

Chap. 8 Equilibrium between phases or chemical species

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1. What will we talk about?



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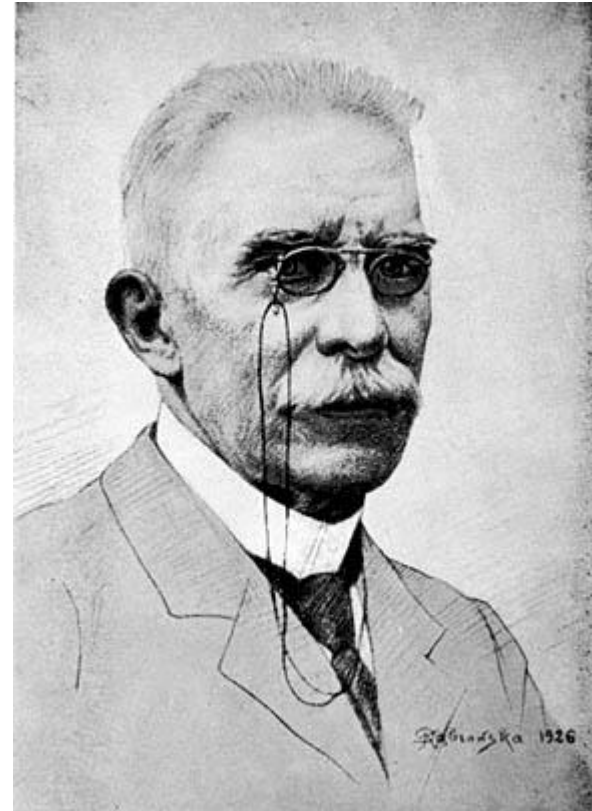
Up to now we have dealt almost exclusively with systems consisting of a single "component" and a single "phase".

However, in this chapter, we will focus our attention on a more general situation, namely, the system consisting of several components in several phases.

2. Background knowledge

2.1 *Le Chatelier's principle*

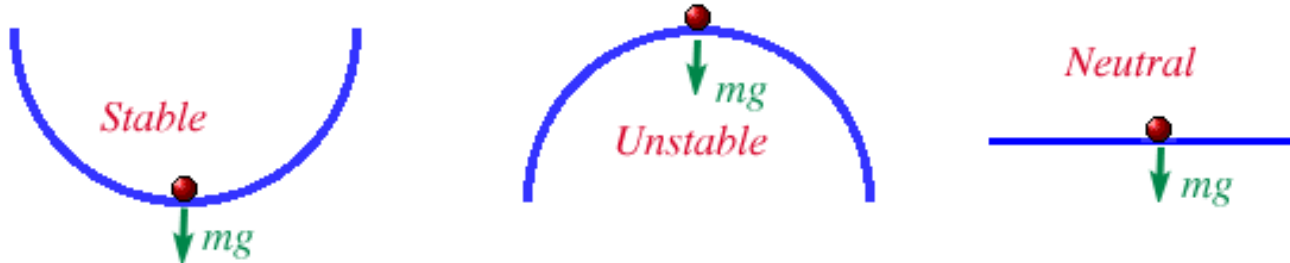
If a system is in ***stable equilibrium***, then any spontaneous change of its parameters must bring about processes which tend to restore the system to equilibrium.



Equilibrium

The picture below illustrates the basic three kinds of equilibrium in mechanics, we can know from the picture that when the system is in stable equilibrium:

$$\begin{cases} \frac{\partial f}{\partial x} = 0 \\ \frac{\partial^2 f}{\partial x^2} > 0 \end{cases}$$



2.2 *Gaussian distribution* (*Normal distribution*)

$$f(x, \mu, \sigma) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$



From some mathematical proof, we can get an important conclusion:(variance)

$$\overline{(x - \bar{x})^2} = \sigma^2$$

3. General Equilibrium Conditions

3.1 Isolated system

3.2 System in contact with a reservoir at constant temperature

3.3 System in contact with a reservoir at constant temperature and pressure

3.4 Stability conditions for a homogeneous substance

3.1 *Isolated system*

We know from the *second law of thermodynamics* that in a natural thermodynamic process, there is an increase in the sum of the entropies of the participating systems.


$$\Delta S \geq 0$$

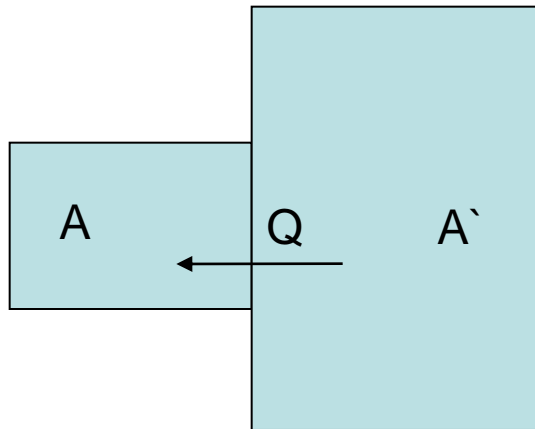
Theorem 1

For a thermally isolated system, the stable equilibrium situation is characterized by the fact that

$$S = \text{maximum}$$

(8.1.2)

3.2 *System in contact with a reservoir at constant temperature*



system A is in contact with the reservoir A' at constant temperature T_0

$$\Delta S^{(0)} = \Delta S + \Delta S' \geq 0$$

$$\Delta S' = \frac{-Q}{T_0}$$

$$\Delta S^{(0)} = \Delta S - \frac{Q}{T_0} = \frac{T_0 \Delta S - (\Delta \bar{E} + W)}{T_0}$$

$$\Delta S^{(0)} = \frac{-\Delta F_0 - W}{T_0} \geq 0$$

where we have introduced the ***Helmholtz free energy***.

$$F = \bar{E} - T_0 S$$

Helmholtz free energy F

$$\Delta S^{(0)} = \frac{-\Delta F_0 - W}{T_0} \geq 0 \quad \longrightarrow \quad -\Delta F_0 \geq W \quad (8.2.5)$$

The maximum work which can be done by a system in contact with a heat reservoir is given by $(-\Delta F_0)$. (That's why F is called "free energy".)

If the external parameters of system A are kept fixed, then $W=0$ and yields the condition

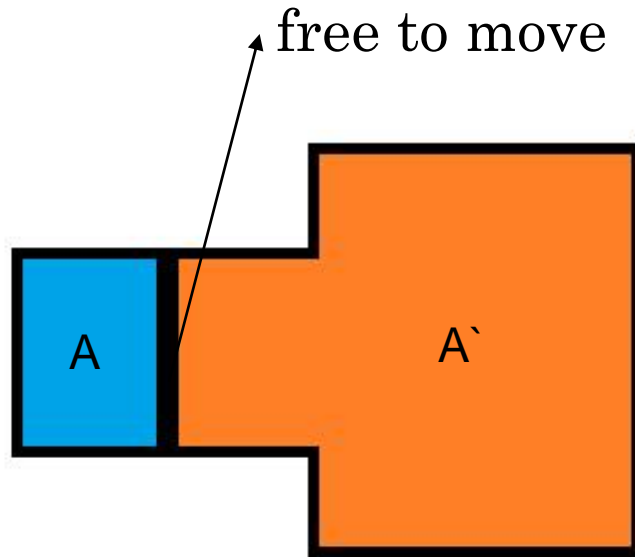
$$\Delta F_0 \leq 0$$

Theorem 2

If a system, whose external parameters are fixed, is in thermal contact with a heat reservoir, the stable equilibrium situation is characterized by the condition that

$$F_0 = \text{minimum} \quad (8.2.7)$$

3.3 *System in contact with a reservoir at constant temperature and pressure*



system A is in contact with the reservoir A' at constant temperature T_0 and pressure p_0

$$\Delta S^{(0)} = \Delta S + \Delta S' \geq 0$$

$$\Delta S' = \frac{-Q}{T_0}$$

$$Q = \Delta \bar{E} + p_0 \Delta V + W^*$$

where W^* denote the work done by A other than $p_0 \Delta V$.

