Fundamental equations of Thermodynamics

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(1) The combined first and second law

From the first law: $dU = dq + dW$

From the second law: $dS \geq \frac{dq}{T}$

Where, $dS > \frac{dq}{T}$ for irreversible system

and, $dS = \frac{dq}{T}$ for reversible system

For a closed system in which only reversible pV work is involved

$dW = -pdV$ and $dS = \frac{dq}{T}$

$\therefore dU = TdS - pdV$ **Fundamental equation**

The internal energy is a function of S and V

Where U, T, S, P, and V are state functions

$$\therefore dU = TdS - pdV$$

The differential of U

$$\therefore dU = \left(\frac{dU}{dS}\right)_V dS + \left(\frac{dU}{dV}\right)_S dV$$

Thus, we can calculate T and p as

$$\therefore T = \left(\frac{dU}{dS}\right)_V \quad \text{and} \quad p = -\left(\frac{dU}{dV}\right)_S$$

S and V are natural variables of U represented as U(S,V)

The enthalpy was defined by: $H = U + pV$

by differential: $dH = dU + pdV + Vdp$

and $dU = TdS - pdV$

$$\therefore dH = TdS - pdV + pdV + Vdp$$

$$\therefore dH = TdS + Vdp$$

The natural variables of H are S and p represented as H(S,p)

The last equation is the fundamental equation for H and for a closed system in which only pV work, and since H is a state function:

$$\therefore T = \left(\frac{dH}{dS}\right)_p \quad \text{and} \quad V = \left(\frac{dH}{dp}\right)_S$$

U and H provide criteria for whether a process can occur spontaneously in a system when the corresponding natural variables are held constant.

From: $$dS \geq \frac{dq}{T}, dW = -p_{ext}dV$$

And substitute in : $$dU = dq + dW$$

We obtain: $$\therefore dU \leq TdS - p_{ext}dV$$

At infinitesimal change (rev.) with constant S and V $$\therefore (dU)_{S,V} \leq 0$$

"A change in a process can occur spontaneously if the internal energy decreases when the change occurs at constant entropy and volume"

The meaning:

dU = zero	equilibrium
dU < zero	spontaneous
dU > zero	non-spontaneous

At constant S and p $$\therefore (dH)_{S,p} \leq 0$$

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Helmholtz Energy (A)

It is defined by: $A = U - TS$

By differentiating: $dA = dU - TdS - SdT$

But $\therefore dU = TdS - pdV$

$$\therefore dA = -SdT - pdV$$

T and V are the natural variables of A

If an infinitesimal change takes place in a system of constant T and V, thus:

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

For irreversible process, A decrease.

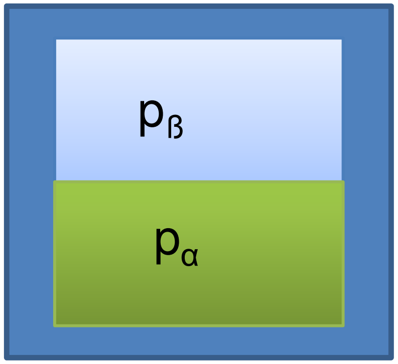
For reversible process, A is constant.

It is more practical to use the criterion $(dA)_{t,V} \leq 0$

The Helmholtz energy can be used to show that the pressures of two phases must be equal at equilibrium

For two-phase system in a container of fixed volume surrounded by a heat reservoir

Suppose that the volume of phase α is increased by dV
and the volume of phase ß is decreased by dV.



So, the total volume is constant

When the system at equilibrium $\therefore dA = -SdT - pdV$

$$\mathbf{dA = 0 = dA_{\alpha} + dA_{ß}}$$

$$\mathbf{-p_{\alpha}dV + p_{ß}\,dV = 0}$$

$$\mathbf{p_{\alpha} = p_{ß}}$$

The Gibbs Energy (G)

It provides a more convenient thermodynamic property than the entropy for applications of the second law at constant T and p.

Example: for an isolated system consisting of system and surrounding at constant T and p

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$ must increase for a spontaneous process

but $$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T}$$ at constant T

So that

$$\Delta S_{sys} - \frac{\Delta H_{sys}}{T} = -\frac{\Delta G_{sys}}{T}$$ Must increase

Or ΔG_{sys} must decrease

This means that it is not required for specification what is happening in the surrounding

The Helmholtz Energy $\mathbf{A \equiv U - TS}$ convenient for a constant V path

The Gibbs Energy $\mathbf{G \equiv H - TS}$ convenient for a constant p path

The differentials of A and G can be written

$dA \equiv dU - TdS - SdT$ $\mathbf{dG \equiv dH - TdS - SdT}$

If the temperature is held constant for the process the result is

$dA \equiv dU - TdS$ $\mathbf{dG \equiv dH - TdS}$

The RHS of these expressions is exactly what was derived for the two new criteria. Thus

constant T, V

$dA_{T,V} \leq 0$

constant T, p

$\mathbf{dG_{T,p} \leq 0}$

Thus for a spontaneous process at constant T and p the Gibbs energy must decrease. If the process is at equilibrium then dG = 0.

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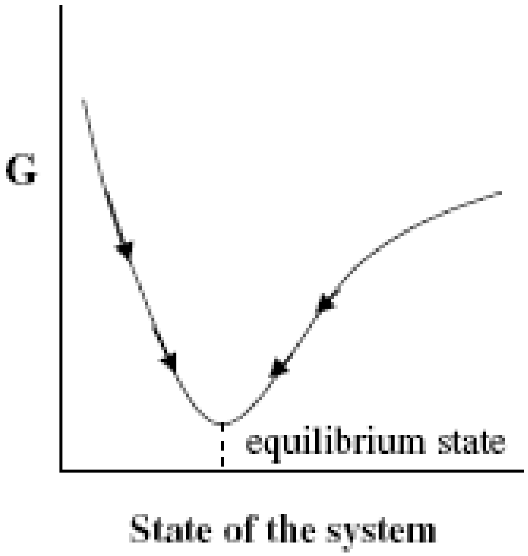
This criteria is the most important developed so far because it leads to all future analyses of spontaneous and equilibrium processes such as equilibrium constants, electrode potentials and the Nernst equation, gas, liquid and solid equilibria, solution processes, etc. etc.

While there are now two separate conditions for the two different paths we will **focus almost exclusively on the Gibbs Energy since the constant pressure path is so much more convenient** to establish experimentally. We only need to do it in the open under constant atmospheric pressure. Thus we will have tables of values for ΔG rather than ΔA. Recall that this is exactly the same reason why we focus on H and not U and why there are tables of ΔH and not ΔU.

