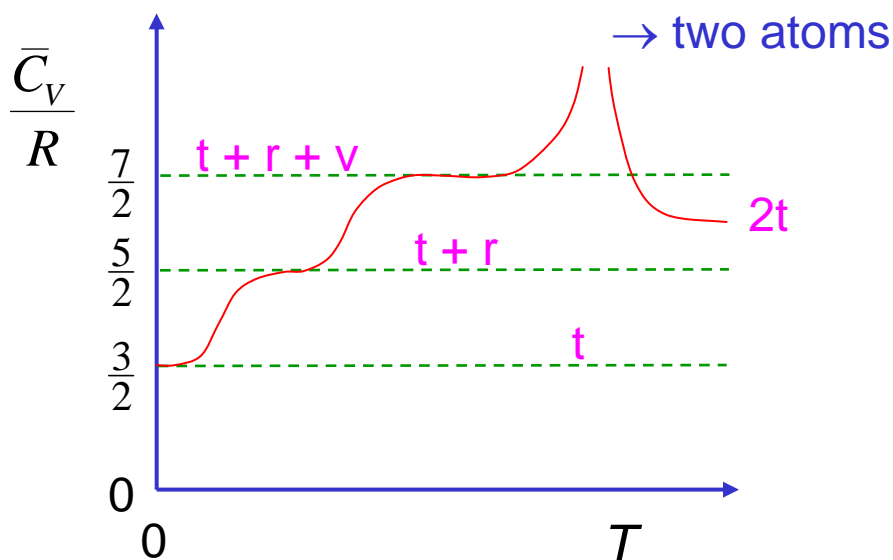
$$\bar{C}_V^{\text{rot}} = \begin{cases} R & \text{-- linear} \\ 1.5R & \text{-- non-linear} \end{cases} \quad \text{for } kT \gg \Delta\varepsilon_{\text{rot}}$$

$$\bar{C}_V^{\text{rot}} = 0 \quad \text{at very low } T, \text{ where } \langle \varepsilon_{\text{rot}} \rangle \rightarrow 0$$

$$\bar{C}_V^{\text{vib}} = R \quad \text{for each vibrational mode, at high } T$$

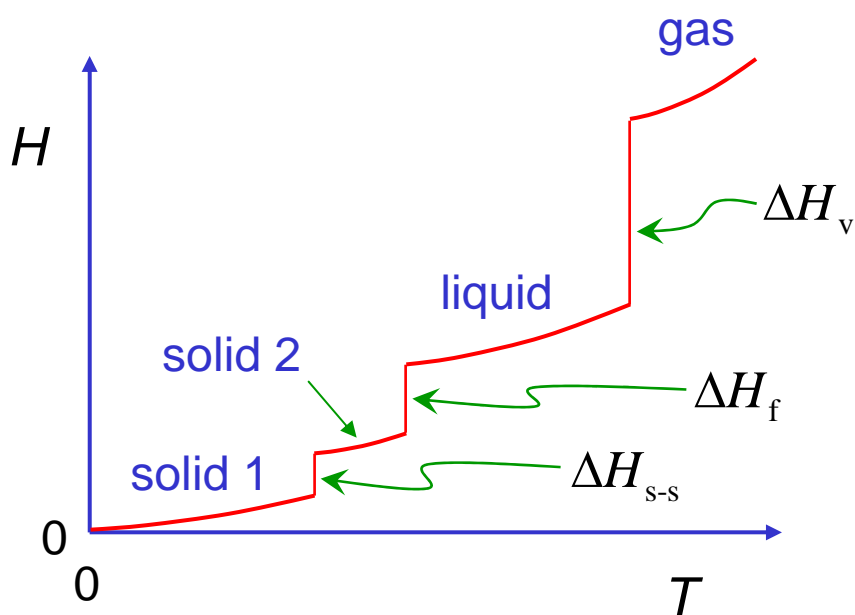
$$\bar{C}_V^{\text{el}} = 0 \quad \text{almost always, since electronic excitation takes great energy}$$

e.g. for a diatomic molecule:



Temperature Dependence of H

Interactions between molecules also contribute to the heat capacity of real systems. In particular, **first-order** phase changes often involve large energy changes. These are usually measured at constant pressure and expressed as **enthalpies**.



In general, $H = a + bT + cT^2 + \dots$ for each phase

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = b + 2cT + \dots$$

Thermochemistry

The study of energy changes that occur during chemical reactions:

- at constant volume $\Delta U = q_V$ no work
- at constant pressure $\Delta H = q_P$ only PV work

For practical reasons most measurements are made at constant P , so thermochemistry mostly deals with ΔH .

$$\Delta H_{\text{reaction}} = \sum_{\text{products}} H - \sum_{\text{reactants}} H$$

If $\Delta H > 0$ the reaction is **endothermic**.

If $\Delta H < 0$ the reaction is **exothermic**.

For comparison purposes we need to refer ΔH to the same T and P . To define a standard reaction enthalpy each component of the reaction must be in its **standard state** – the most stable form at **1 bar** pressure and (usually) **25°C**.

$$1 \text{ bar} = 10^5 \text{ Pa}$$

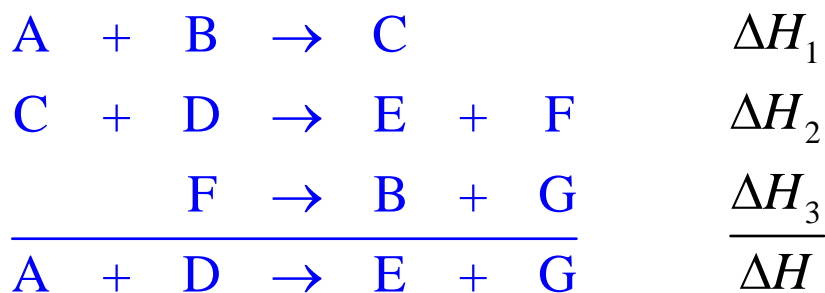
$$1 \text{ atm} = 1.01325 \text{ bar}$$

Reaction Enthalpy 1

Hess's Law

The standard enthalpy change in any reaction can be expressed as the sum of the standard enthalpy changes, at the same temperature, of a series of reactions into which the overall reaction can be formally divided.

Combine chemical equations as if mathematical equations, e.g.



$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Standard Reaction Enthalpy

ΔH° reaction enthalpy at 1 bar

ΔH_{298}° ... and at standard T

ΔH_{500}° or some other T

Reaction Enthalpy 2

Standard (molar) enthalpy of formation $\Delta H_f^\circ \equiv \Delta_f H^\circ$

Heat of formation of a substance from its elements, all substances being in their standard state.

By definition, for all elements $\Delta H_f^\circ = 0$

Enthalpy of combustion $\Delta H_c^\circ \equiv \Delta_c H^\circ$

ΔH° for total oxidation of a substance

e.g. $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$ $\Delta_c H^\circ = -2808 \text{ kJ mol}^{-1}$

Enthalpy of hydrogenation

ΔH° when an unsaturated organic compound becomes fully saturated

e.g. $\text{C}_6\text{H}_6 + 3\text{H}_2 \rightarrow \text{C}_6\text{H}_{12}$ $\Delta H^\circ = -246 \text{ kJ mol}^{-1}$

Enthalpy of atomization \equiv Bond dissociation enthalpy

ΔH° for the dissociation of a molecule into its constituent gaseous atoms

e.g. $\text{C}_2\text{H}_6(\text{g}) \rightarrow 2\text{C}(\text{g}) + 6\text{H}(\text{g})$ $\Delta H^\circ = 2883 \text{ kJ mol}^{-1}$

Bond strength \equiv single bond enthalpy

An average value taken from a series of compounds and often combined *for a rough estimate*

e.g. $\Delta H^\circ(\text{C}_2\text{H}_6) = \Delta H^\circ(\text{C-C}) + 6 \Delta H^\circ(\text{C-H})$

Temperature Dependence of ΔH°

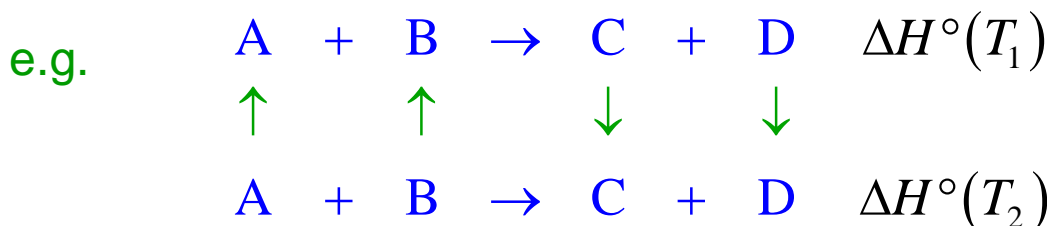
The temperature dependence of reaction enthalpies can be expressed in terms of the T dependence of the enthalpies of the reaction components:

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$

$$\therefore \Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$$

$$\text{where } \Delta C_p = \sum_{\text{products}} C_p - \sum_{\text{reactants}} C_p$$

This is known as **Kirchoff's Law**.



$$\begin{aligned} \Delta H^\circ(T_2) &= (C_p(A) + C_p(B))(T_1 - T_2) \\ &\quad + \Delta H^\circ(T_1) \\ &\quad + (C_p(C) + C_p(D))(T_2 - T_1) \\ &= \Delta H^\circ(T_1) + \left(\sum_{\text{products}} C_p - \sum_{\text{reactants}} C_p \right) \Delta T \end{aligned}$$

assuming that the C_p values are T independent.