$$\Delta S^{(0)} = \frac{-\Delta G_0 - W^*}{T_0} \geq 0$$

$$G_0 = \bar{E} - T_0 S + p_0 V$$

Gibbs free energy G

$$\Delta S^{(0)} = \frac{-\Delta G_0 - W^*}{T_0} \geq 0 \quad \longrightarrow \quad -\Delta G_0 \geq W^* \quad (8.3.4)$$

If all the external parameters of system A, except its volume, are kept fixed, then $W^*=0$ and yields the condition

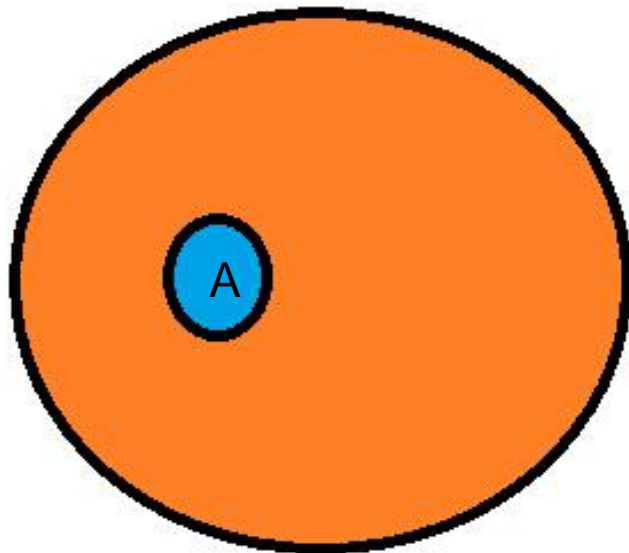
$$\Delta G_0 \leq 0$$

Theorem 3

If a system is in contact with a reservoir at constant temperature and pressure and if its external parameters are fixed so that it can only do the work $p_0\Delta V$, then the stable equilibrium situation is characterized by the condition that

$$G_0 = \text{minimum} \quad (8.3.6)$$

3.4 *Stability conditions for a homogeneous substance*



Let's first consider a one-component system in a single phase. Focus attention on some small, but macroscopic, part A of this system where A consists of some fixed number of particles. The rest of the system is then relatively very large and acts like *a reservoir at some constant temperature T_0 and constant pressure p_0* .

1) Let V and T be the two independent parameters specifying the macrostate of A .

$$\text{then } G_0 = G_0(V, T) = \bar{E} - TS + pV$$

2) By Theorem 3, we know that the condition for equilibrium is

$$G_0 = \text{minimum}$$

which means

$$\left\{ \begin{array}{l} \left(\frac{\partial G_0}{\partial T} \right)_V = 0 \quad \text{for } T = \bar{T} \\ \left(\frac{\partial^2 G_0}{\partial T^2} \right)_V \geq 0 \quad \text{for } T = \bar{T} \end{array} \right. \quad \left\{ \begin{array}{l} \left(\frac{\partial G_0}{\partial V} \right)_T = 0 \\ \left(\frac{\partial^2 G_0}{\partial V^2} \right)_T \geq 0 \end{array} \right.$$

3) First, keep V a constant.

$$G_0 = \bar{E} - T_0 S + p_0 V$$

$$\left(\frac{\partial G_0}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V - T_0 \left(\frac{\partial S}{\partial T}\right)_V = 0$$

$$T dS = d\bar{E} + \bar{p} dV$$

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

$$\left(\frac{\partial G_0}{\partial T}\right)_V = \left(1 - \frac{T_0}{T}\right) \left(\frac{\partial \bar{E}}{\partial T}\right)_V = 0$$

Hence we arrive at the obvious conclusion that a necessary condition for equilibrium is that the temperature of the subsystem A is the same as that of the surrounding medium.

$$\bar{T} = T_0$$

4) Next, let's keep T a constant.

similarly, we can get the condition

$$\left(\frac{\partial G_0}{\partial V}\right)_T = -\bar{p} + p_0 = 0 \quad \longrightarrow \quad \bar{p} = p_0$$

5) *Isothermal compressibility*

$$\left(\frac{\partial G_0}{\partial V}\right)_T = -\bar{p} + p_0$$

$$\left(\frac{\partial^2 G_0}{\partial V^2}\right)_T = -\left(\frac{\partial \bar{p}}{\partial V}\right)_T \geq 0$$

This is a physically quite reasonable result consistent with ***Le Chatelier's principle***.

We define the ***isothermal compressibility***

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \geq 0$$

In physics, compressibility is a measure of the relative volume change of a fluid or solid as a response to a pressure (or mean stress) change.

6) *Density fluctuations*

Let $\varphi(V)dV$ denote the probability that the volume of A lies between V and $V+dV$.

$$\varphi(V)dV \propto e^{-G_0(V)/KT} dV$$

When $\Delta V = V - \bar{V}$ is small, we can get

$$G_0(V) = G_{\min} - \frac{1}{2} \left(\frac{\partial \bar{p}}{\partial V} \right)_T (\Delta V)^2 = G_{\min} + \frac{(\Delta V)^2}{2\bar{V}\kappa}$$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

$$\varphi(V)dV = B \exp\left[-\frac{(V - \bar{V})^2}{2KT_0\bar{V}\kappa}\right] dV$$

The probability is simply a ***Gaussian distribution***, so we can get

$$\overline{(\Delta V)^2} = \overline{(V - \bar{V})^2} = KT_0\bar{V}\kappa$$

The density of A is $n = N / V$, then $\Delta n = -(N/\bar{V}^2)\Delta V = -(\bar{n} / \bar{V})\Delta V$