Thus to determine if a constant T, p process will be spontaneous we only need to find whether the change in one state function dG is negative i.e. that the state function G decreases.

How does G behave overall as the state of a system changes?

Since the new criteria for spontaneous change is that G must decrease, we can sketch how it must behave as a system changes spontaneously. From the plot we can see that the system naturally tends to roll down a Gibbs energy hill until it reaches the lowest point. The system is then at equilibrium. We can see that a system tends to stay in a state **G** of equilibrium because it must climb a Gibbs energy hill to get out. Thus the reason for change, the lowering of the Gibbs free energy can be viewed as a **"driving force" or a tendency for change. The steeper** the hill the greater the tendency for the system to change.



The **Gibbs (free) energy driving force is relatively simple in that it is made up of two** recognizable factors, the enthalpy and entropy. It is useful in analyzing how each of these factors separately behaves when a change occurs i.e. the Gibbs energy changes.

$$G = H - TS$$

In general, any process in which the enthalpy (or energy) decreases is favorable to a decrease in G and any process in which the entropy goes up is also favorable to a decrease in G.

In other words, systems, like most people, seek a position of minimum energy and maximum disorder.

This leads to minimum Gibbs energy and a state from which a system is reluctant to move.

Thus the Gibbs energy, enthalpy (energy) and entropy are the three main properties to keep uppermost in mind when thinking about a change of state.

Maximum Useful Work

We can show that for a constant temperature and pressure process, a finite change in the Gibbs energy ΔG is of great physical significance because it is identical to the maximum work that we can extract out of a system. This would be very useful in calculating the efficiency of a process and would set an upper limit as to the maximum useful work available. This has wide applications in assessing the efficiency of processes and reactions.

$H = U + pV$ **and** $G = H - TS$

For a constant T and p process $dT = 0$ and $dp = 0$ and thus

$dH = dU + pdV$ $\quad dG = dH - TdS = dU + pdV - TdS$

Also $dU = dq_{rev} + dw_{rev}$ **and** $TdS = dq_{rev}$.

Substituting for dU and TdS

$$dG = dq_{rev} + dw_{rev} + pdV - TdS = dw_{rev} + pdV$$

Let $dw_{rev} = pdV + dw_{e,max}$

Where $dw_{e,max}$ represents all other types of possible work e.g. electrical

$$dw_{rev} = - pdV + dw_{e,max} \longrightarrow dG = dw_{e,max}$$

When a process is carried out in the open under constant atmospheric pressure, pV work is done by the system against atmospheric pressure [e.g. in expanding the volume of the system] and this work is wasted because it is not controlled.

Thus any useful work done by the system is above and beyond this pV work and is given by the change in the Gibbs energy.

For example in some electrochemical cells gases are evolved which expand against the atmosphere to do pV work which is not used.

It is only the electrical energy generated, $dwe_{,max}$ equal to dG which is utilized.

Thus the maximum useful net work that we can get from any constant T and p process is

$$\boxed{\Delta G = w_{e,max} = \Delta H - T\,\Delta S}$$

ANALYSIS OF ΔG IN TERMS OF ΔH AND ΔS

For useful work to be done, w, ΔG and (almost always) ΔH must be negative.

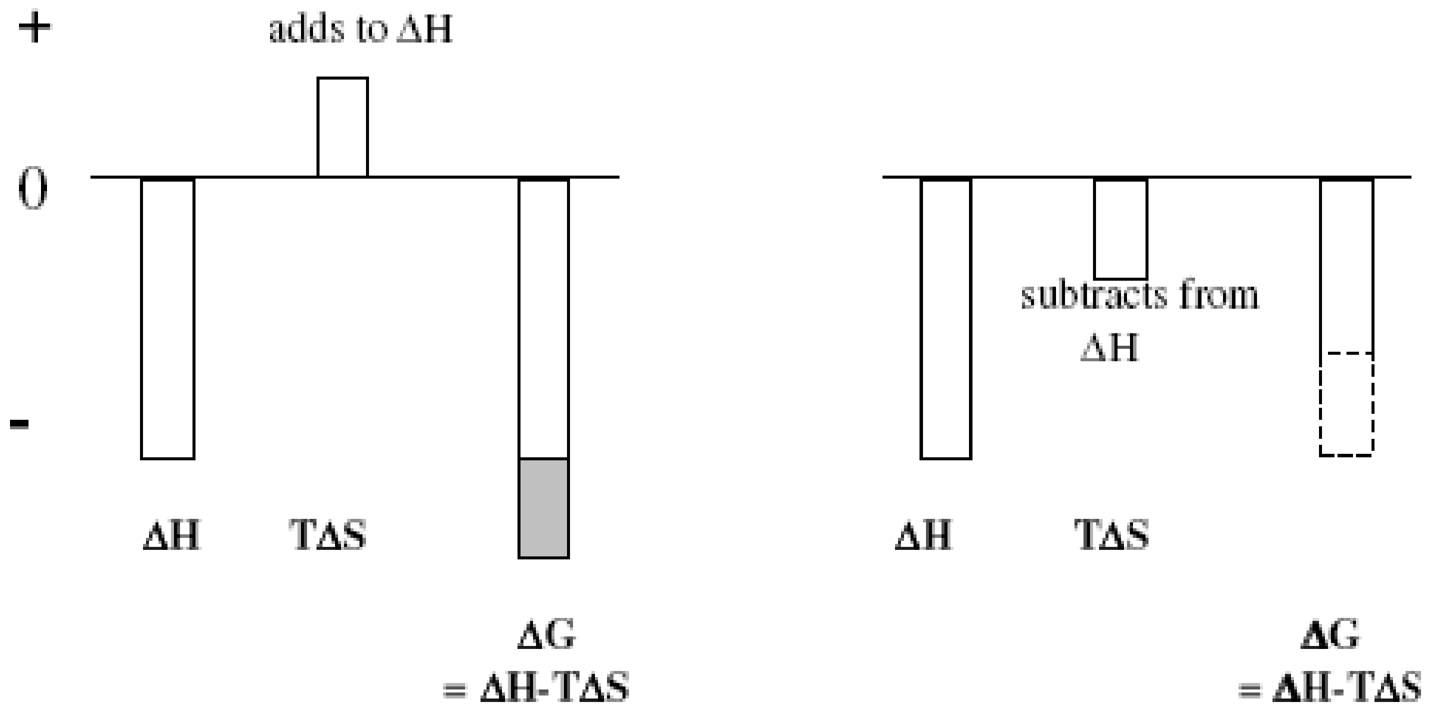
If the entropy term TΔS is positive [then - TΔS will be negative] it makes ΔG more negative than just ΔH and so increases the work done for us.