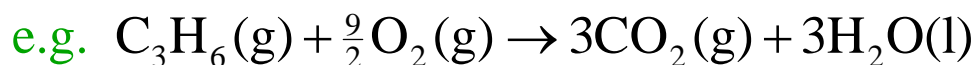
Reactions at Constant Volume

$$\Delta H_r = \Delta U_r + (PV)_{\text{products}} - (PV)_{\text{reactants}}$$

For solids and liquids $\Delta(PV) \approx 0$, so $\Delta H \approx \Delta U$

For ideal gases $\Delta(PV) = \Delta n_{\text{gas}} RT$,

so $\Delta H \approx \Delta U + \Delta n_{\text{gas}} RT$



$$\Delta H_r = \Delta U_r + \left(-\frac{5}{2}\right) RT$$

The relationship between ΔH and ΔU is particularly important when relating thermochemical enthalpies to molecular properties,

e.g. for a single bond energy $\Delta U = \Delta H - RT$

as seen in the case of $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$.

In practice, RT is usually so much smaller than ΔH that it is often ignored.

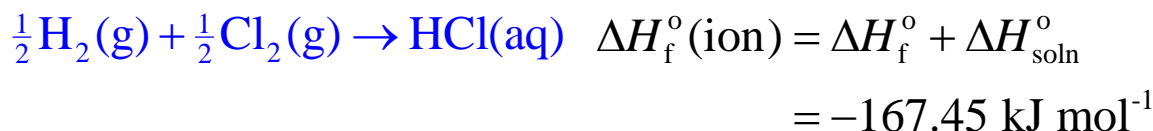
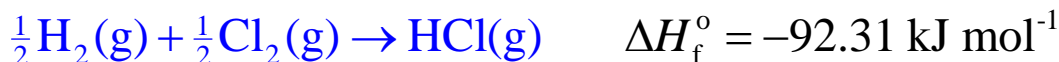
Enthalpies of Ions in Solution

Enthalpy of solution ΔH° for solution of a substance in a *stated* amount of solvent

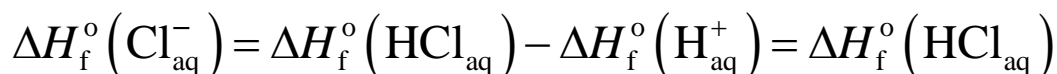
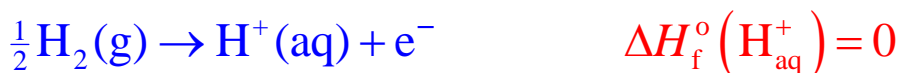
Enthalpy of dilution ΔH° for dilution of a solution to a lower concentration

Enthalpy of solution to infinite dilution $\Delta H_{\text{soln}}^\circ$ for an *infinite* amount of solvent

The enthalpy of formation for a species in solution can be found by combining $\Delta H_{\text{soln}}^\circ$ with the ΔH_f° of the gaseous species:



ΔH_f° for individual ions in solution can only be found if one is arbitrarily fixed. By **convention** this is $\text{H}^+(\text{aq})$.

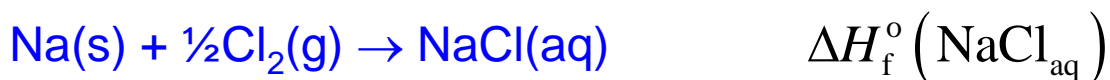


The **standard state** for a substance in solution (**not just ions**) is a concentration of 1 mole solute in 1 kg solution (1 **molal**).

Enthalpy of Formation of an Ionic Solid

Consider individual steps in the formation of NaCl.

1. $\text{Na(s)} \rightarrow \text{Na(g)}$ $\Delta H_{\text{subl}}^{\circ}(\text{Na})$
2. $\text{Na(g)} \rightarrow \text{Na}^{\text{+}}(\text{g}) + \text{e}^{-}$ $\Delta H^{\circ} = I(\text{Na}) + RT$
3. $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl(g)}$ $\frac{1}{2}\Delta H^{\circ}(\text{Cl-Cl})$
4. $\text{Cl(g)} + \text{e}^{-} \rightarrow \text{Cl}^{-}(\text{g})$ $\Delta H^{\circ} = -E_{\text{A}}(\text{Cl}) - RT$
5. $\text{Na}^{\text{+}}(\text{g}) + \text{Cl}^{-}(\text{g}) \rightarrow \text{Na}^{\text{+}}(\text{aq}) + \text{Cl}^{-}(\text{aq})$
 $\equiv \text{NaCl(aq)}$ $\Delta H_{\text{sol}}^{\circ}(\text{Na}^{\text{+}}) + \Delta H_{\text{sol}}^{\circ}(\text{Cl}^{-})$

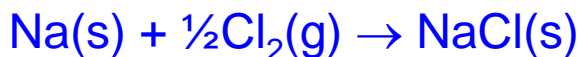


$$\Delta H_{\text{f}}^{\circ}(\text{NaCl}_{\text{aq}}) = \Delta H_{\text{subl}}^{\circ}(\text{Na}) + I(\text{Na}) + \frac{1}{2}\Delta H^{\circ}(\text{Cl-Cl}) - E_{\text{A}}(\text{Cl}) + \Delta H_{\text{sol}}^{\circ}(\text{Na}^{\text{+}}) + \Delta H_{\text{sol}}^{\circ}(\text{Cl}^{-})$$

Step 5 could be creation of solid NaCl instead of solution



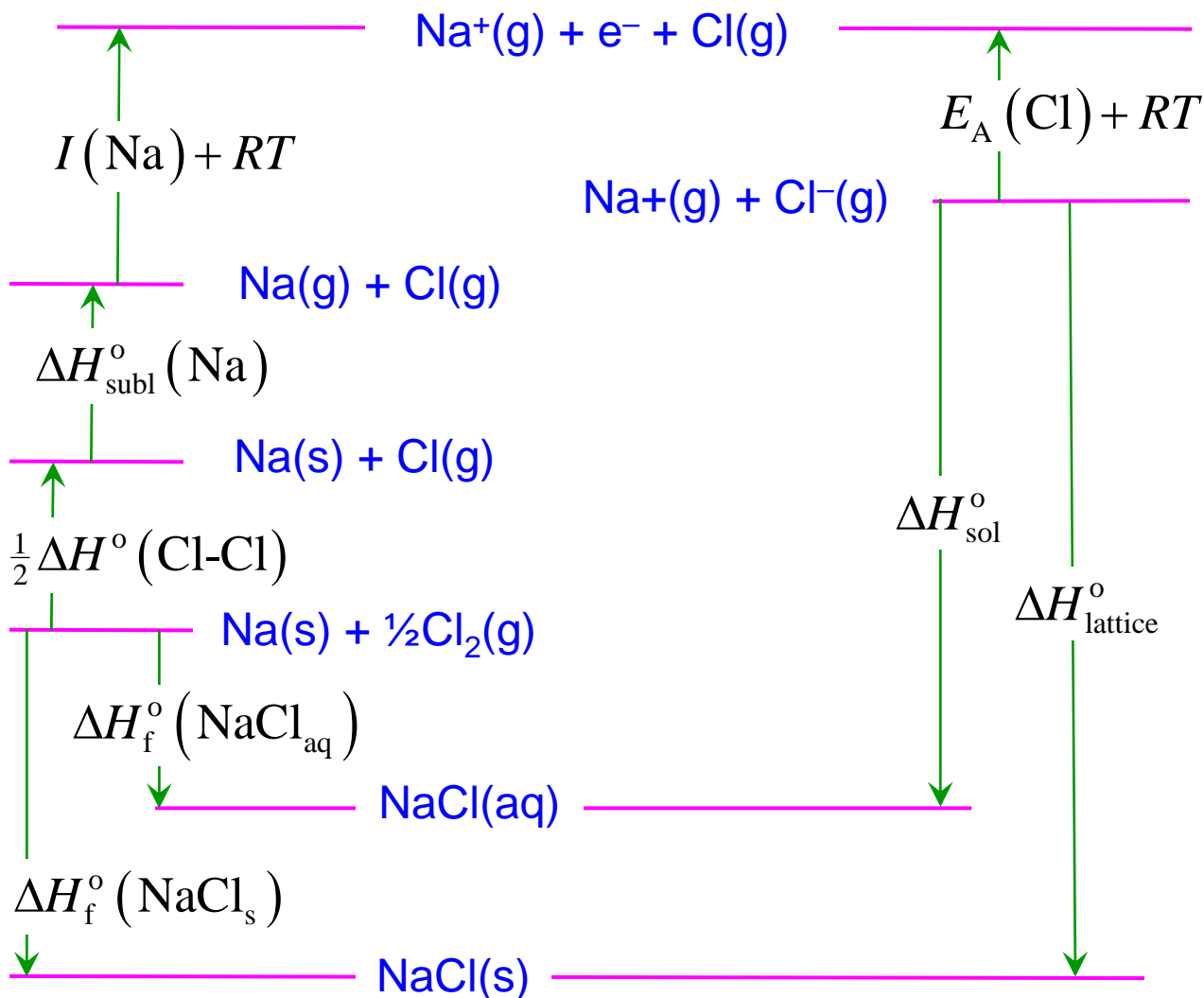
leading us to the enthalpy of formation of solid NaCl:



$$\Delta H_{\text{f}}^{\circ}(\text{NaCl}_{\text{s}}) = \Delta H_{\text{subl}}^{\circ}(\text{Na}) + I(\text{Na}) + \frac{1}{2}\Delta H^{\circ}(\text{Cl-Cl}) - E_{\text{A}}(\text{Cl}) + \Delta H_{\text{lattice}}^{\circ}(\text{NaCl})$$

The Born-Haber Cycle

Enthalpy changes can also be expressed in a diagram, e.g.