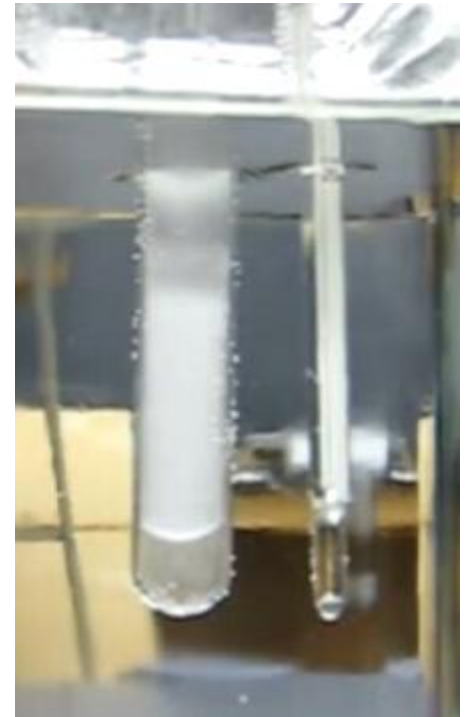
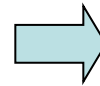
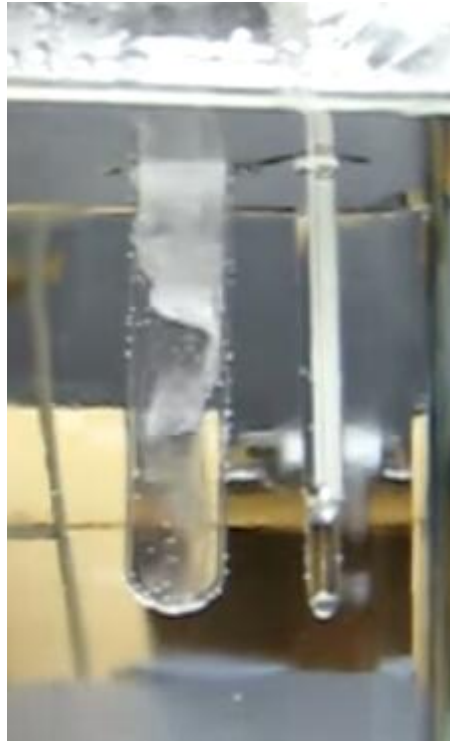
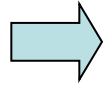
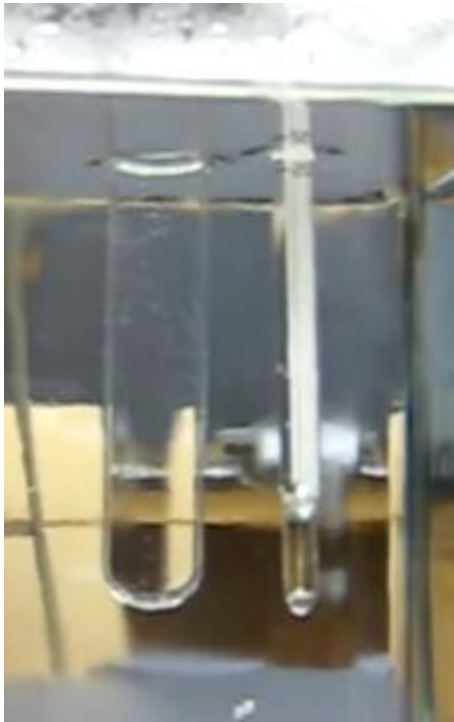
$$\longrightarrow \overline{(\Delta n)^2} = \left(\frac{\bar{n}}{\bar{V}}\right)^2 \overline{(\Delta V)^2} = \bar{n}^2 \left(\frac{KT_0}{\bar{V}} \kappa\right)$$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$

An interesting case arises when $\left(\frac{\partial \bar{p}}{\partial V}\right)_T \rightarrow 0$, then $K \rightarrow \infty$ and the ***density fluctuations*** become very large.

We define the temperature and pressure as the "***critical point***" of a substance where $(\partial \bar{p} / \partial V) = 0$.

The very large density fluctuations at this point lead to a very large ***scattering of light***. As a result the substance, which is ordinarily transparent, will assume a milky white appearance at its critical point. This impressive phenomenon is known as "***critical point opalescence***".



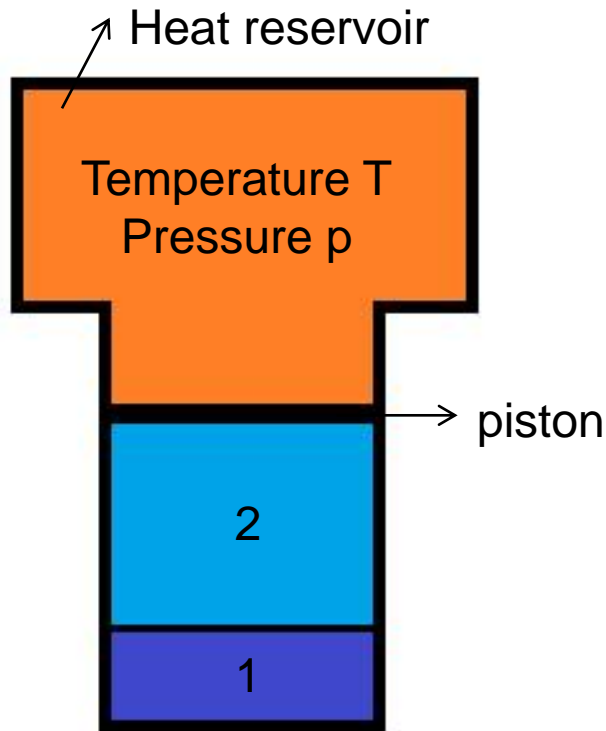
Change the temperature and the substance will get the ***critical point opalescence*** at the critical point (p,T), where $(\partial \bar{p} / \partial V) = 0$.

4. Equilibrium between Phases

4.1 Equilibrium conditions and the *Clausius-Clapeyron equation*

4.2 Phase transformations and the equations of state

4.1 *Equilibrium conditions and the Clausius-Clapeyron equation*



System A consists of two phases of a single component 1 and 2. It is in equilibrium with a reservoir at the constant temperature T and constant pressure p .

Then by theorem 3, the equilibrium condition is that the Gibbs free energy G of the system is a minimum.

$$G = E - TS + pV = \text{minimum}$$

Let

ν_i = the number of moles of phase i present in the system
 $g_i(T, p)$ = the Gibbs free energy per mole of phase i at this temperature T and pressure p

Then G can be written

$$G = \nu_1 g_1 + \nu_2 g_2$$

The conservation of matter implies that

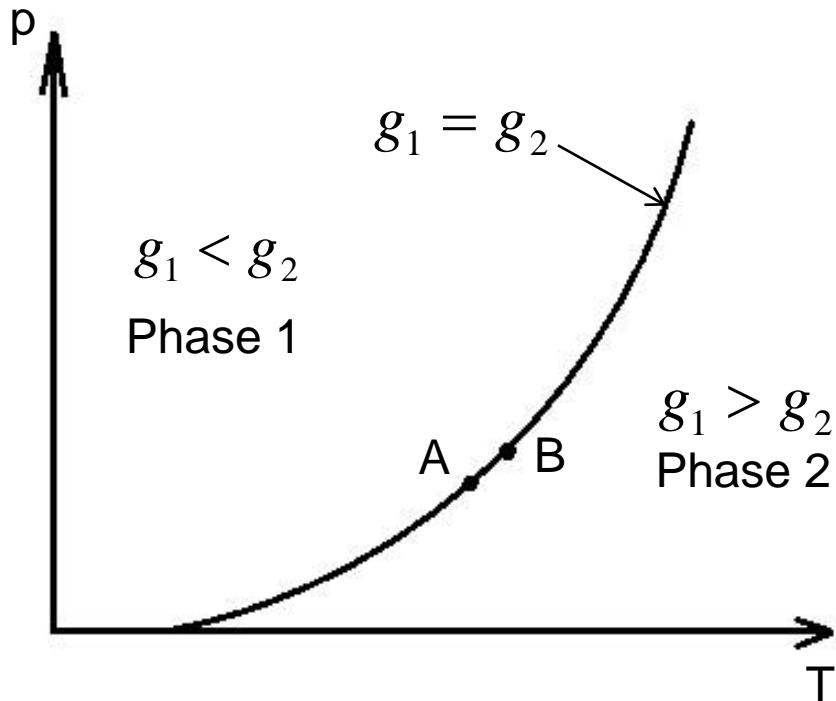
$$\nu_1 + \nu_2 = \nu = \text{constant}$$