In this case $T\Delta S = q_{rev} > 0$ i.e. heat is transferred from the surrounding to the system to help fuel the work.

In the reverse case where the system entropy decreases $T\Delta S < 0$ [$-T\Delta S$ is positive and ΔG is not as negative as ΔH] heat must flow from the system to the surroundings and so all of the ΔH is not available to do work..

The heat flowing to the surroundings increases the entropy of the surroundings sufficiently so that the process **remains** spontaneous.

Thus part of the energy of the system has to be sacrificed in order to maintain spontaneity.



For	$\Delta S = 0$	maximum net work ΔG	equal to	$\lvert \Delta H \rvert$
	$\Delta S > 0$		more than	$\lvert \Delta H \rvert$
	$\Delta S < 0$		less than	$\lvert \Delta H \rvert$

Example: Check if this process is spontaneous or not?

$NH_4Cl(s) + H_2O \rightarrow$ aqueous solution at 25 ^{o}C

ΔH^{θ}(solution) = + 34.7 kJ mol^{-1} (endothermic) **unfavorable to spontaneity**

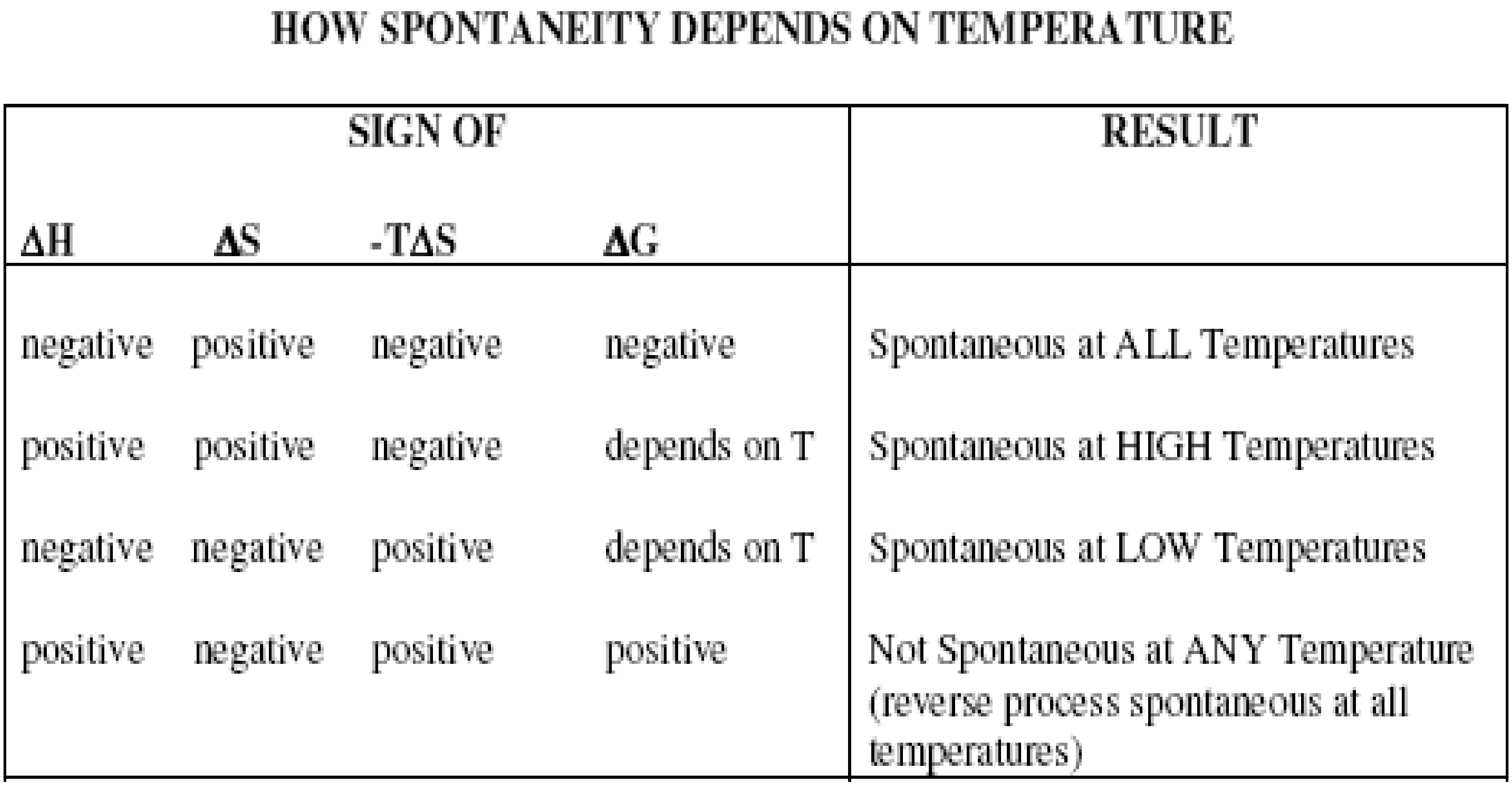
ΔS^{θ}(solution) = + 167.1 J K^{-1} mol^{-1} **favorable to spontaneity**

ΔG^{θ}(solution) =ΔH^{θ} (solution) - TΔS^{θ} (solution)
= 34.7 kJ mol^{-1} – 298 K (.1671 kJ K-1 mol^{-1})
= -15.1 kJ mol-1

In this case a favorable entropy change overcomes an unfavorable energy change.

In fact, this process is spontaneous at any temperature above:

$$T = \frac{\Delta H^{\theta}}{\Delta S^{\theta}} = \frac{34.7 \quad kJ \quad mol^{-1}}{.167 \quad kJ \quad K^{-1} \quad mol^{-1}} = 208 \quad K \quad \text{at which point} \quad \Delta G^{\theta} = 0.$$



HOW SPONTANEITY DEPENDS ON TEMPERATURE

SIGN OF				RESULT
ΔH	ΔS	$-T\Delta S$	ΔG	
negative	positive	negative	negative	Spontaneous at ALL Temperatures
positive	positive	negative	depends on T	Spontaneous at HIGH Temperatures
negative	negative	positive	depends on T	Spontaneous at LOW Temperatures
positive	negative	positive	positive	Not Spontaneous at ANY Temperature (reverse process spontaneous at all temperatures)

Example: One mole of an ideal gas at 300 K and 10 atm is isothermally and reversibly expanded to 1 atm. Calculate q, w, ΔU, ΔH, ΔS and ΔG.