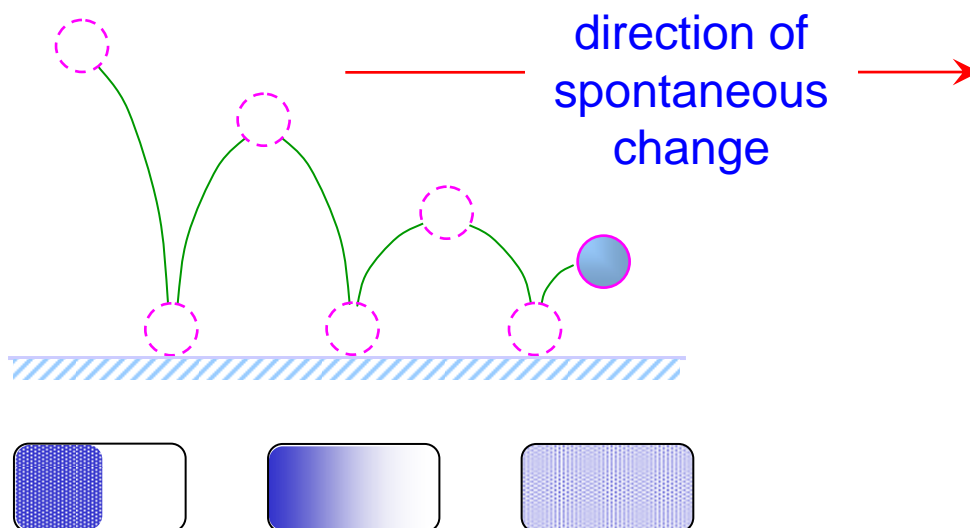


Since H is a state variable, the sum of enthalpy changes around the cycle must be zero. Consequently, if all but one of the enthalpy changes is known, it can be readily calculated.

This is equivalent to using Hess's Law to sum reaction steps.

Spontaneous Change

Who needs entropy, anyway?



The direction of spontaneous change is that which

- leads to chaotic dispersal of the total energy
- moves from a state of low intrinsic probability towards one of greater probability.

Work is needed to reverse a spontaneous process.

We need a quantity – **entropy** – to describe energy dispersal, i.e. the probability of a state.

Spontaneous processes are irreversible.

They “generate” entropy

Reversible processes do not generate entropy – **but they may transfer it from one part of the universe to another.**

Entropy 1

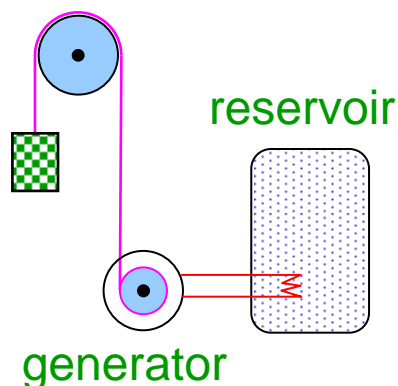
- ❖ Entropy is a state variable (property) which determines if a state is accessible from another by a spontaneous change.
- ❖ Entropy is a measure of chaotic dispersal of energy.
- ❖ The natural tendency of spontaneous change is towards states of higher entropy.
- ❖ There are both thermodynamic (how much heat is produced?) and statistical definitions (how probable is a state?). They both become equivalent when statistics is applied to a large number of molecules.

Consider a falling weight which drives a generator and thus results in heat q being added to the reservoir (the surroundings).

Define a system variable S

$$dS(\text{surr}) = -\delta q / T$$

Use stored energy to restore the weight to its original height. The reservoir gives up δq_{rev} to the system, and there is no overall change in the universe.



$$dS(\text{sys}) = -dS(\text{surr}) = \frac{\delta q_{\text{rev}}}{T}$$

Entropy 2

In general, $dS(\text{sys}) + dS(\text{surr}) \geq 0$
 $dS(\text{sys}) \geq -dS(\text{surr})$

Equality for reversible processes only

or, for the system, $dS \geq \frac{\delta q}{T}$ Clausius inequality

For an isolated system, $q = 0$ hence $\Delta S \geq 0$

Isothermal Processes $\Delta S = q_{\text{rev}} / T$

e.g. $\Delta S(\text{fusion}) = \frac{\Delta H_{\text{fus}}}{T_m}$ $\Delta S(\text{vap}) = \frac{\Delta H_{\text{vap}}}{T_b}$

Trouton's Rule: $\Delta S(\text{vap}) \approx 85 \text{ J K}^{-1} \text{ mol}^{-1}$

Can be used to estimate ΔH_{vap} if T_b is known. Not good for associated liquids.

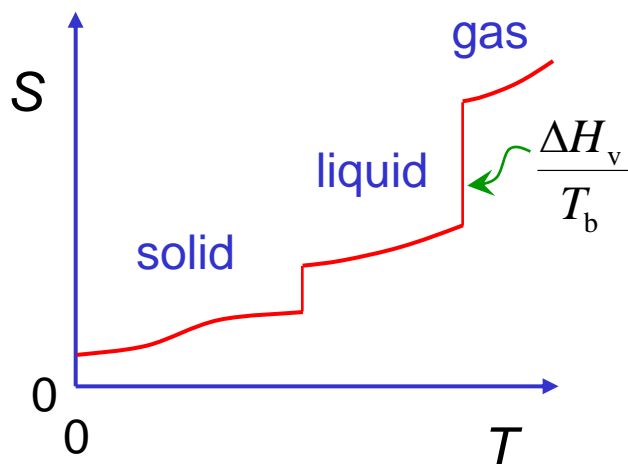
Temperature Variation $\delta q_{\text{rev}} = CdT$

$$(\Delta S)_V = \int_{T_1}^{T_2} \frac{C_V}{T} dT$$

and $(\Delta S)_P = \int_{T_1}^{T_2} \frac{C_P}{T} dT$

Absolute Entropy

$$S(T) = S(0) + \int_0^T \frac{C_P}{T} dT$$

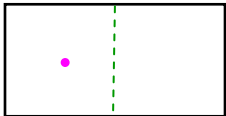
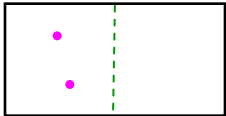
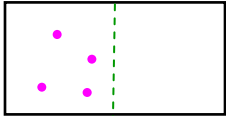
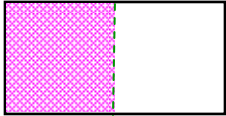


Entropy 3

Entropy depends on Probability.

Consider the number of ways Ω of arranging n molecules between two sides (A and B) of a container.

The probability P_A that all molecules are on side A depends on the ratio of Ω_A to the total number of arrangements.

A	B			
		$\Omega_A = 1$	$\Omega_{\text{tot}} = 2$	$P_A = \frac{1}{2}$
		$\Omega_A = 1$	$\Omega_{\text{tot}} = 4$	$P_A = \frac{1}{4}$
		$\Omega_A = 1$	$\Omega_{\text{tot}} = 16$	$P_A = \frac{1}{16}$
		$\Omega_A = 1$	$\Omega_{\text{tot}} = 2^n$	$P_A = 2^{-n}$

State A becomes less and less probable as n increases. Conversely, the probability of the less ordered, roughly evenly distributed states, increases.

Since entropy is a measure of disorder, it follows that S depends on Ω .

Boltzmann equation $S = k \ln \Omega$

Since $P(x \text{ AND } y) = P_x \cdot P_y$, $\ln P_{x+y} = \ln P_x + \ln P_y$

The Second Law of Thermodynamics

- “An isothermal cyclic process in which there is a net conversion of heat into work is impossible.”
- “No process is possible in which the sole result is the absorption of heat from a reservoir and its conversion into work.” It is possible to convert all work into heat!
- “It is impossible for heat to be transformed from a body at a lower temperature to one at a higher temperature unless work is done.”
- “The entropy of an isolated system increases during any natural process.” The universe is an isolated system.
 $\Delta S(\text{sys}) < 0$ is allowed provided $\Delta S(\text{sys}) + \Delta S(\text{surr}) > 0$
- “All reversible Carnot cycles operating between the same two temperatures have the same thermodynamic efficiency.”
- “There is a state function called entropy S that can be calculated from $dS = \delta q_{\text{rev}}/T$. The change in entropy in any process is given by $dS \geq \delta q/T$, where the inequality refers to a spontaneous (irreversible) process.”

The 1st Law uses U to identify permissible changes of state.

The 2nd Law uses S to identify natural changes among the permissible ones.

The Third Law of Thermodynamics

- “If the entropy of every element in its stable state at $T = 0$ is taken as zero, every substance has a positive entropy which at $T = 0$ may become zero, and does become zero for all perfect crystalline substances, including compounds.”

Nernst Heat Theorem “The entropy change accompanying transformation between condensed phases in equilibrium, including chemical reactions, approaches zero as $T \rightarrow 0$.”

$$\lim_{T \rightarrow 0} \Delta S = 0$$

Practical consequence: Set $S(0) = 0$ for elements by convention. Apply Nernst to determine $S(0)$ for all else.

- “It is impossible to reach absolute zero in a finite number of steps.”

The **1st Law** says U cannot be created or destroyed.

The **2nd Law** says S cannot decrease.

The **3rd Law** says zero Kelvin cannot be reached.

The Clausius Inequality

Given $dS = \frac{\delta q_{\text{rev}}}{T}$ and $\delta w_{\text{rev}} = -PdV$

Substitute into the 1st Law:

$$dU = TdS - PdV$$

Fundamental Equation
of Thermodynamics

All exact differentials, so path independent.