Equilibrium requires that G be stationary for changes in ν_1 :
thus $dG = g_1 d\nu_1 + g_2 d\nu_2 = (g_1 - g_2) d\nu_1 = 0$

Hence we obtain as ***a necessary condition for equilibrium*** that

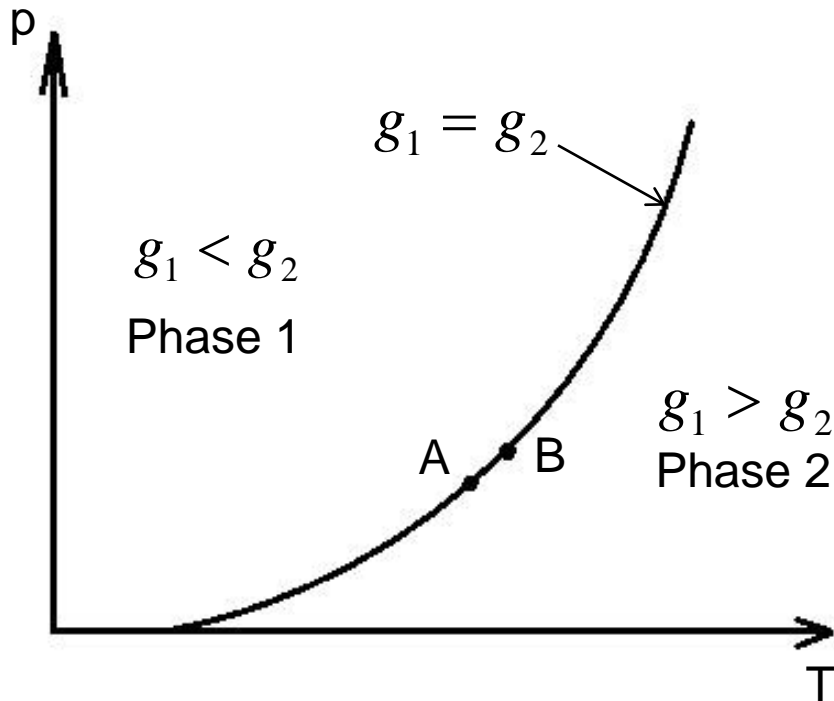
$$g_1 = g_2 \quad (8.5.4)$$

Phase-equilibrium line



Along the phase-equilibrium line, $g_1 = g_2$ and the two phases can coexist in equilibrium. This line divides the p - T plane into two regions: one where $g_1 < g_2$, so the phase 1 is the stable one and the other where $g_1 > g_2$, so the phase 2 is the stable one.

Clausius-Clapeyron equation



Consider point A, we have:

$$g_1(T, p) = g_2(T, p)$$

Consider now a neighboring point, such as B:

$$g_1(T + dT, p + dp) = g_2(T + dT, p + dp)$$

$$\longrightarrow dg_1 = dg_2$$

where

$$dg_i = \left(\frac{\partial g_i}{\partial T}\right)_p dT + \left(\frac{\partial g_i}{\partial p}\right)_T dp$$

By using *the fundamental thermodynamic relation*

$$d\varepsilon = Tds - pdv$$

Hence $dg = d(\varepsilon - Ts + pv) = -sdT + vdp$

$$-s_1 dT + v_1 dp = -s_2 dT + v_2 dp$$

Then we can get the *Clausius-Clapeyron equation*

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v}$$

This equation relates the slope of the *phase-equilibrium line* at this point to the entropy change Δs and volume change Δv of the substance in “crossing the line” at this point, i.e., in undergoing a change of phase at this temperature and pressure.

vapor pressure

We define the “***latent heat of transformation***” L_{12} as the heat absorbed when a given amount of phase 1 is transformed to phase 2.

Then we have
$$\frac{dp}{dT} = \frac{l}{T\Delta v}$$

Let 1 refer to liquid (or solid) phase and 2 to the vapor.

Then

$$\Delta v = v_2 - v_1 \approx v_2$$

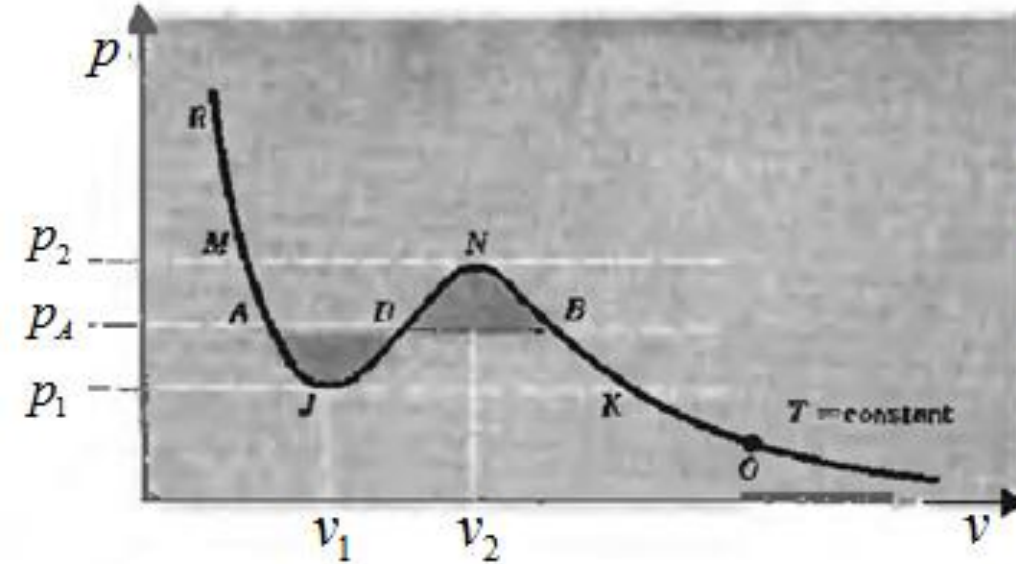
Let us assume that the vapor can be adequately treated as an ideal gas, so its ***equation of state*** is simply

$$pv_2 = RT$$

Then $\Delta v = RT / p \quad \Rightarrow \quad \frac{1}{p} \frac{dp}{dT} = \frac{l}{RT^2} \quad \Rightarrow \quad p = p_0 e^{-l/RT}$

This shows that the vapor pressure p is a very rapidly increasing function of T , the temperature dependence being determined by the magnitude of the ***latent heat of vaporization***.

4.2 Phase transformation and the equation of state



Consider a single-component system. For a constant temperature T, the diagram of van der Waals equation is shown on the left.

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

(1) if the pressure is sufficiently low that $p < p_1$, the curve yields, correspondingly, a unique value of v . There exists a well-defined single phase. Here the slope of the curve $\partial p / \partial v \leq 0$ as is necessary by the **stability condition**. Also, $|\partial p / \partial v|$ is relatively small, so that the **compressibility** of this phase is relatively large, as would be the case for a **gas phase**.