Analysis

ΔU , ΔH - *since gas is ideal and process is isothermal* $\Delta U = 0 = \Delta H$

w - *since gas expands, work is done by gas* $w < 0$

$$w_{rev} = -nRT \ln\left(\frac{V_f}{V_i}\right) = -nRT \ln\left(\frac{p_i}{p_f}\right)$$

q - *since isothermal, heat must be absorbed to offset energy loss due to work done* $q > 0$

$\Delta U = 0$ *so* $q = -w$

ΔS - *since gas expands and T is constant have greater disorder* $\Delta S > 0$

$$\Delta S = \frac{q_{rev}}{T}$$

ΔG - *since* $\Delta H = 0$ *there is only the* $-T\Delta S$ *term* $\Delta G < 0$

$$\Delta G = -T\,\Delta S$$

$$q_{rev} = -w_{rev} = nRT \ \ln\left(\frac{p_i}{p_f}\right)$$

$$= 1 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \ln(10/1) = 5.74 \text{ kJ}$$

$$\Delta S = \frac{q_{rev}}{T} = \frac{5.74 \ \text{kJ}}{300 \ \text{K}} = .019 \ \text{kJ} \ \text{K}^{-1}$$

$$\Delta G = \Delta H - T\Delta S = 0 - 300 \text{ K} \times .019 \text{ kJ K}^{-1} \text{ mol}^{-1} = -5.74 \text{ kJ}$$

STANDARD MOLAR GIBBS ENERGY

In the same way that standard heats of formation were defined for compounds we define standard molar Gibbs free energy of formation.

This will allow us to calculate free energies of reactions at 298 K and hence whether a reaction will be spontaneous IF the reaction is carried out at constant temperature and pressure.

$\Delta_f G^\theta$ ≡ Standard Gibbs (free energy) of formation of a compound [formed from constituent elements in their standard state]. Values in tables are given for T = 298 K

$\Delta_f G^\theta = 0$ for elements in their standard state i.e. for $O_2(g)$, $I_2(s)$, C(s; graphite)

The standard free energy of the reaction is obtained in the same manner as the heat of reaction and the entropy of reaction.

$$\Delta_r G^\theta = \sum_{\text{products}} \nu \ \Delta_f G^\theta - \sum_{\text{reactants}} \nu \ \Delta_f G^\theta$$

The standard Gibbs energy of formation of a compound and the standard Gibbs energy of a reaction at constant temperature can also be calculated from heats of reaction and entropies of reaction using:

$$\boxed{\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta}$$

ΔH^θ is almost **independent** of the temperature
ΔS^θ is **moderately dependent on the temperature**
$\Delta G^\theta$is **strongly dependent on the temperature**

Example: oxidation of α-D glucose

$$C_6H_{12}O_6(s) + 6\ O_2(g) \quad \rightarrow \quad 6\ CO_2(g) + 6\ H_2O(l)$$

If the ΔG^θ for $CO_2(g)$ = -394.4 kJ mol^{-1}, ΔG^θ for $H_2O(g)$= -237.2 kJ mol^{-1} , ΔG^θ for $C_6H_{12}O_6(s)$ = -910.9 kJ mol^{-1}

Is this reaction is spontaneous or not?

Calculate ΔG^θ **=** ΔG^θProduct - ΔG^θReactants

ΔG^θ =[6 ΔG^θ $CO_2(g)$ + 6 ΔG^θ $H_2O(l)$)]- [ΔG^θ $C_6H_{12}O_6(s)$ + 6 ΔG^θ $O_2(g)$]

ΔG^θ = 6(-394.4) + 6(-237.2) - 1(-910.9) - 0 = -2879 kJ mol^{-1}

If this reaction is carried out at constant temperature and pressure it would be spontaneous.

Example: Iodine sublimes at 25 °C as $I_2(s) \rightarrow I_2(g)$ where the heat and entropy of sublimation are ΔH = 39.37 kJ mol^{-1} and ΔS = 86.19 J K^{-1} mol^{-1}. What is equilibrium sublimation temperature if ΔH and ΔS are assumed to be independent of temperature.

We use the fact that at equilibrium $\Delta G = \Delta H - T\,\Delta S = 0$

$$T = \frac{\Delta H}{\Delta S} = \frac{39370\ \ J\ \ mol^{-1}}{86.19\ \ J\ \ K^{-1}\ \ mol^{-1}} = 457\ \ K\ \ or\ \ 184\ ^\circ C$$

Maxwell Relations

(1) The combined first and second law

From the first law: $dU = dq + dW$

From the second law: $dS \geq \frac{dq}{T}$

Where, $dS > \frac{dq}{T}$ for irreversible system

and, $dS = \frac{dq}{T}$ for reversible system

For a closed system in which only reversible pV work is involved

$dW = -pdV$ and $dS = \frac{dq}{T}$

$\therefore dU = TdS - pdV$ **Fundamental equation**

The internal energy is a function of S and V

Where U, T, S, P, and V are state functions

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$$\therefore dU = \left(\frac{dU}{dS}\right)_V dS + \left(\frac{dU}{dV}\right)_S dV$$

Thus, we can calculate T and p as

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Equation I

S and V are natural variables of U represented as U(S,V)

Also since U is a state function we can apply the state function condition

$$\left[\frac{\partial}{\partial \mathrm{V}}\left(\frac{\partial \mathrm{U}}{\partial \mathrm{S}}\right)_\mathrm{V}\right]_\mathrm{S} = \left[\frac{\partial}{\partial \mathrm{S}}\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_\mathrm{S}\right]_\mathrm{V} \Longrightarrow \left(\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_\mathrm{S} = -\left(\frac{\partial \mathrm{p}}{\partial \mathrm{S}}\right)_\mathrm{V}$$

This is a Maxwell Relation

Using the fundamental equation we can obtain new equations for dH, dA and dG and use the same procedures as above to obtain three more equations like [I] as well as three other Maxwell Relations. These turn out to be particularly useful in manipulating partials as will be shown shortly.

H = U + pV and G = H – TS

For a constant T and p process dT = 0 and dp = 0 and thus

G = U – TS + pV $\therefore$ **dG = dU – TdS –SdT + pdV + Vdp**

Substitute the fundamental equation dU = TdS – pdV into the equation for dG to get: **dG = Vdp – SdT**

This equation for dG suggests that we take p and T as the variables for the Gibbs energy.