But $dU = \delta q + \delta w = \delta q - P_{\text{ex}} dV$

In general,
i.e. any path

$$TdS - PdV = \delta q - P_{\text{ex}} dV$$

$$\Rightarrow dS = \frac{\delta q}{T} + \frac{(P - P_{\text{ex}})}{T} dV$$

If $P > P_{\text{ex}}$, $dV > 0$; if $P < P_{\text{ex}}$, $dV < 0$

$$\therefore (P - P_{\text{ex}})dV \geq 0$$

Clausius Inequality

$$dS \geq \frac{\delta q}{T}$$

Equal for
reversible
change

Even more generally,

$$dS_{\text{univ}} = \left(\frac{T - T_{\text{surr}}}{T} \right) dS_{\text{surr}} + \frac{(P - P_{\text{surr}})}{T} dV$$

Conditions for: thermal equilibrium mechanical equilibrium

The Fundamental Equation of Thermodynamics

Combine $dU = \delta q - PdV$ with $dS = \frac{\delta q_{\text{rev}}}{T}$

$$\Rightarrow dU = TdS - PdV$$

$$\text{or } dS = \left(\frac{1}{T}\right)dU + \left(\frac{P}{T}\right)dV$$

Reversible change but true for all paths since dV exact

This fundamental equation generates many more relationships.

Example 1: Comparison with $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$

$$\Rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Example 2: Consider that dU is exact and cross differentiate.

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \text{a Maxwell relation}$$

Example 3: $\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial S}{\partial T}\right)_V$ cyclic rule

$$= \left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{and again!}$$

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

$$= \alpha / \kappa$$

How Entropy Depends on T and V

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{P}{T}\right) dV$$

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

$$\Rightarrow dS = \frac{C_V}{T} dT + \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right] dV$$

Compare with $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

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

$$\Delta S_V = \int \frac{C_V}{T} dT$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

0 for ideal gases

$$\begin{aligned} \Delta S_T &= \int \frac{P}{T} dV = nR \int \frac{1}{V} dV \\ &= nR \ln(V_2 / V_1) \end{aligned}$$

For any substance,

$$dS = \frac{C_V}{T} dT + \frac{\alpha}{\kappa} dV$$

For ideal gases,

$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

assuming C_V is T independent

How Entropy Depends on T and P

$$dS = \left(\frac{1}{T}\right)dU + \left(\frac{P}{T}\right)dV$$

First problem: replace dU ; second problem: replace dV .

Use $dU = dH - PdV - VdP$ and both are solved!

$$dS = \left(\frac{1}{T}\right)dH - \left(\frac{V}{T}\right)dP$$

But $dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$

$$\Rightarrow dS = \frac{C_P}{T} dT + \frac{1}{T} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right] dP$$

Compare with $dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\Delta S_P = \int \frac{C_P}{T} dT$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right]$$

0 for ideal gases

$$\Delta S_T = - \int \frac{V}{T} dP = -nR \int \frac{1}{P} dP$$

$$\Delta S_T = -nR \ln(P_2 / P_1) = nR \ln(V_2 / V_1)$$

Entropy Changes in Spontaneous Processes

Entropy is a state function, so

$$\Delta S(\text{sys}) = S_2 - S_1 \quad \text{independent of path}$$

This can be used to calculate ΔS for an irreversible process.

❖ Consider isothermal expansion of a gas from V_1 to V_2 :

$$\Delta S(\text{sys}) = nR \ln(V_2 / V_1) \quad \text{reversible and irreversible cases}$$

For the reversible case $\Delta S(\text{surr}) = -\Delta S(\text{sys})$

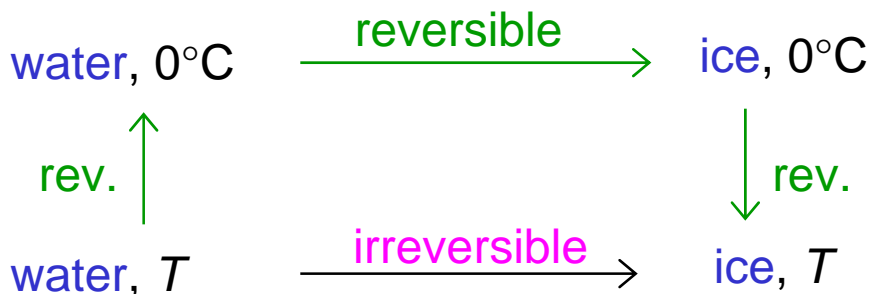
For the irreversible case $\Delta S(\text{surr}) > -\Delta S(\text{sys})$

$$\Delta S(\text{surr}) = -\frac{q}{T} = \frac{w}{T}$$

e.g. for free expansion, $w = 0$

$$\Rightarrow \Delta S(\text{surr}) = 0, \quad \Delta S(\text{univ}) = \Delta S(\text{sys}) > 0$$

❖ Consider freezing of supercooled water at $T < 273 \text{ K}$

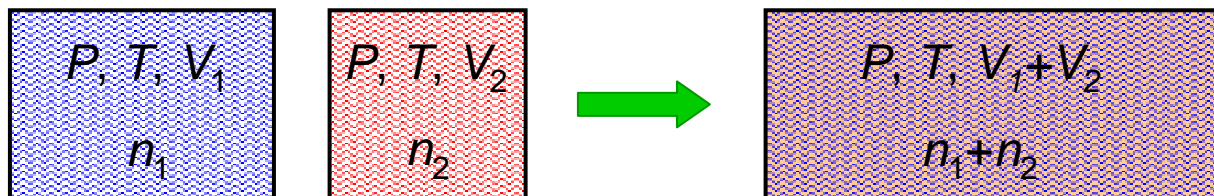


$$\Delta S(\text{sys}) = C_P(\text{l}) \ln\left(\frac{273}{T}\right) + \frac{(-\Delta H_{\text{fus}}^\circ)}{273} + C_P(\text{s}) \ln\left(\frac{T}{273}\right)$$

$$\Delta S(\text{surr}) = \frac{\Delta H_{\text{fus}}(T)}{T} = \frac{1}{T} \left\{ \Delta H_{\text{fus}}(273) + [C_P(\text{l}) - C_P(\text{s})](T - 273) \right\}$$

Entropy of Mixing

❖ Consider the mixing of two ideal gases :



$$\Delta S_1 = -n_1 R \ln \frac{V_1}{V_1 + V_2} = -n_1 R \ln \frac{n_1}{n_1 + n_2} = -n_1 R \ln \chi_1$$

$$\Delta S_2 = -n_2 R \ln \frac{V_2}{V_1 + V_2} = -n_2 R \ln \frac{n_2}{n_1 + n_2} = -n_2 R \ln \chi_2$$

$$\Delta S_{\text{mix}} = -n_1 R \ln \chi_1 - n_2 R \ln \chi_2 = -(n_1 + n_2) R (\chi_1 \ln \chi_1 + \chi_2 \ln \chi_2)$$

In general

$$\Delta S_{\text{mix}} = -n_{\text{tot}} R \sum_i \chi_i \ln \chi_i$$

This expression applies to the arrangement of objects (molecules) just as well as fluids (gases and liquids).

For example, arrange N identical atoms in N sites in a crystal:

$$\Omega = N! / N! = 1 \quad S = k \ln \Omega = 0$$

Compare with the arrangement of two types of atom, A and B.

$$\Omega = \frac{N!}{N_A! N_B!} \quad \Delta S = k (\ln N! - \ln N_A! - \ln N_B!)$$

Application of Stirling's approximation $\ln(z!) = z \ln z - z$

leads to $\Delta S_{\text{config}} = -kN (\chi_A \ln \chi_A + \chi_B \ln \chi_B)$

Using Entropy to Achieve Low T

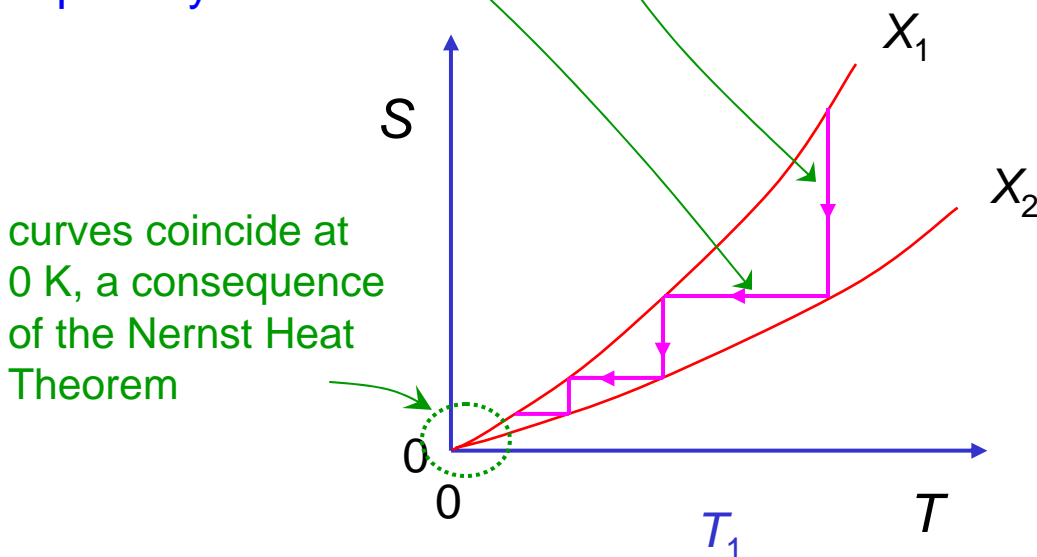
$$\Delta S_P = \int \frac{C_P}{T} dT \approx C_P \ln(T_2/T_1) \quad \text{if } C_P \text{ is } \approx \text{constant}$$

To achieve lower temperatures, S must be reduced.