5) *Isothermal compressibility*

$$\left(\frac{\partial G_0}{\partial V}\right)_T = -\bar{p} + p_0$$

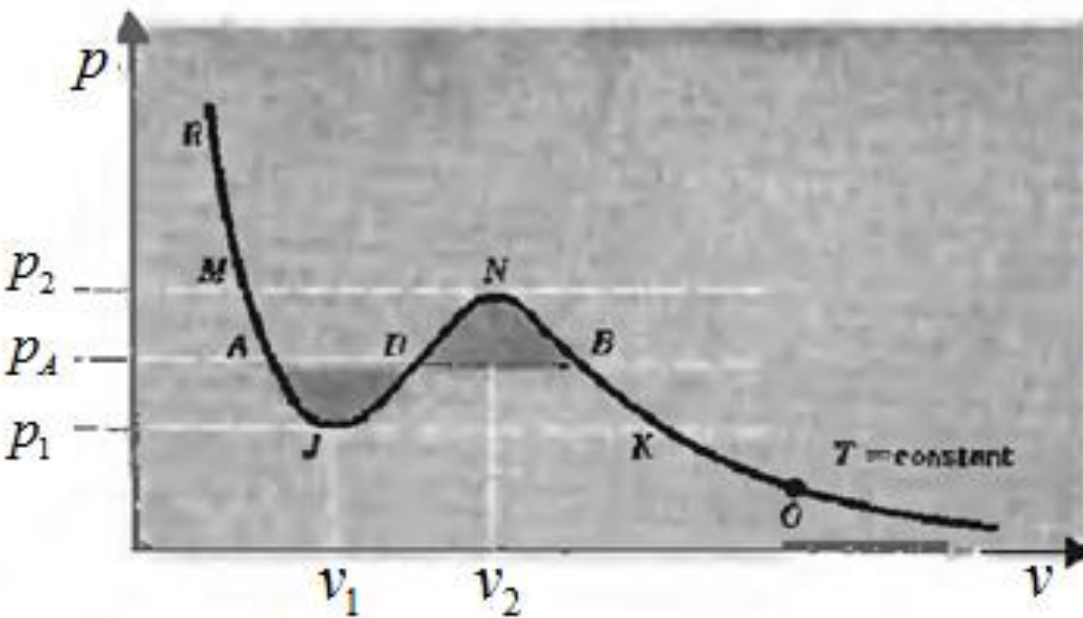
$$\left(\frac{\partial^2 G_0}{\partial V^2}\right)_T = -\left(\frac{\partial \bar{p}}{\partial V}\right)_T \geq 0$$

This is a physically quite reasonable result consistent with *Le Chatelier's principle*.

We define the *isothermal compressibility*

$$k = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \geq 0$$

In physics, compressibility is a measure of the relative volume change of a fluid or solid as a response to a pressure (or mean stress) change.



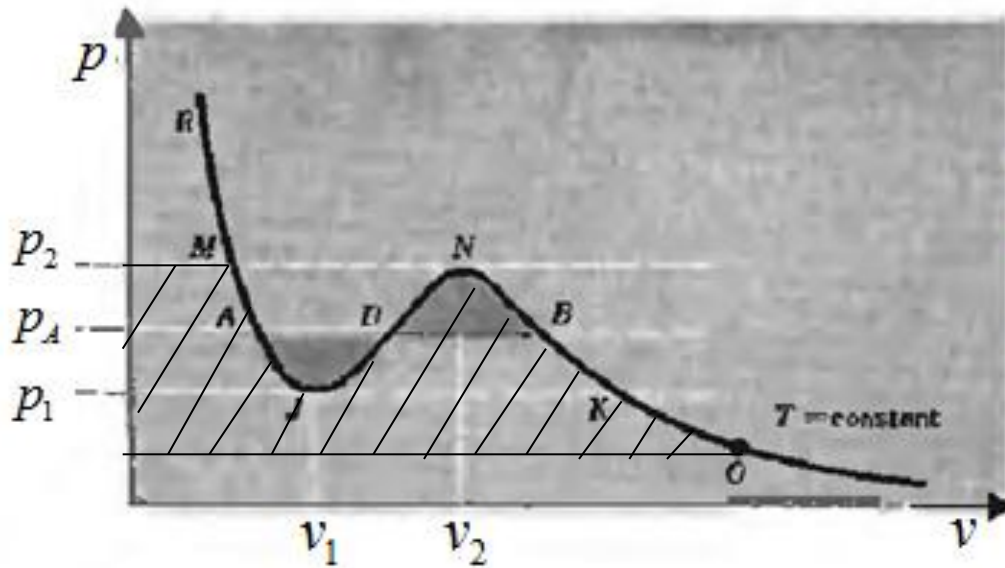
(2) if the pressure is sufficiently high that $p > p_2$. There exists again a single phase with a unique value of v . The stability condition $\partial p / \partial v \leq 0$ is again satisfied, but $|\partial p / \partial v|$ is relatively large. Hence the **compressibility** of this phase is relatively small, as would be the case for a **liquid phase**.

(3) Now consider the intermediate pressure range $p_1 < p < p_2$.

There are now, for each pressure p , three possible values of volume v . It's obvious that v_D violates **the stability condition** $\partial p / \partial v \leq 0$. Hence we have to decide whether v_A or v_B is more stable, which needs us to compare the **molar-free energies** g_A and g_B .

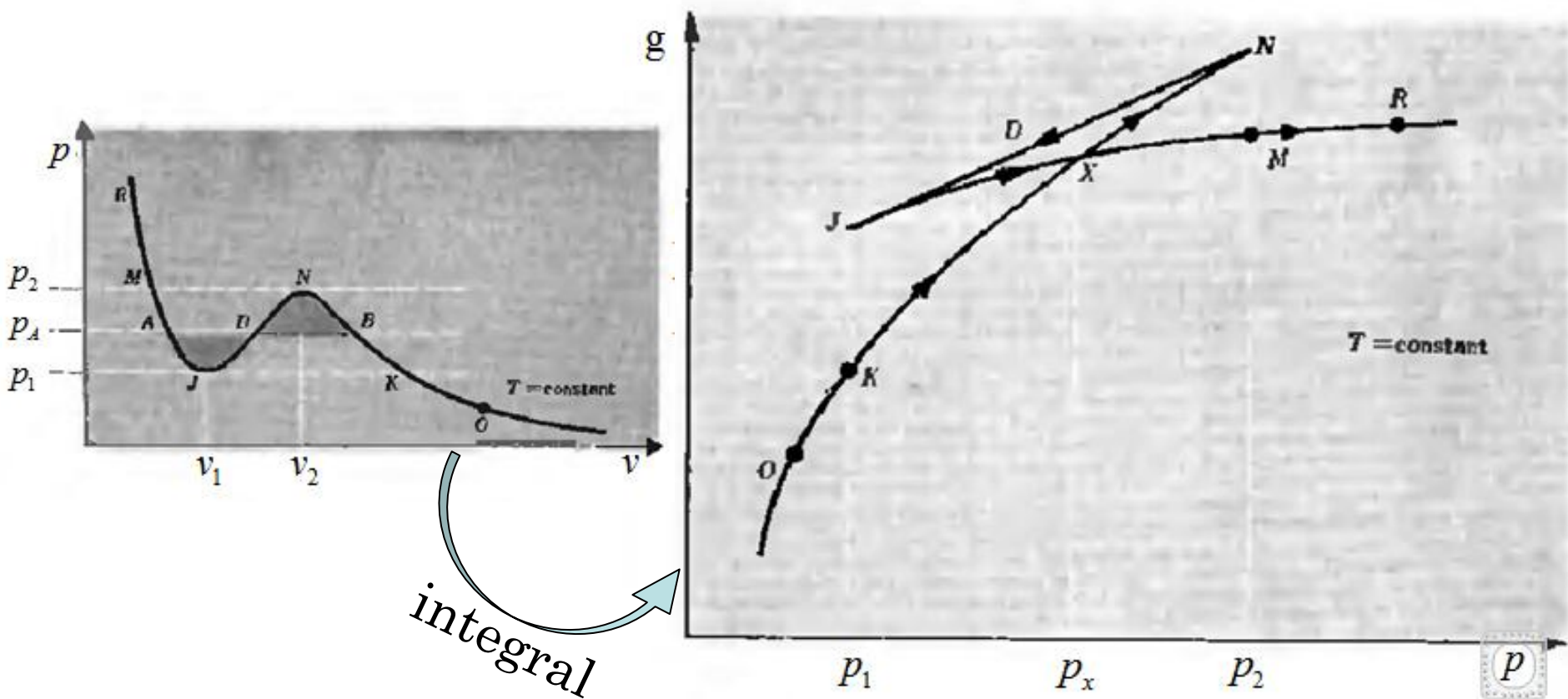
T is a constant here.