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

Comparing coefficients of dp and dT for the two equations gives

$$\left(\frac{\partial \mathbf{G}}{\partial \mathbf{p}}\right)_{\mathbf{T}} = \mathbf{V} \quad \textbf{and} \quad \left(\frac{\partial \mathbf{G}}{\partial \mathbf{T}}\right)_{\mathbf{p}} = -\mathbf{S}$$

Applying the state function condition for G

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

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The four Maxwell relations are

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

Maxwell relations allow us to develop different equations

Start with the fundamental equation $dU = TdS - pdV$.

Proof that $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$

To get the LHS partial of the above equation we divide dU by dV and hold T constant

$$\left.\frac{dU}{dV}\right|_T = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

Substitute the Maxwell relation $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ to obtain the equation

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

The physical significance of the LHS. It is the change in the energy when the volume of a system, say a gas, is changed. i.e, when the distance between gas molecules is increased or decreased. Thus it is a measure of the change in the potential energy of molecules.

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The physical significance of the LHS. It is the change in the energy when the volume of a system, say a gas, is changed. ie when the distance between gas molecules is increased or decreased. Thus it is a measure of the change in the potential energy of molecules.

THE CHANGE of GIBBS ENERGY WITH T AND p

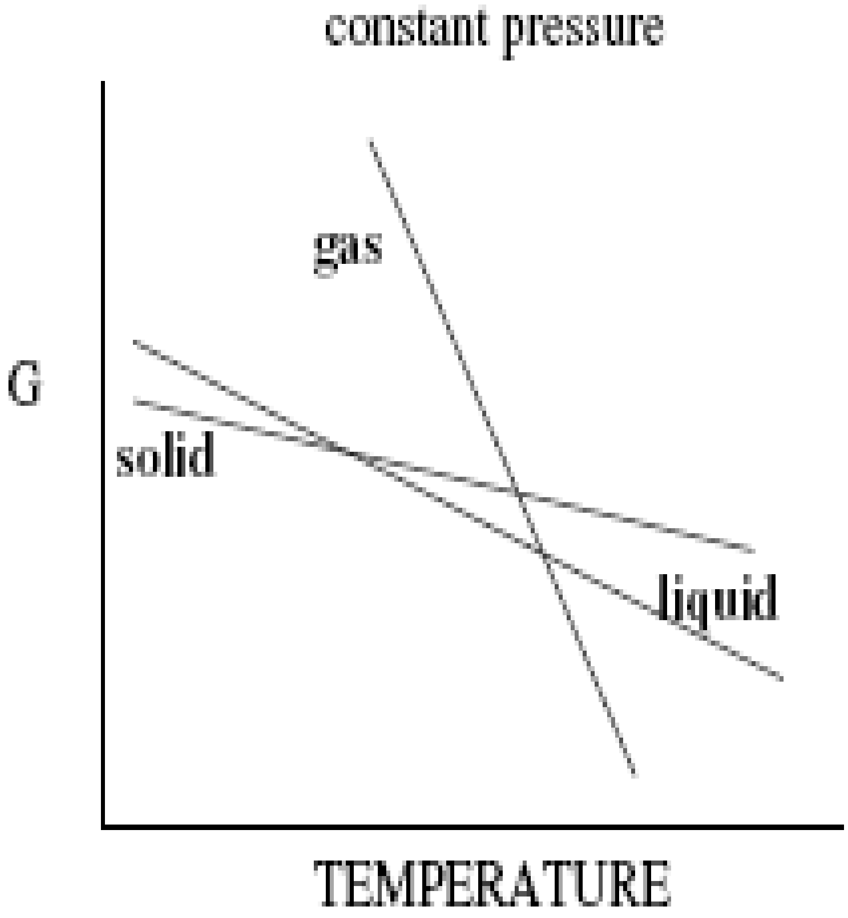
It is easy to determine the spontaneity of a reaction at 1 atm and 298 K since we can get the free energy of a reaction from the free energy of formation of compounds given in tables.

But, there are many reactions that are carried out at very different temperature and pressure conditions.

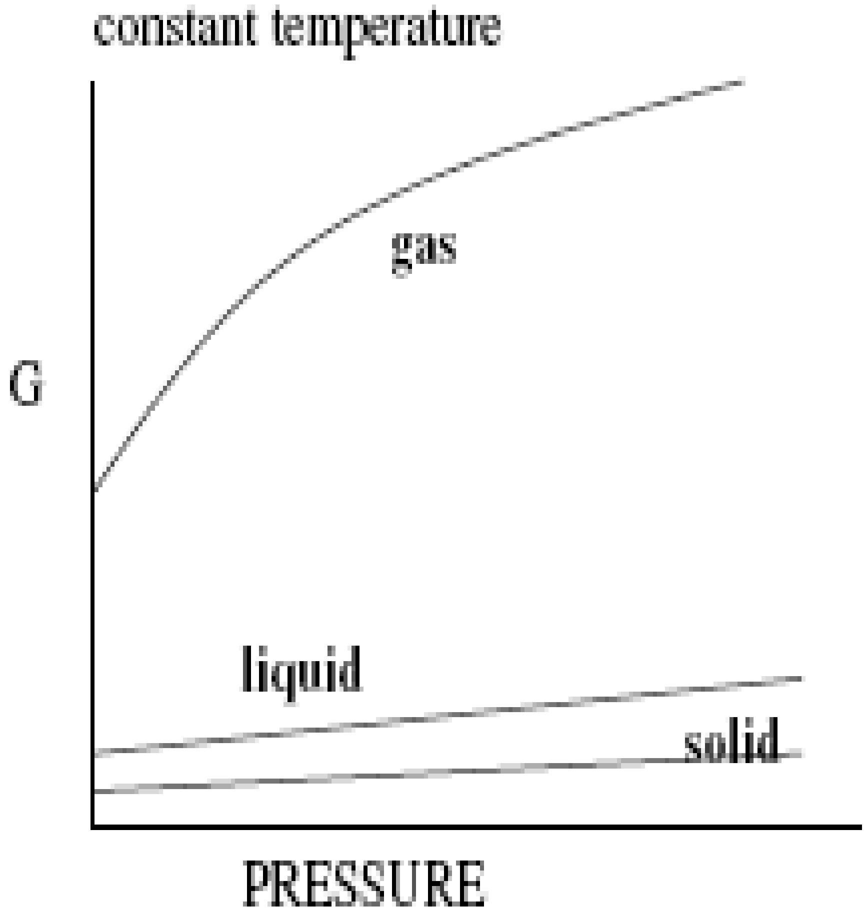
It is important to know how the free energy changes with temperature and pressure if we want to determine spontaneity at <u>any</u> temperature and pressure.