Choose some property X that varies with S , i.e. $S = f(X, T)$.

This could be the pressure of a gas or, for example, the magnetic moment of a paramagnetic salt (whose energy varies with magnetic field).

1. Alter X isothermally. Entropy changes. $\Delta S_T \approx \left(\frac{\partial S}{\partial X} \right)_T \Delta X, \quad q = T \Delta S$
2. Restore X by a reversible adiabatic process. $q = 0, \quad \Delta S = 0$
3. Repeat cycle.



Spontaneous Change

For a system in thermal equilibrium with its surroundings,

$$dS \geq \frac{\delta q}{T} \quad \text{Clausius inequality}$$

At constant volume:

$$dq_V = dU \quad \text{no work}$$

$$TdS - dU \geq 0$$

$$(dS)_{U,V} \geq 0 \quad \text{isolated system}$$

$$(dU)_{S,V} \leq 0$$

At constant pressure:

$$dq_P = dH \quad \text{PV work only}$$

$$TdS - dH \geq 0$$

$$(dH)_{S,P} \leq 0$$

For convenience, define:

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

Then the conditions for spontaneous change become:

$$(dA)_{T,V} \leq 0$$

$$(dG)_{T,P} \leq 0$$

Helmholtz Energy A

Helmholtz energy; Helmholtz free energy; Helmholtz function;
Maximum work function A for Arbeit

For spontaneous change at constant T and V

$$dA = dU - TdS \leq 0$$

Note that it is the *total* function A that tends to a minimum;
this is *not* the same as minimizing U and maximizing S .

Maximum Work

Combine $dU = \delta q + \delta w$ and $TdS \geq \delta q$

$$\Rightarrow dU \leq TdS + \delta w$$

equality for
reversible change

Word done by
the system

$$(-\delta w) \leq TdS - dU$$

$$(-\delta w)_{\max} = TdS - \delta q_{\text{rev}} - \delta w_{\text{rev}} = -\delta w_{\text{rev}}$$

A system does maximum work when it is operating reversibly.

But $(dA)_T = dU - TdS = dU - \delta q_{\text{rev}} = \delta w_{\text{rev}}$

Therefore, for macroscopic changes

$$-w_{\max} = -\Delta A = T\Delta S - \Delta U \quad \text{constant } T$$

$(-w)$ can be more or less than ΔU according to the sign of ΔS .

For $\Delta S > 0$, heat flows into the system to fuel the extra work.

Gibbs Energy G

Gibbs free energy, Gibbs function

- ❖ Very important in chemistry since it tells whether a particular reaction can proceed at a given T and P .

For spontaneous change,

$$(dG)_{T,P} \leq 0 \quad \Delta G = G_{\text{products}} - G_{\text{reactants}} \leq 0$$

$\Delta G_{T,P}$ for reactions can be calculated from tabulated data

$$\Delta G^\circ(T) = \Delta H^\circ(T) - T\Delta S^\circ(T)$$

If ΔH is	and ΔS is	then ΔG	the reaction proceeds
-ve	+ve	< 0	at all temperatures
+ve	-ve	> 0	at no temperatures
-ve	-ve	...	if $T < \Delta H / \Delta S$
+ve	+ve	...	if $T > \Delta H / \Delta S$

Maximum Work:

$$(dG)_T = dH - TdS$$

$$(dG)_{T,P} = dU + PdV - TdS$$

$$= \delta q_{\text{rev}} + \delta w_{\text{rev}} + PdV - TdS$$

$$= \delta w_{\text{rev}} + PdV$$

$$= \delta w_{\text{max}} (\text{non-PV})$$

$$\Delta w_{\text{max}} (\text{non-PV}) = \Delta G \quad \text{constant } T, P$$

Basic Thermodynamic Relations 1

Laws $dU = \delta q - PdV$... (1)

$$dS = \delta q_{\text{rev}} / T \quad \dots (2)$$

Definitions $H = U + PV$... (3)

$$A = U - TS \quad \dots (4)$$

$$G = H - TS \quad \dots (5)$$

Fundamental Equations

$$dU = TdS - PdV \quad \dots (6)$$

$$dH = TdS + VdP \quad \dots (7)$$

$$dA = -SdT - PdV \quad \dots (8)$$

$$dG = -SdT + VdP \quad \dots (9)$$

Partial Differentials

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

Basic Thermodynamic Relations 2

Maxwell Relations

From (6) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \dots(10)$

From (7) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \dots(11)$

From (8) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \dots(12)$

From (9) $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \dots(13)$

Thermodynamic Equation of State

$$dU = TdS - PdV \dots(6)$$

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

Substituting (12) $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\alpha}{\kappa}\right) - P$$

How Free Energy Depends on T

$$G = H - TS \quad \dots(1) \quad \text{definition}$$

$$\Delta G = \Delta H - T\Delta S \quad \dots(2) \quad \text{constant } T$$

$$dG = VdP - SdT \quad \dots(3) \quad \text{fundamental eqn.}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S = \frac{G - H}{T} \quad \text{from (1)}$$

$$\therefore \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T} = -\frac{H}{T} \quad \dots(4)$$

$$\text{But} \quad \left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} \quad \dots(5)$$

Gibbs-Helmholtz
Equation

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{H}{T^2}$$

substitute
(4) in (5)

alternative form:

$$\left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P = H$$

By applying the Gibbs-Helmholtz equation to both reactants and products of a chemical reaction,

$$\Rightarrow \left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$

How Free Energy Depends on P

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

$$\Delta G = G_2 - G_1 = \int_1^2 V dP$$

For solids and liquids V does not change much with P , so

$$G_2(T) \approx G_1(T) + V(P_2 - P_1)$$

For a perfect gas $V = \frac{nRT}{P}$

$$\Delta G_T = nRT \ln(P_2 / P_1)$$

$$G = G^\circ(T) + nRT \ln(P / P^\circ)$$

where G° is the **standard free energy** defined at $P^\circ=1$ bar

The chemical potential for a pure substance is the molar Gibbs energy:

$$\mu = \bar{G} = \frac{G}{n}$$

\therefore For a perfect gas

$$\mu = \mu^\circ + RT \ln(P / P^\circ)$$

The Chemical Potential

So far, our thermodynamic relations apply to **closed** systems. However, G , U , H , etc. are **extensive** properties.

Partial molar quantities are used to describe quantities which depend on composition.

$$\bar{J}_i = \left(\frac{\partial J}{\partial n_i} \right)_{T,P,n_{j \neq i}} \quad J = U, H, S, A, G, V$$

$$J = \sum_i n_i \bar{J}_i$$

In general

$$dG = \left(\frac{\partial G}{\partial P} \right)_{T,n_1,n_2,\dots} dP + \left(\frac{\partial G}{\partial T} \right)_{P,n_1,n_2,\dots} dT + \left(\frac{\partial G}{\partial n_1} \right)_{T,P,n_2,\dots} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{T,P,n_1,n_3,\dots} dn_2 + \dots$$

Chemical Potential

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_{j \neq i}}$$

Fundamental Equations

$$dU = TdS - PdV + \sum \mu_i dn_i$$
$$dH = TdS + VdP + \sum \mu_i dn_i$$

etc.

$$\Rightarrow \mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{V,S} = \left(\frac{\partial H}{\partial n_i} \right)_{P,S} = \left(\frac{\partial A}{\partial n_i} \right)_{V,T}$$

Free Energy of Mixing 1

Consider the mixing of two *ideal* gases A and B at constant T and P .

Before: $G_1 = n_A \mu_A (\text{pure}) + n_B \mu_B (\text{pure})$

where $\mu_A (\text{pure}) = \mu_A^\circ + RT \ln(P / P_0)$

After mixing: $G_A = n_A \left\{ \mu_A^\circ + RT \ln(p_A / P_0) \right\}$
 $= n_A \left\{ \mu_A^\circ + RT \ln(P / P_0) + RT \ln \chi_A \right\}$

$$= n_A \mu_A (\text{pure}) + n_A RT \ln \chi_A$$

$$G_2 = G_A + G_B < G_1$$

negative

Change: $\Delta G_{\text{mix}} = G_2 - G_1$
 $= n_A RT \ln \chi_A + n_B RT \ln \chi_B$
 $= nRT (\chi_A \ln \chi_A + \chi_B \ln \chi_B)$