$$\begin{cases} g = \varepsilon - Ts + pv \\ Tds = d\varepsilon + pdv \end{cases} \longrightarrow dg = d(\varepsilon - Ts + pv) = vdp$$



$$g - g_0 = \int_{p_0}^p v dp$$

If we perform the integral from point O along the curve to Point M, we will get the shaded area on the left.

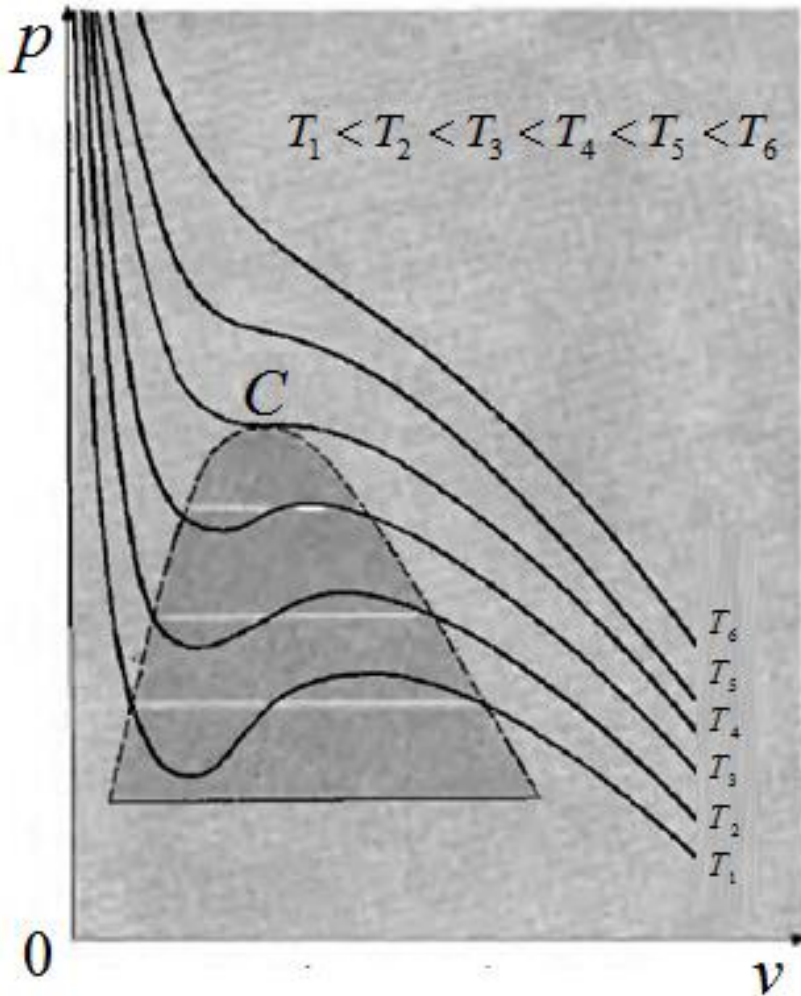


At point X the free energies g of both phases become equal. This p_X then is the pressure where both these phases can **coexist** and where the **phase transformation** occurs.

OKXN $\longrightarrow v > v_2$

NDJ $\longrightarrow v_1 < v < v_2$

JXMR $\longrightarrow v < v_1$

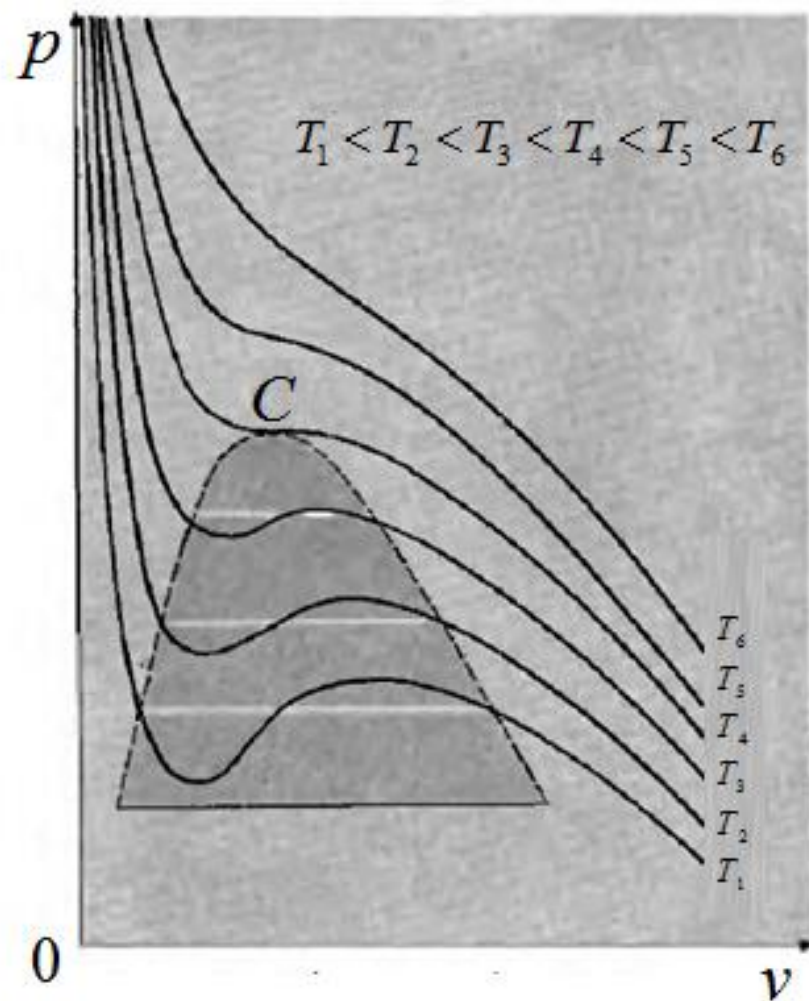


As one goes to higher temperature the two extremum points where $(\partial p / \partial v)_T = 0$ move closer, which implies that the volume change Δv in the phase transformation decreases.

