Tutorial 4 - chemical reactions

Mixture of substances among which chemical reactions are possible.

Thermo. equil (chemical equil.) - Quantity of each substance doesn't change anymore.

(Tot. No. of particles of each of the reacting substances = const).

Thermo. equil. for mixture of substances @ $T, P = \text{const}$:

Recall Gibbs free energy: $G = E - TS + PV$

$$\partial G = -S\partial T + V\partial P + \mu \partial N$$

We have several substances $\Rightarrow$ $\mu \partial N \to \sum_i \mu_i \partial N_i$ and

$$\frac{\partial G}{\partial N_i} = \mu_i$$

~~(Note: using Euler formulation one has $G(P,T,N_i) = \sum \mu_i(T,P) N_i$)~~

Description of a chemical reaction:

A symbolic equation $\sum_i \nu_i A_i = 0$

A_i - chemical symbols of reacting substances

ν_i - positive/negative integers

($2H_2 + O_2 = 2H_2O \rightarrow 2H_2 + O_2 - 2H_2O = 0$ $\nu_{H_2} = 2$, $\nu_{O_2} = 1$, $\nu_{H_2O} = -2$)

To find the equil. we need to minimize the Gibbs potential for given P, T (need to find $N_1, N_2, \dots$)

N_i - no. of particles of substance i in reaction.

Need $\left(\frac{\partial G}{\partial N_i}\right)_{P,T} = 0$ take N_1 for example

$$\Rightarrow \frac{\partial G}{\partial N_1} + \frac{\partial G}{\partial N_2}\frac{dN_2}{dN_1} + \frac{\partial G}{\partial N_3}\frac{dN_3}{dN_1} + \cdots = 0$$

N_i, N_j connected by chemical reaction:

Reaction equation $\Rightarrow$ N_1 changes by ν_1 then each N_i changes by ν_i: $dN_i = \frac{\nu_i}{\nu_1} dN_1 \Rightarrow \frac{dN_i}{dN_1} = \frac{\nu_i}{\nu_1}$

We get $\sum_i \frac{\partial G}{\partial N_i}\frac{\nu_i}{\nu_1} = 0 \underset{\overset{\uparrow}{\frac{\partial G}{\partial N_i} = \mu_i}}{\Rightarrow} \boxed{\sum \nu_i \mu_i = 0}$ Condition for chemical equil.

Law of mass action

Apply the result to a mixture of ideal gases.

Recall for ideal gas (classical)

$$\underset{\overset{\nearrow}{\text{free energy}}}{F} = -NT \ln\left[\frac{eV}{N}\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\sum_k e^{-\varepsilon_k/T}\right]$$

We will write this as $F = -NT\ln\left(\frac{eV}{N}\right) + Nf(T)$

The Gibbs free energy: $G = F + PV$

Need to express $V(P) = \frac{NT}{P}$

$$\Rightarrow G = -NT\ln\left(\frac{eT}{P}\right) + Nf(T) + NT = NT\ln P + N\chi(T)$$

$$\chi(T) = f(T) - T\ln T$$

For a mixture of ideal gasses G is a sum of thermo. potentials of a gas with N_i particles with temp T and volume V (without other gasses)

Then can write $P_i = \frac{N_i T}{V}$ because $p = \frac{NT}{V}$

the partial pressure $P_i = \frac{N_i}{N} p = C_i p$

where c_i – concentration of substance.

Sum up:

$$G = \sum_i N_i T \ln P_i + N_i \chi_i(T)$$

$$\Rightarrow \mu_i = T \ln P_i + \chi_i(T)$$

Condition for chemical equil:

$$\sum \nu_i \mu_i = T \sum_i \nu_i \ln P_{0i} + \sum \nu_i \chi_i = 0$$

P_{0i} – partial pressure @ equil.

$\Rightarrow \ln\left[\prod_i P_{0i}^{\nu_i}\right] = -\frac{\sum \nu_i \chi_i}{T}$ Define $K_p(T) = e^{-\sum \nu_i \chi_i / T}$

Get $\boxed{\prod_i P_{0i}^{\nu_i} = K_p(T)}$

Can rewrite if use $P_{0i} = p C_{0i}$ $\left(C_{0i} = \frac{\overset{\circ}{N}_i}{N}\right)$ ← concentration @ equil.

Use $\prod P_{0i}^{\nu_i} = \prod_i p^{\nu_i} \prod C_{0i}^{\nu_i} = p^{\sum \nu_i} \prod C_{0i}^{\nu_i}$ to get

$\prod_i C_{0i}^{\nu_i} = p^{-\sum \nu_i} K_p(T) \equiv K_c(P,T)$ ← independent on initial amounts of reacting gases

K_c – chemical equil. constant.