This is especially true for temperature changes since G is strongly dependent on temperature for solids, liquids, gases and solutions.

Pressure effects on G are substantial only for gases.



constant pressure

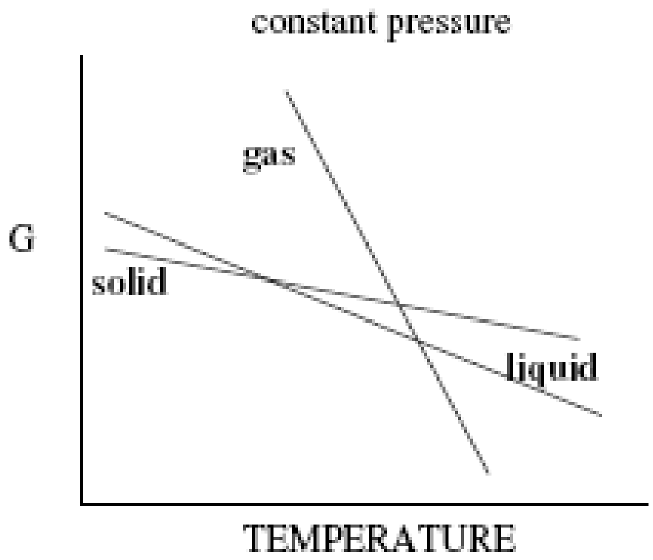


constant temperature

Change of G with temperature

The change of G with T was given by $\left(\frac{\partial G}{\partial T}\right)_{]} = -S$

This is the slope of the plots of G vs T



The fact that the slope is just the negative of the entropy makes the interpretation of the plots very simple.

The entropy of a gas is much larger than that of a liquid which in turn is larger than that of the solid. Thus, it is easy to rationalize the relative steepness of the G vs T lines for gas, liquid and solid.

For the change of ΔG with T we can write $\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$

"what will happen to the equilibrium which exits between water → steam at 100 °C and 1 atm if we raise the temperature to 110 °C"?

It is known that: at 100 °C, 1 atm there is equilibrium and $\Delta G^\theta = G^\theta(\text{steam}) - G^\theta(\text{water}) = 0$.

We need to see whether the value of ΔG^θ becomes positive or negative when the temperature increases by +10 °C.

From $\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$, write the equation for a small finite change δ as

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p \approx \frac{\delta \Delta G^\theta}{\delta T} = -\Delta S^\theta \qquad \therefore\ \delta \Delta G^\theta = (-\Delta S^\theta)\delta T$$

Since ΔS^θ [= S^θ(steam)> S^θ(water)] > 0 and that $\delta T > 0$, $\delta \Delta G^\theta < 0$ at 110 °C, 1 atm and hence , the process water → steam will be spontaneous.

a) The Gibbs Helmholtz Equation

$$\frac{\delta\Delta G^{\theta}}{\delta T} = -\Delta S^{\theta} \qquad \therefore\ \delta\Delta G^{\theta} = (-\Delta S^{\theta})\delta T$$

The above temperature dependence of the Gibbs energy on entropy is OK but it would be even better if it depended on enthalpy since we usually have more heat data than entropy data. This can be shown as follows:

$$G = H - TS \quad \therefore S = \frac{H-G}{T} = -\left(\frac{\partial G}{\partial T}\right)_p$$

Consider $\left(\frac{\partial\ \ G/T}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p + G\left(\frac{\partial\ \ 1/T}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2}$

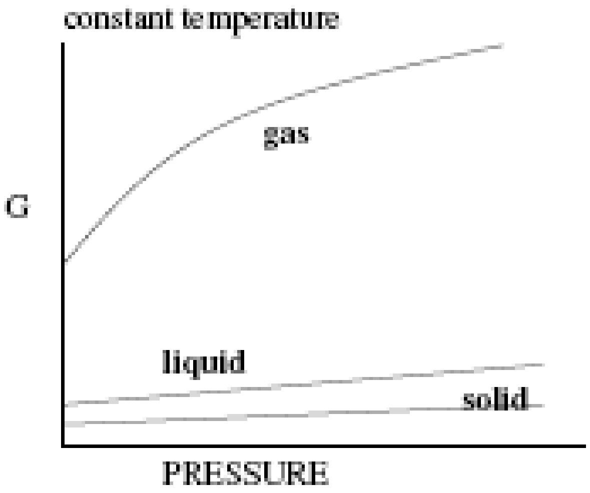
Substitute for $\left(\frac{\partial G}{\partial T}\right)_p = \frac{G-H}{T} \qquad \therefore \quad \left(\frac{\partial\ \ G/T}{\partial T}\right)_p = \frac{-H}{T^2}$

For any process: initial state → final state with $\Delta G = G_i - G_f$ and $\Delta H = H_i - H_f$

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

This is Gibbs Helmholtz Equation

Change of G with pressure:



It was proved before that $\left(\frac{\partial G}{\partial p}\right)_T = V$

The slope of the plot of G vs p is just the volume of the system. Since V is always positive, the free energy must always increase with pressure.

The slopes of the plot for the gas, liquid and solid should decrease in that order since the molar volumes of these phases decreases as we go from gas to liquid to solid.

For a finite change in ΔG when p changes : $\left(\frac{\partial \Delta G}{\partial p}\right)_T = \Delta V$

This equation can be applied to the water ↔ steam equilibrium at 100 °C, 1 atm.

What will happen to the equilibrium if the pressure is decreased to 0.5 atm?

$$\left(\frac{\partial \Delta G}{\partial p}\right)_T \approx \frac{\delta \Delta G}{\delta p} = \Delta V \quad \therefore \delta \Delta G = (\Delta V) \quad \delta p$$

BUT ΔV = V(steam) – V(water) >> 0 and δp = 0.5 – 1.0 = - 0.5 < 0 and as a result

$\delta\Delta G < 0$

Water turning into steam (water vapor) will occur spontaneously

Deriving equation for the change of Gibbs energy with pressures at constant temperature:

From the above partial derivative, at constant temperature:

$$\left(\frac{\partial G}{\partial p}\right)_T = \left.\frac{dG}{dp}\right|_T = V \quad \text{and} \quad dG\,|_T = Vdp\,|_T$$