As the temperature is increased further, the two extremum points coincide and the ***phase transformation*** has barely disappeared. (Critical point C)

Since $(\partial p / \partial v)_T = 0$ at the critical point C, it follows from our previous discussion that the density fluctuations become very large, i.e., the substance “cannot quite make up its mind” whether to be a liquid or a gas.

At still higher temperature $(\partial p / \partial v)_T < 0$ everywhere so there is no phase transformation. There is only a single ***fluid phase*** from ***high compressibility*** to ***low compressibility*** as the pressure increases.



5. Systems with several components; chemical equilibrium

5.1 General relations for a system with several components

5.2 General conditions for *chemical equilibrium*

5.3 Chemical equilibrium between ideal gases

5.1 *General relations for a system with several components*

Consider a homogeneous system, of energy E and of volume V , which consists of m different kinds of molecules.

$$S = S(E, V, N_1, N_2, \dots, N_m)$$

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \sum_{i=1}^m \left(\frac{\partial S}{\partial N_i}\right)_{E,V,N} dN_i$$

When all the numbers N are kept fixed, the ***fundamental thermodynamic relation*** asserts that

$$dS = \frac{dQ}{T} = \frac{dE + pdV}{T}$$

Compare the coefficients then we have

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} \quad \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{p}{T}$$

Let us introduce the “*chemical potential per molecule*”

$$\mu_i \equiv -T \left(\frac{\partial S}{\partial N_i} \right)_{E,V,N}$$

Then we have

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \sum \frac{\mu_i}{T} dN_i$$

$$dE = TdS - pdV + \sum_{i=1}^m \mu_i dN_i$$

Hence we have

$$\mu_i = \left(\frac{\partial E}{\partial N_i} \right)_{S,V,N} = \left(\frac{\partial F}{\partial N_i} \right)_{T,V,N} = \left(\frac{\partial G}{\partial N_i} \right)_{T,p,N}$$

$(F = E - TS, G = E - TS + pV)$

Hence we can conclude that *the chemical potential per molecule* is just equal to *the Gibbs free energy per molecule*.

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T,p,N} = g'(T, p)$$

5.2 *General conditions for chemical equilibrium*

A system consists of H_2 , O_2 and H_2O molecules in the gas phase.

We change the reaction $2H_2 + O_2 \rightarrow 2H_2O$
into the standard form $-2H_2 - O_2 + 2H_2O = 0$

We use B_1, B_2, \dots, B_m to represent the chemical symbols and let b_i denote the coefficient of B_i .

Then a general chemical equation can be written in the form

$$\sum_{i=1}^m b_i B_i = 0$$

Under the assumed conditions of constant V and E

$$dS = \sum_{i=1}^m \mu_i dN_i = 0 \quad \left(dS = \frac{1}{T} dE + \frac{p}{T} dV - \sum \frac{\mu_i}{T} dN_i \right)$$

The changes in the numbers N_i should be

$$dN_i = \lambda b_i$$

where λ is a constant of proportionality.

$$\text{Hence } dS = \sum_{i=1}^m \mu_i dN_i = \sum_{i=1}^m b_i \mu_i = 0 \quad (8.9.7)$$

This is ***the general condition for chemical equilibrium.***

5.3 *Chemical equilibrium between ideal gases*

5.3.1 *The relationship between the mean numbers of the reacting molecules*

In equilibrium

$$F = F(T, V, N_1, \dots, N_m)$$

$$\Delta F = \sum_i \left(\frac{\partial F}{\partial N_i} \right)_{T,V,N} b_i = \sum_i \mu_i b_i = 0$$

The partition function is

$$Z = \sum_{s_1, s_2, \dots} \exp[-\beta(\varepsilon_1(s_1) + \varepsilon_2(s_2) + \dots)]$$

$$Z = \left(\sum_{s_1} \exp[-\beta \varepsilon_1(s_1)] \right) \left(\sum_{s_2} \exp[-\beta \varepsilon_2(s_2)] \right) \dots$$

Where the possible states of the k th molecule is labeled by s_k and the energy of the molecule in this state is denoted by $\varepsilon_k(s_k)$.

$$Z = \left(\sum_{s_1} \exp[-\beta \varepsilon_1(s_1)] \right) \left(\sum_{s_2} \exp[-\beta \varepsilon_2(s_2)] \right) \dots$$

In this product there will be N_i equal factors for all molecules of type i , each of these factors being equal to

$$\xi_i \equiv \sum_s \exp[-\beta \varepsilon_i(s)]$$

Thus

$$Z = \xi_1^{N_1} \xi_2^{N_2} \dots \xi_m^{N_m}$$

But this is inconsistent with ***the essential indistinguishability*** of the molecules in quantum mechanics to count these gas states as distinct. Therefore the equation must be divided by the $(N_1! N_2! \dots N_m!)$ possible permutations of like molecules among themselves. Thus we get

$$Z = \frac{\xi_1^{N_1} \xi_2^{N_2} \dots \xi_m^{N_m}}{N_1! N_2! \dots N_m!} \quad (8.10.7)$$

This can also be written

$$Z = Z_1 Z_2 \dots Z_m$$

Where

$$Z_i = \frac{\xi_i^{N_i}}{N_i!}$$

is the partition function of a gas of Ni molecules occupying the given volume V by itself in the absence of all other gases.

From this, we can get a variety of important results.