$$\Delta G_{\text{mix}} = nRT (\chi_A \ln \chi_A + \chi_B \ln \chi_B)$$

$$\Delta G_{\text{mix}} < 0 \quad \text{Mixing is spontaneous.}$$

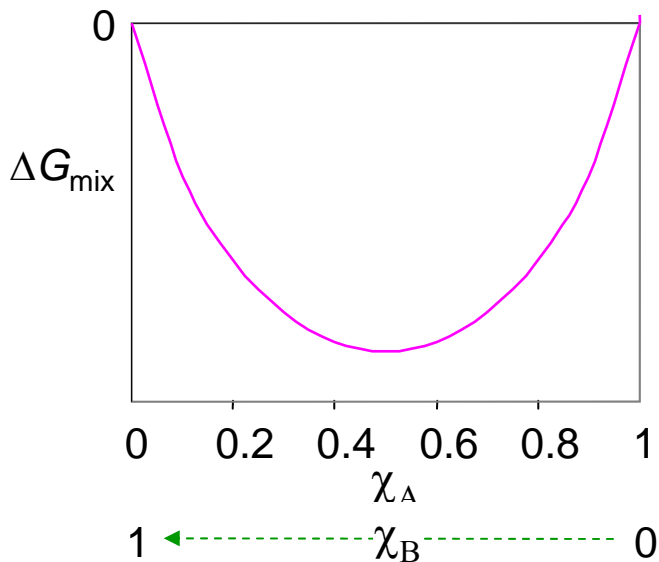
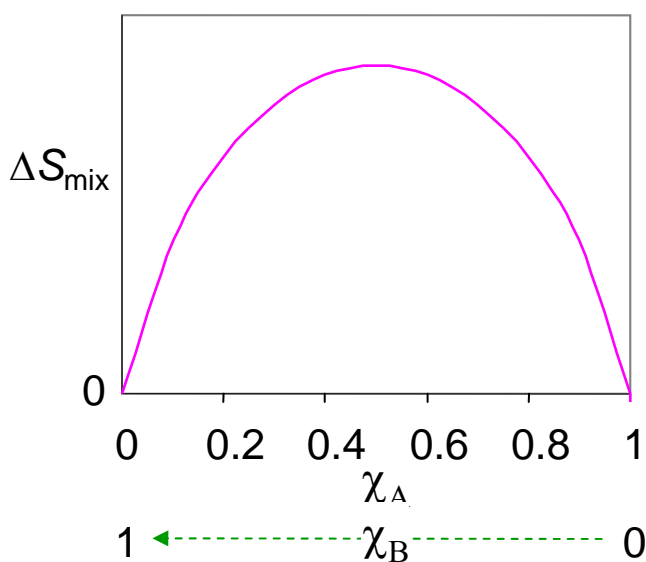
Entropy of Mixing $\Delta S_{\text{mix}} = -(\partial \Delta G_{\text{mix}} / \partial T)_{P, n_i} = -nR \sum \chi_i \ln \chi_i$

Enthalpy of Mixing $\Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T \Delta S_{\text{mix}} = 0$

Similarly, $\Delta U_{\text{mix}} = \Delta V_{\text{mix}} = 0$ for ideal gases and solutions

Free Energy of Mixing 2

For a binary system, ΔG_{mix} is at its **minimum** and ΔS_{mix} at its **maximum** when $\chi_A = \chi_B = 0.5$

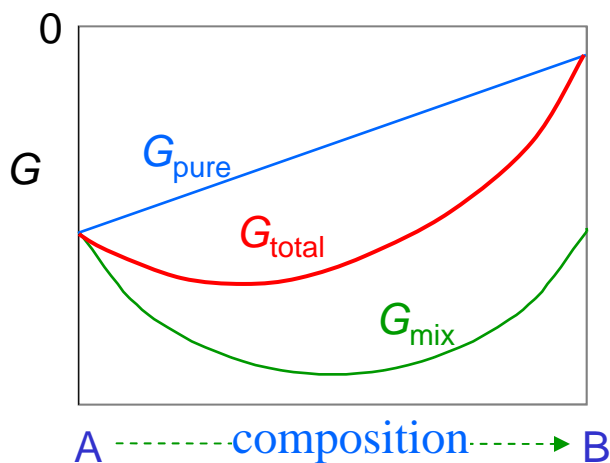


Equilibrium and Mixing:

Consider an equilibrium between two ideal gases $A \rightleftharpoons B$

$$G = G_A(\text{pure}) + G_B(\text{pure}) + \Delta G_{\text{mix}}$$

$$= n(\chi_A \mu_A + \chi_B \mu_B) + nRT(\chi_A \ln \chi_A + \chi_B \ln \chi_B)$$



The equilibrium composition is determined by the minimum in G_{total} .

Reaction Equilibrium 1

Consider $A \rightleftharpoons B$

Suppose an amount dx of A turns into B.

Then $(dG)_{T,P} = \mu_A dn_A + \mu_B dn_B = -\mu_A dx + \mu_B dx$

$$\Rightarrow \left(\frac{\partial G}{\partial x} \right)_{T,P} = \mu_B - \mu_A$$

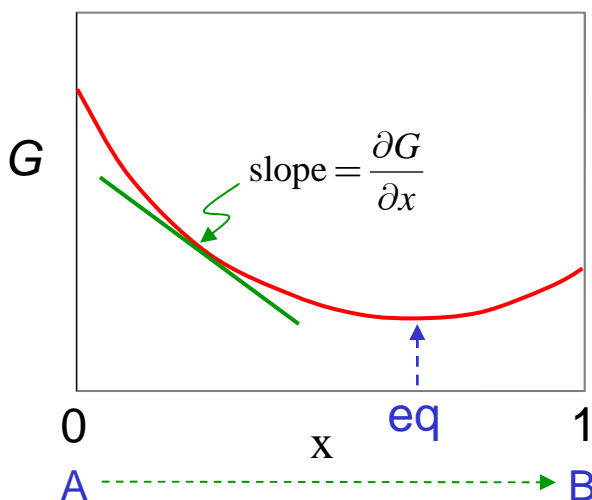
μ_A and μ_B depend on composition, and therefore change during the reaction.

If $\mu_A > \mu_B$ the reaction proceeds from $A \rightarrow B$.

If $\mu_A < \mu_B$ the reaction proceeds from $B \rightarrow A$.

At equilibrium

$$\mu_A = \mu_B$$



$$\mu_A^\circ + RT \ln(p_A^{\text{eq}} / P^\circ) = \mu_B^\circ + RT \ln(p_B^{\text{eq}} / P^\circ)$$

$$RT \ln(p_A^{\text{eq}} / p_B^{\text{eq}}) = \mu_B^\circ - \mu_A^\circ = \Delta \bar{G}_{\text{rxn}}^\circ$$

$$\frac{p_B^{\text{eq}}}{p_A^{\text{eq}}} = \exp(-\Delta \bar{G}_{\text{rxn}}^\circ / RT)$$

Reaction Equilibrium 2

A reaction such as $2A + 3B \rightarrow C + 2D$ can be written as

$$0 = -2A - 3B + C + 2D$$

or completely generally as $0 = \sum_i \nu_i R_i = 0$

Then
$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \sum_i \nu_i \mu_i$$

and at equilibrium,
$$\sum_i \nu_i \mu_i = 0$$

$$\sum_i \left(\nu_i \mu_i^\circ + \nu_i RT \ln \frac{p_i^{\text{eq}}}{P^\circ} \right) = 0$$

$$\Delta \bar{G}_{\text{rxn}}^\circ + RT \ln \left[\prod_i \left(\frac{p_i}{P^\circ} \right)_{\text{eq}}^{\nu_i} \right] = 0$$

$$\Delta \bar{G}_{\text{rxn}}^\circ = -RT \ln K$$

$$K = \prod_i \left(\frac{p_i}{P^\circ} \right)_{\text{eq}}^{\nu_i}$$

Equilibrium Constants

Consider $aA + bB \rightleftharpoons yY + zZ$ $\Delta v = y + z - a - b$

Thermodynamic Equilibrium Constant

$$K^\circ = \prod_i \left(\frac{p_i}{P^\circ} \right)_{\text{eq}}^{\nu_i} = \frac{\left(p_Y / P^\circ \right)_{\text{eq}}^y \left(p_Z / P^\circ \right)_{\text{eq}}^z}{\left(p_A / P^\circ \right)_{\text{eq}}^a \left(p_B / P^\circ \right)_{\text{eq}}^b}$$

Some books still refer to the pressure equilibrium constant

$$K_p = \frac{\left(p_Y \right)_{\text{eq}}^y \left(p_Z \right)_{\text{eq}}^z}{\left(p_A \right)_{\text{eq}}^a \left(p_B \right)_{\text{eq}}^b} \quad \text{which in general has pressure units}$$

The equilibrium constant can also be expressed in mole fractions:

$$K^\circ = \frac{\left(\chi_C P_{\text{tot}} / P^\circ \right)_{\text{eq}}^y \left(\chi_D P_{\text{tot}} / P^\circ \right)_{\text{eq}}^z}{\left(\chi_A P_{\text{tot}} / P^\circ \right)_{\text{eq}}^a \left(\chi_B P_{\text{tot}} / P^\circ \right)_{\text{eq}}^b} = K_x \left(\frac{P_{\text{tot}}}{P^\circ} \right)^{\Delta v}$$

and in concentrations:

$$p_i = n_i RT / V = c_i RT$$

$$K^\circ = \prod_i \left(\frac{p_i}{P^\circ} \right)_{\text{eq}}^{\nu_i} = \prod_i \left(\frac{c_i RT}{P^\circ} \right)_{\text{eq}}^{\nu_i} = \left(\frac{c^\circ RT}{P^\circ} \right)^{\sum \nu} K_c$$

where

$$K_c = \frac{\left([C] / c^\circ \right)_{\text{eq}}^y \left([D] / c^\circ \right)_{\text{eq}}^z}{\left([A] / c^\circ \right)_{\text{eq}}^a \left([B] / c^\circ \right)_{\text{eq}}^b}$$

for this example

Equilibrium Calculations

	2 NO	+	Cl ₂	→	2NOCl
stoichiometry	-2		-1		+2
initial moles	2		1		0
during reaction	2(1-a)		1-a		2a
mole fraction	$\frac{2(1-a)}{3-a}$		$\frac{1-a}{3-a}$		$\frac{2a}{3-a}$
partial pressure	$\frac{2(1-a)}{3-a} \frac{P}{P^\circ}$		$\frac{1-a}{3-a} \frac{P}{P^\circ}$		$\frac{2a}{3-a} \frac{P}{P^\circ}$

$$K_x = \frac{\left\{ \frac{2a}{3-a} \right\}^2}{\left\{ \frac{2(1-a)}{3-a} \right\}^2 \left\{ \frac{1-a}{3-a} \right\}} = \frac{a^2(3-a)}{(1-a)^3}$$

$$K^\circ = K_x \left(\frac{P^\circ}{P} \right)$$

The value of a at equilibrium (and thus the equilibrium composition of the reaction mixture) depends on pressure.