Thus $\int dG = \int Vdp$ the understanding that for this integration, T is constant

$$\boxed{\mathbf{G(p_f) - G(p_i) = \int_{p_i}^{p_f} V(p,T)dp}}$$

Always true for any isothermal process

$$\boxed{G(p_f) - G(p_i) = \int_{p_i}^{p_f} V(p,T)\,dp}$$

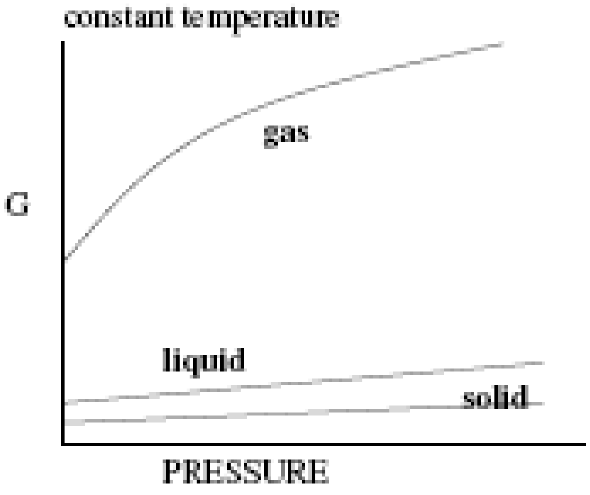
a) For solids and liquids (V is independent of p)

$$\therefore G_2 = G_1 + V(p_2 - p_1) \longrightarrow G = G^o + V(p - p^o)$$

Where, G^o and p^o are the standard value

Since for most solids and liquid, the molar volume is small the value of ΔG is also very small unless the pressure change is huge.

Thus as a first approximation we can say that G is independent of pressure for solids and liquids. This is seen in the plot of G vs p where the lines for liquid and solid are almost flat.



$$\boxed{G(p_f) - G(p_i) = \int_{p_i}^{p_f} V(p,T)dp}$$

b) For gasses (V is dependent of p), ideal gas

$$V = \frac{nRT}{P} \quad \Longrightarrow \quad \int_{G_1}^{G_2} G = nRT \int_{p_1}^{p_2} \frac{p}{dp}$$

$$\therefore G_2 = G_1 + nRT \ln \frac{p_2}{p_1}$$

$$\therefore \Delta G = nRT \ln \frac{V_1}{V_2} = -nRT \ln \frac{V_2}{V_1} = W$$

$$\boxed{G = G^{o} + nRT \ln \frac{p}{p^{o}}}$$

This equation shows that at constant temperature the free energy goes up with the pressure. This means that for an isothermal expansion the Gibbs energy decreases (due to a dispersal of energy)

The effect on G of a gas due to changing the pressure is much greater the the effect on G of the corresponding liquid or solid, because the molar volume of the gas is much larger.

Example: Calculate the free energy change ΔG when one mol of an ideal gas at a constant temperature of 300 K is compressed from 1 atm to 100 atm.

Analysis:
ΔG should be positive since this is a compression which concentrates energy.

$$\Delta G = nRT \ln(p_f/p_i)$$
$$= 1 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \ln(100/1) = 11.5 \text{ kJ}$$

$\Delta_f G^O$ (Standard Gibbs energy of formation) for liquid CH_3OH at 298K is -166.27 $kJmol^{-1}$, and that for gaseous CH_3OH is -161.96 $kJmol^{-1}$. The density of the liquid methanol at 298K is 0.7914 $g.cm^{-3}$.

Calculate $\Delta_f G$ (CH_3OH, g) and $\Delta_f G$ (CH_3OH, liq) at 10 bar at 298 K and

$\Delta_f G$ (CH_3OH, g)

$\Delta_f G = \Delta_f G^o + nRT \ln(p/p^o)$

$= -161.96\ kJmol^{-1} + (1\ mol \times 8.314 J\ K^{-1}\ mol^{-1} \times 298K \ln(10/1)$

$= -156.25\ kJmol^{-1}$

$\Delta_f G$ (CH_3OH, liq)   1 bar = 100 kPa

$\Delta_f G = \Delta_f G^o + V_m(p-p^o)$ and

V_m= molar mass/ density = 32 g mol^{-1} / 0.7914 $g.cm^{-3}$= 40.49 $cm^3\ mol^{-1}$

V_m= 40.49 x $10^{-6}\ m^3\ mol^{-1}$

$V_m(p-p^o)$ = 40.49 x $10^{-6}\ m^3\ mol^{-1}$ (10 x 10^5- 1 x 10^5)Pa x (1 x 10^{-3} kJJ^{-1})

$\Delta_f G$ = -166.27 $kJmol^{-1}$+ 40.49 x $10^{-6}\ m^3\ mol^{-1}$ (10 x 10^5- 1 x 10^5)Pa x (1 x 10^{-3} kJJ^{-1}) = -166.23 $kJmol^{-1}$

An ideal gas at 27^{o}C expands isothermally and reversibly from 10 to 1 bar against a pressure that is gradually reduced. Calculate q, W, ΔU, ΔH, ΔG, ΔA, and ΔS.

Analysis: Isothermally and reversibly, ΔU, ΔH, equal zero
Gas expand, W is negative, q = -W, ΔA is negative, ΔS is positive and ΔG is negative

Calculations:

$W_{max} = \Delta A = -RT\ln(p_1/p_2) = -(8.314\ JK^{-1}\ mol^{-1})(300\ K)\ \ln(10/1) = -5746\ J\ mol^{-1}$

$q = -W_{max} = 5746\ J\ mol^{-1}$

$\Delta U = \Delta H = 0$

$\Delta S = (q_{rev}/T) = (5746\ J\ mol^{-1})/(300\ K) = 19.14\ J\ K^{-1}\ mol^{-1}$

$\Delta G = \Delta H - T\Delta S = 0 - (300\ K)(19.14\ J\ K^{-1}\ mol^{-1}) = 5746\ Jmol^{-1}$

OR $\Delta G = RT\ln(p_2/p_1) = (8.314\ JK^{-1}\ mol^{-1})(300\ K)\ \ln(1/10) = 5746\ Jmol^{-1}$

INTRODUCTION OF THE CHEMICAL POTENTIAL

The change in number of moles of any substance must be considered.

Starting with pure substances and determine how the Gibbs function will change if infinitesimal amount of the same substance is added at constant temperature and pressure.

This partial derivative is defined as the **Chemical Potential** : $\mu \equiv \left(\frac{\partial G}{\partial n}\right)_{T,p}$

For a pure substance , μ is just the molar free energy **G_m**.

$G = n\,G_m$

$$\mu \equiv \left(\frac{\partial n G_m}{\partial n}\right)_{T,p} = G_m + n\left(\frac{\partial G_m}{\partial n}\right)_{T,p}$$

But for a pure substance **G_m** is constant with respect to the **n** and thus **$\mu = G_m$.**

This is true of any molar quantity.