$$\bar{E} = (-\partial \ln Z / \partial \beta)$$

$$F = -kT \ln Z$$

$$\bar{p} = \beta^{-1} (\partial \ln Z / \partial V)$$



$$\bar{E}(T, V) = \sum_i \bar{E}_i(T, V)$$

$$F(T, V) = \sum_i F_i(T, V)$$

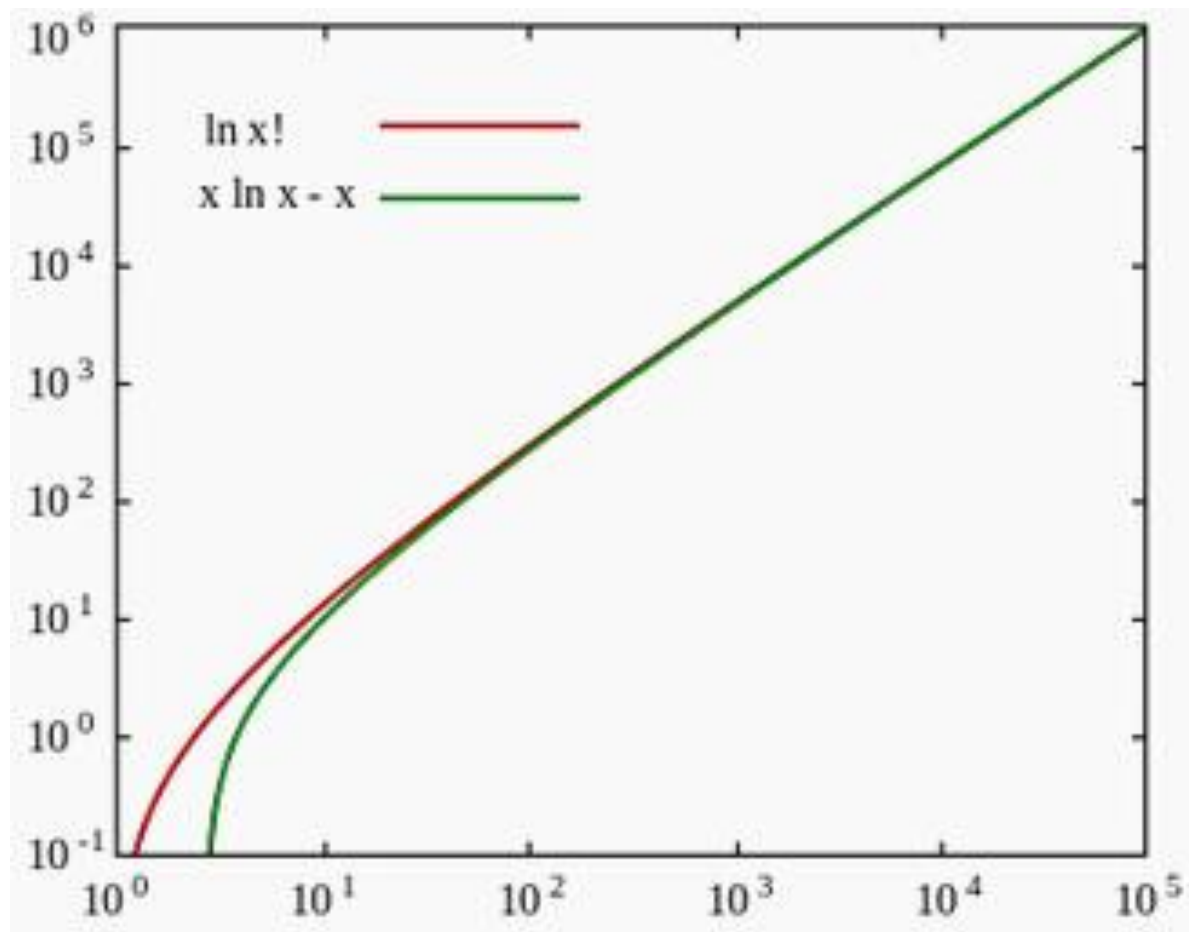
$$\bar{p} = \sum_i \bar{p}_i$$

Where \bar{p}_i is the “***partial pressure*** of the ith gas”.

$$Z_i = \frac{\xi_i^{N_i}}{N_i!} \quad \longrightarrow \quad \ln Z_i = N_i \ln \xi_i - \ln N_i!$$

$$F = -kT \ln Z = -kT \sum_i N_i (\ln \xi_i - \ln N_i + 1)$$

Where we have used *Stirling's formula* $\ln N! = N \ln N - N$.



$$(F = -kT \ln Z = -kT \sum_i N_i (\ln \xi_i - \ln N_i + 1))$$

The ***chemical potential*** of the jth kind of molecules is simply given by

$$\mu_j = \left(\frac{\partial F}{\partial N_j} \right)_{T,V,N} = -kT (\ln \xi_j - \ln N_j)$$

$$\text{Then } \Delta F = -kT \sum_i b_i (\ln \xi_i - \ln N_i) = \Delta F_0 + kT \sum_i b_i \ln N_i = 0$$

$$(\Delta F = \sum_i \left(\frac{\partial F}{\partial N_i} \right)_{T,V,N} b_i = \sum_i \mu_i b_i)$$

$$\text{where } \Delta F_0 = -kT \sum_i b_i \ln \xi_i$$

$$(\xi_i \equiv \sum_s \exp[-\beta \varepsilon_i(s)])$$

is a quantity (the so-called “***standard free-energy change of the reaction***”) which depends on T and V, but not on the numbers N_i of molecules.

$$\Delta F = -kT \sum_i b_i (\ln \xi_i - \ln N_i) = \Delta F_0 + kT \sum_i b_i \ln N_i = 0$$



$$\sum_i \ln N_i^{b_i} = -\frac{\Delta F_0}{kT}$$



$$N_1^{b_1} N_2^{b_2} \dots N_m^{b_m} = K_N(T, V)$$

(8.10.21)

Where $K_N(T, V) = \exp[-\Delta F_0 / kT] = \xi_1^{b_1} \xi_2^{b_2} \dots \xi_m^{b_m}$

is independent of the numbers of molecules present and is called the “***equilibrium constant***”.

$N_1^{b_1} N_2^{b_2} \dots N_m^{b_m} = K_N(T, V)$ is the explicit relation between the mean numbers of molecules present in equilibrium. And this equation is called the “***law of mass action***”.

5.3.2 *Temperature dependence of the equilibrium constant*

$$\ln K_N(T, V) = -\frac{\Delta F_0}{kT}$$

$$\left(\frac{\partial \ln K_N}{\partial T}\right)_V = -\left(\frac{\partial}{\partial T}\right)_V \left(\frac{\Delta F_0}{kT}\right) = -\left(\frac{\partial}{\partial T}\right)_{V,N} \frac{\Delta F}{kT}$$

$$(\Delta F = \Delta F_0 + kT \sum_i b_i \ln N_i)$$

$$\left(\frac{\partial \ln K_N}{\partial T}\right)_V = \frac{\Delta F}{kT^2} - \frac{1}{kT} \left(\frac{\partial \Delta F}{\partial T}\right)_{V,N}$$

$$\text{But } -\left(\frac{\partial}{\partial T}\right) \Delta F = -\sum_i \left(\frac{\partial}{\partial T}\right) \left(\frac{\partial F}{\partial N_i}\right) b_i = -\sum_i \left(\frac{\partial}{\partial N_i}\right) \left(\frac{\partial F}{\partial T}\right) b_i = \sum_i \frac{\partial S}{\partial N_i} b_i = \Delta S$$

$$(F = E - TS)$$

ΔS denotes the entropy change of the reaction when $|b_i|$ of each of the reactant molecules are transformed into b_i of each of the product molecules.

$$\left(\frac{\partial \ln K_N}{\partial T}\right)_V = \frac{\Delta F}{kT^2} - \frac{1}{kT} \left(\frac{\partial \Delta F}{\partial T}\right)_{V,N}$$

$$-\left(\frac{\partial}{\partial T}\right)\Delta F = -\sum_i \left(\frac{\partial}{\partial T}\right)\left(\frac{\partial F}{\partial N_i}\right)b_i = -\sum_i \left(\frac{\partial}{\partial N_i}\right)\left(\frac{\partial F}{\partial T}\right)b_i = \sum_i \frac{\partial S}{\partial N_i} b_i = \Delta S$$

$$\longrightarrow \left(\frac{\partial \ln K_N}{\partial T}\right)_V = \frac{1}{kT^2} (\Delta F + T\Delta S) = \frac{\Delta E}{kT^2}$$

$$\longrightarrow \boxed{\frac{d \ln K_n}{dT} = \frac{\Delta E}{kT^2}}$$

If $\Delta E > 0$, this equation asserts that K_n increases as T is increased. This result is again in accord with what would be expected from ***Le Chatelier's principle***.

$$\frac{d \ln K_n}{dT} = \frac{\Delta E}{kT^2}$$



When $\Delta E > 0$, heat is absorbed as a result of the reaction.

If the temperature T increases, more molecules must then be produced in order to absorb heat and thus to restore the original temperature. Thus K_n must increase.

The background of the slide features four overlapping circles, each with a radial line extending from its center towards the corners of the frame. The circles are light blue and the radial lines are a slightly darker shade of blue, creating a subtle pattern against the dark blue background.

Questions?

Thanks for your attention!