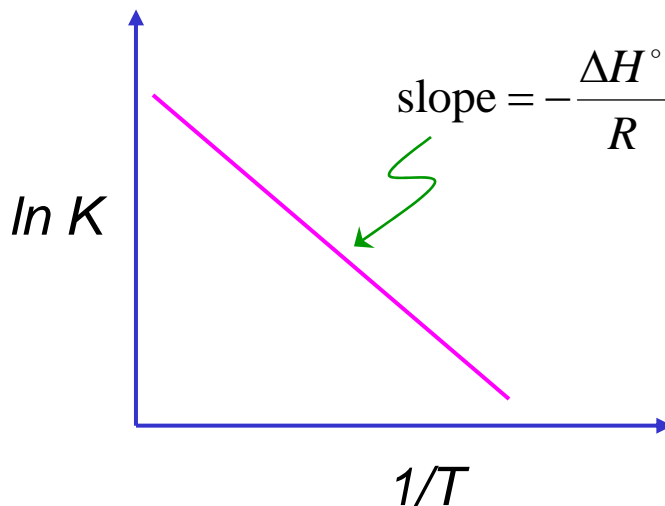
Temperature Dependence of K_P

Gibbs-Helmholtz $\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$

substitute $\Delta G_{\text{rxn}}^\circ = -RT \ln K$

van't Hoff Equation $\left(\frac{\partial(\ln K)}{\partial T}\right)_P = \frac{\Delta_r H^\circ}{RT^2}$

or $\left(\frac{\partial(\ln K)}{\partial(1/T)}\right)_P = -\frac{\Delta_r H^\circ}{R}$



Exothermic reactions: $\Delta H < 0$ so K falls with increasing T .

Endothermic reactions: $\Delta H > 0$ so K rises with increasing T .

Integrating, $\ln \left\{ \frac{K(T_2)}{K(T_1)} \right\} = -\frac{\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$

or from $\Delta G_{\text{rxn}}^\circ = -RT \ln K$ $\ln K(T) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$

Pressure Dependence of Equilibrium

Since $K^\circ = \exp(-\Delta G^\circ / RT)$, $\left(\frac{\partial K^\circ}{\partial P}\right)_T = 0$

But, $K_x = K^\circ (P / P^\circ)^{-\Delta v}$

$$\begin{aligned}\ln K_x &= \ln K^\circ - \Delta v \ln(P / P^\circ) \\ &= \ln K^\circ - \Delta v \ln P + \Delta v \ln P^\circ\end{aligned}$$

$$\left(\frac{\partial \ln K_x}{\partial \ln P}\right)_T = -\Delta v$$

$$\left(\frac{\partial \ln K_x}{\partial P}\right)_T = -\frac{\Delta v}{P} = -\frac{\Delta V}{RT} \quad \text{ideal gas}$$

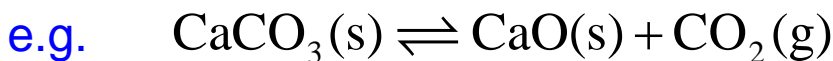
Although the thermodynamic equilibrium constant does not depend on pressure, the K for mole fraction does if $\Delta v \neq 0$

The equilibrium composition depends on pressure if $\Delta v \neq 0$

Le Chatelier's Principle

A system at equilibrium, when subjected to a perturbation, responds in a way that tends to minimize the effect.

Equilibria Involving Condensed Matter



$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = -\mu(\text{CaCO}_3) + \mu(\text{CaO}) + \mu(\text{CO}_2)$$

where $\mu(\text{CO}_2) = \mu^\circ(\text{CO}_2) + RT \ln(p_{\text{CO}_2} / P^\circ)$

but $\mu(\text{CaCO}_3) \approx \mu^\circ(\text{CaCO}_3)$

$$\mu(\text{CaO}) \approx \mu^\circ(\text{CaO})$$

At equilibrium, $\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = 0$

$$\Rightarrow \Delta \bar{G}^\circ + RT \ln(p_{\text{CO}_2}^{\text{eq}} / P^\circ) = 0$$

$$K^\circ = (p_{\text{CO}_2}^{\text{eq}} / P^\circ)$$

K depends only on the partial pressures of the gaseous reaction components.

A special case is the evaporation of a liquid: $\text{L}(\text{l}) \rightleftharpoons \text{G}(\text{g})$

$$K^\circ = (p_{\text{G}}^{\text{eq}} / P^\circ)$$

$$\frac{\partial \ln K^\circ}{\partial T} = \frac{\partial \ln P}{\partial T} = \frac{\Delta H_{\text{vap}}^\circ}{RT^2}$$

Phase Equilibria

Consider a closed system of a single component.

The **chemical potential** determines which phase is stable at a particular T and P . μ tends to a minimum.

At the melting point T_m , $\mu(s) = \mu(l)$

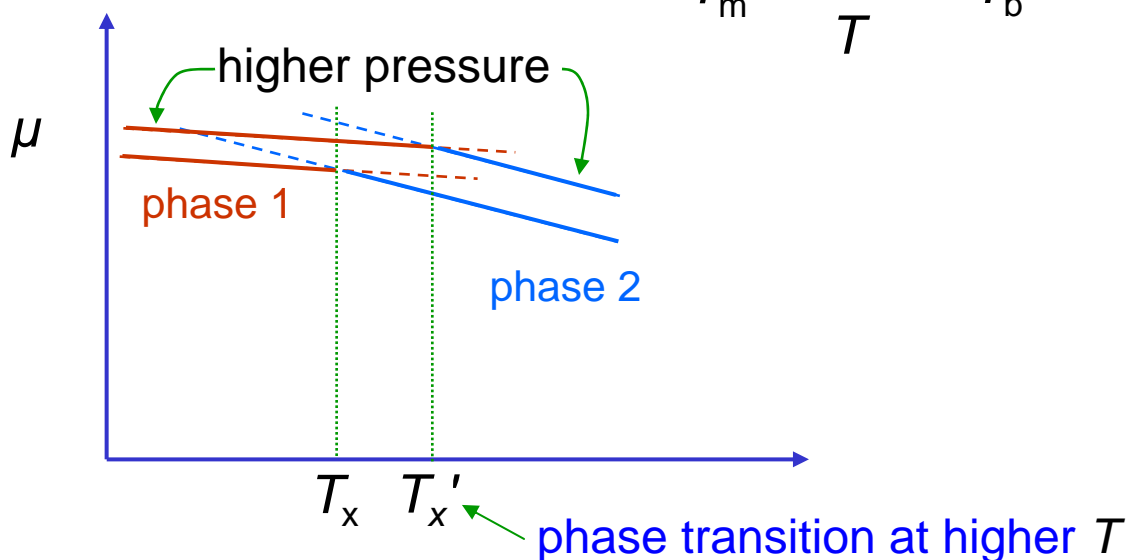
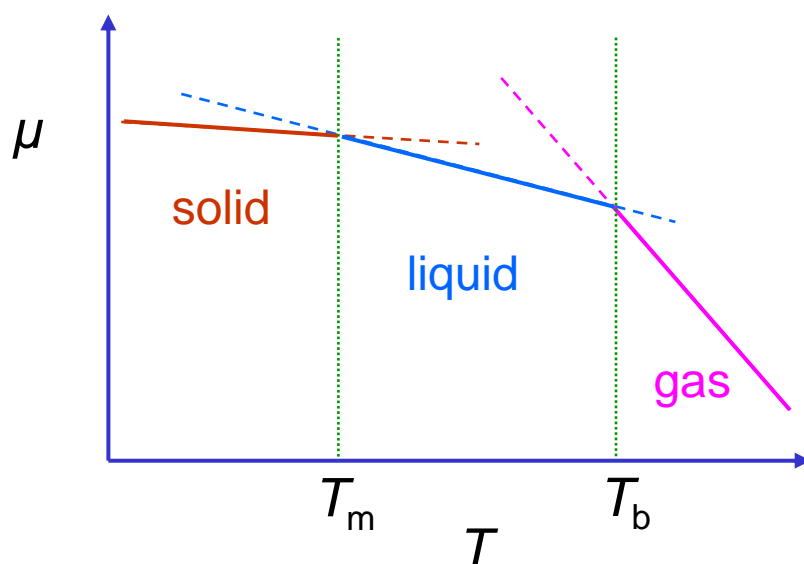
At the boiling point T_b , $\mu(l) = \mu(g)$

These points depend on temperature and pressure.

$$dG = VdP - SdT$$

$$\left(\frac{\partial\mu}{\partial T}\right)_P = -\bar{S}$$

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



The Clapeyron Equation

Consider two phases α and β in equilibrium:

$$\mu(\alpha, T, P) = \mu(\beta, T, P)$$

If small changes in T and P are made such that α and β are still in equilibrium:

$$d\mu(\alpha, T, P) = d\mu(\beta, T, P)$$

$$-\bar{S}(\alpha)dT + \bar{V}(\alpha)dP = -\bar{S}(\beta)dT + \bar{V}(\beta)dP$$

$$[\bar{V}(\alpha) - \bar{V}(\beta)]dP = [\bar{S}(\alpha) - \bar{S}(\beta)]dT$$

$$\frac{dP}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}} = \frac{\Delta\bar{H}}{T\Delta\bar{V}}$$

Melting

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_m}{T_m \Delta\bar{V}_m}$$

Integrating,

$$P_2 - P_1 = \frac{\Delta\bar{H}_m}{\Delta\bar{V}_m} \ln \left\{ \frac{T_m(P_2)}{T_m(P_1)} \right\}$$
$$\approx \frac{\Delta\bar{H}_m}{\Delta\bar{V}_m} \frac{\Delta T}{T_m}$$

$$\Delta\bar{H}_m > 0 \quad \text{and usually} \quad \Delta\bar{V}_m > 0$$

$\Rightarrow T_m$ increases with pressure *not for water!*

The Clausius-Clapeyron Equation

Vaporization

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\text{vap}}}{T\Delta\bar{V}_{\text{vap}}} \approx \frac{\Delta\bar{H}_{\text{vap}}}{T\bar{V}(g)}$$

Assuming the vapour is an ideal gas, $\bar{V}(g) = RT / P$

$$\frac{d \ln P}{dT} = \frac{\Delta\bar{H}_{\text{vap}}}{RT^2}$$

Integrating,

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta\bar{H}_{\text{vap}}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

The normal boiling point is the temperature at which the vapour pressure becomes standard, i.e. 1 bar.