For example, the molar volume V_m of water is 0.018 L mol^{-1} and is independent of whether we are talking about 1 mole or 23 moles. Molar quantities are “intensive” like density - they don’t depend on the amount.

The chemical potential is the most fundamentally important function for general systems because it indicates how a system will change with a change in temperature, pressure AND composition.

As applied to ideal gases we can obtain the chemical potential of an ideal gas at any temperature and pressure p,T from the previous equation for G:

$$\mu = \mu^{\theta} + RT \ln \frac{p}{p^{\theta}} \quad OR \qquad \mu = \mu^{\theta} + RT \ln \frac{p}{1atm}$$

In the most general formulation μ is a function of **T, p** and moles of each component in the system ie

$$\mu = \mu\,(T, p, n_1, n_2, n_3, \ \ldots\ldots\ldots)$$

Also <u>rewrite the equilibrium criteria</u> for a constant T and p process

$\Delta G = 0$ as $\qquad \Delta\mu = 0$

FUGACITY

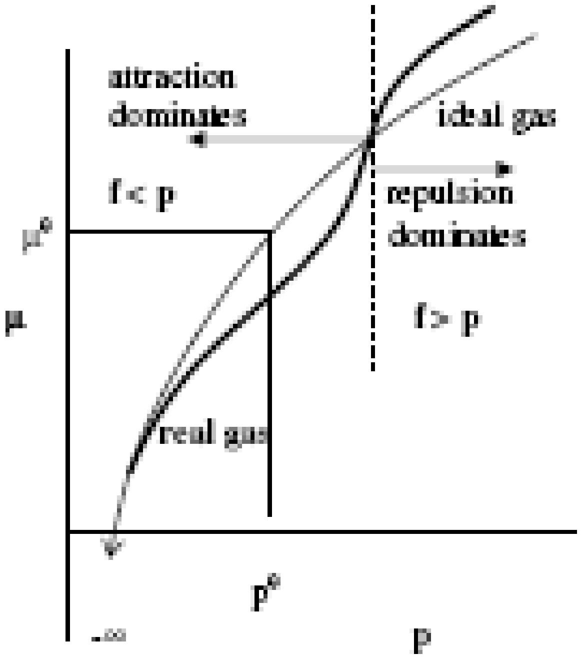
It is simply a measure of molar Gibbs energy of a real gas .

Modify the simple equation for the chemical potential of an ideal gas by introducing the concept of a **fugacity f.** The fugacity is an " effective pressure" which forces the equation below to be true for real gases:

$$\mu(p,T) = \mu^{\theta}(T) \quad + \quad RT\ln\left(\frac{f}{p^{\theta}}\right)$$

where $p^{\theta} = 1$ atm

A plot of the chemical potential for an ideal and real gas is shown as a function of the pressure at constant temperature.



The fugacity has the units of pressure. As the pressure approaches zero, the real gas approach the ideal gas behavior and f approaches the pressure.

If fugacity is an "effective pressure" ie the pressure that gives the right value for the chemical potential of a real gas. The only way we can get a value for fugacity and hence for μ is from the gas pressure. Thus <u>we must find the relation between the effective pressure f and the measured pressure p.</u>

let **$f = \phi p$**

ϕ is defined as the **fugacity coefficient.** ϕ is the "fudge factor" that modifies the actual measured pressure to give the true chemical potential of the real gas.

$$\mu(p,T) = \mu^{\theta}(T) + RT \ln\left(\frac{f}{p^{\theta}}\right)$$

By introducing ϕ we have just put off finding f directly. Thus, now we have to find ϕ. Substituting for ϕ in the above equation gives:

$$\mu(p,T) = \mu^{\theta}(T) + RT \ln\left(\frac{p}{p^{\theta}}\right) + RT \ln\phi = \mu(\text{ideal gas}) + RT \ln\phi$$

$$\mu(p,T) - \mu(\text{ideal gas}) = RT\ln\phi$$

This equation shows that the difference in chemical potential between the real and ideal gas lies in the term **RT ln** ϕ. This is the term due to molecular interaction effects.

The equation relating f or ϕ to the measured pressure p:

Note that as **p $\to$ 0**, the real gas → ideal gas, so that **f$\to$p** and $\phi \to$ **1**

The chemical potential for an ideal gas and a real gas at two pressures p and p′ is

$$\int_{p'}^{p} V_{\mathrm{ideal,m}} dp = \int d\mu_{\mathrm{ideal}} = \mu_{\mathrm{ideal}}(p,T) - \mu_{\mathrm{ideal}}(p',T) = RT \ \ln \left(\frac{p}{p'}\right)$$

$$\int_{p'}^{p} V_{m} dp = \int d\mu = \mu(p,T) - \mu(p',T) = RT \ \ln \left(\frac{f}{f'}\right)$$

Subtracting the first equation from the second gives

$$\int_{p'}^{p} \left(V_m - V_{\mathrm{ideal,m}}\right) \ dp = RT \ \ln \left(\frac{f}{f'}\right) - RT \ \ln \left(\frac{p}{p'}\right)$$

or $$\ln\left(\frac{f/p}{f'/p'}\right) = \frac{1}{RT}\int_{p'}^{p} \left(V_m - V_{\mathrm{ideal,m}}\right) \ dp$$

Let **p′ $\to$ 0**, then in the initial state the real gas → **the ideal gas. Thus f′ $\to$ p′**

$$\ln\left(\frac{f}{p}\right) = \frac{1}{RT}\int_{0}^{p} \left(V_m - V_{\mathrm{ideal,m}}\right) \ dp$$

Since for an ideal gas $V_{ideal,m} = \frac{RT}{p}$ and for a real gas $V_m = \left(\frac{RT}{p}\right)Z$

where Z is the compressibility factor

$$\ln\left(\frac{f}{p}\right) = \frac{1}{RT}\int_0^p\left[\left(\frac{RT}{p}\right)Z - \left(\frac{RT}{p}\right)\right] dp = \int_0^p\left[\frac{Z(p,T)-1}{p}\right]dp = \ln\ \phi$$

$$f = p\ \exp\left\{\int_0^p\left[\frac{Z(p,T)-1}{p}\right]dp\right\}$$

The fugacity coefficient **ϕ = f/p** is given by

$$\boldsymbol{\phi = \exp\left\{\int_0^p\left[\frac{Z(p,T)-1}{p}\right]dp\right\}}$$

Thus the fugacity of a gas is readily calculated at same pressure p if Z is known as a function of pressure up to that particular pressure.