Sublimation solid \leftrightarrow gas

The liquid is not stable at any temperature.

Triple Point: solid, liquid and gas are all in equilibrium

This happens at the pressure where the sublimation temperature and the boiling temperature coincide.

At the triple point,

vapour pressure of liquid = vapour pressure of solid

T_{triple} and P_{triple} are fixed.

The Phase Rule

How many intensive variables are needed to describe fully a system of C components and P phases?

- Two for temperature and pressure.
- How many for the composition of each phase?

Take mole fractions of each component in each phase

$$\Rightarrow P \times (C - 1) \quad \text{C-1 because for each phase } \sum \chi_i = 1$$

but since the phases are in equilibrium,

$$\mu(\text{phase 1}) = \mu(\text{phase 2}) = \dots$$

$(P - 1)C$ variables are redundant

$$\therefore \text{Number of independent concentration variables} = P(C - 1) - (P - 1)C = C - P$$

$$\therefore \text{Total number of variables (degrees of freedom)} \quad F = C - P + 2$$

Phase: A state of matter that is uniform throughout, in both chemical composition and physical state.

Component: The number of components is the minimum number of independent species necessary to define the composition of all phases in the system.

Reactions and phase equilibria must be taken into account.

Phase Diagrams of Pure Materials

$$F = C - P + 2 \quad \text{with } C = 1 \Rightarrow F = 3 - P$$

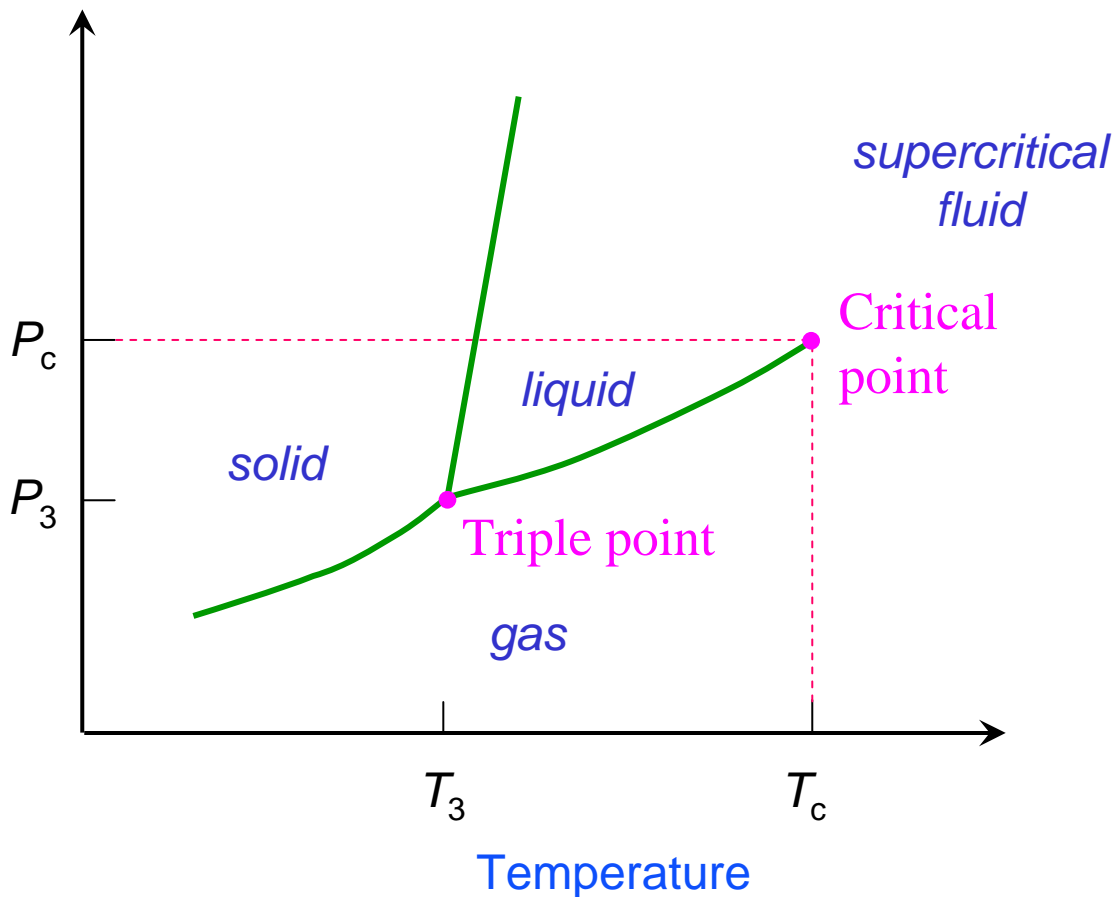
For single phase regions there are 2 degrees of freedom.

For phase boundaries there is 1 degree of freedom.

At the triple point there is no freedom.

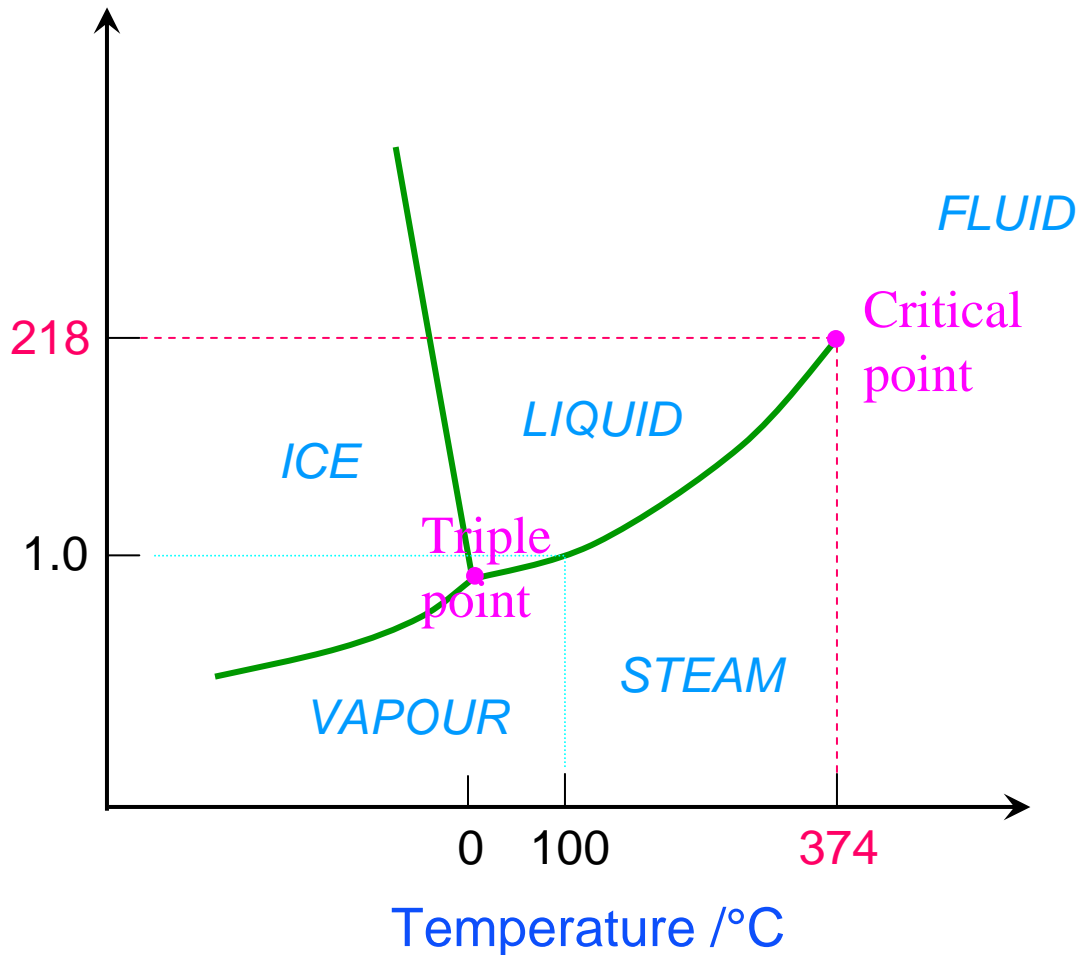
e.g. CO_2

Pressure



The Phase Diagram of Water

Pressure / atm



There are other solid phases at much higher pressures.