<u>Example</u>

Gasses having constant specific heat:

Recall $E = F - T\frac{\partial F}{\partial T} \underset{\substack{\uparrow \\ \text{in previous notations}}}{=} N f(T) - NT f'(T)$

constant c_v $\Rightarrow$ $c_v = \left(\frac{\partial E}{\partial T}\right)_V = -T f''(T)$ → solve the equation and get

$$N f(T) = -N c_v T \ln T - N \underset{\substack{\uparrow \\ \text{chemical} \\ \text{constant} \\ \text{of the gas}}}{\zeta} T + N \underset{\substack{\uparrow \\ \text{ground} \\ \text{state} \\ \text{energy}}}{\varepsilon_0}$$

$$(E = N\varepsilon_0 + N c_v T)$$

Can write

$$\chi_i(T) = \varepsilon_{0i} - c_{pi} T \log T - T \zeta_i$$

using $c_p = c_v + 1$ for ideal gas $\left[c_p = \left(\frac{\partial S}{\partial T}\right)_p \frac{T}{N} \right]$

Get $K_p(T) = e^{-\sum \nu_i \chi_i / T} = e^{-\sum \nu_i \varepsilon_{0i}/T} \cdot T^{(\sum c_{pi} \nu_i)} \cdot e^{\sum \nu_i \zeta_i}$

Heat of reaction

Chemical reaction → absorption/evolution of heat.

Absorption - "endothermic reaction"

Evolution - "exothermic -"- "."

(The opposite of an endoth. react. is exoth.)

Want to find the maximum work that can be obtained by means of the chemical reaction.
(and then will find the heat flux)

Maximum work the system does in a reaction (transition) is equal to minimum work that needs to be done on the system for the opposite reaction.

T, P const, not equil. because of N_i

[redacted]

This corresponds to the change in the Gibbs potential

$(\Delta E_{tot} = \Delta E + \Delta E_r = \Delta E + T\Delta S_r - P\Delta V_r = \Delta E - T\Delta S + P\Delta V = \Delta(E - TS + PV) = \Delta G|_{P,T})$

⇒ Need to calculate change in $G(T, P, N_i)$ when a small no. δn of elementary reactions takes place.

$$\delta G = \sum_i \frac{\partial G}{\partial N_i}\delta N_i = \sum_i \mu_i \delta N_i$$

$\delta N_i = -\nu_i \delta n$ $\quad (\delta N_i = N_i^{final} - N_i^{initial}$ → the equation from right to left)

⇒ $\delta G = -\delta n \sum_i \nu_i \mu_i$ - Minimal work to be done to bring about δn reactions. || Maximal work that can be obtained from that no. of opposite reactions.

(We see agian that in equil. $\frac{\delta G}{\delta n} = 0$)

For gases: $\delta G = -\delta n \left(T \sum_i \nu_i \ln P_i + \sum \nu_i \chi_i\right) =$

$$= T\delta n \left[-\sum_i \nu_i \ln P_i + \ln(K_p(T))\right] =$$

$$= T\delta n \left[-\sum_i \nu_i \ln C_i + \ln(K_c(T))\right]$$

Note: needed δn small so that can keep C_i const. in reaction.

$\delta G < 0$ → reaction occurs in forward direction

$\delta G > 0$ → " — in backward "

(equil. at δG minimal)

Another way to see this: $\delta G = T\delta n \left[\ln\left[\frac{K_p(T)}{\Pi P_i^{\nu_i}}\right]\right]$

If $\Pi P_i^{\nu_i} > K_p$ → reaction in forward direction to reduce partial pressure of substances with $\nu_i > 0$ (increase P_i of $\nu_i < 0$)

Heat absorbed/evolved:

Note that $G = \underset{\substack{\uparrow \\ \text{enthalpy} \\ \text{heat function}}}{W} - TS$, $\Delta W = \Delta(E+PV)$ = heat gained by the body

$$\Rightarrow \Delta W = \Delta G - T\underset{\substack{\uparrow \\ \frac{\partial \Delta S}{\partial T}}}{\left(\frac{\partial \Delta G}{\partial T}\right)_p} = -T^2\left(\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right)$$

$$\Rightarrow \delta Q_p = -T^2 \frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right) = -T^2 \delta n \frac{\partial \ln K_p(T)}{\partial T}$$ – heat absorbed by the system

Doesn't depend on the concentrations C_i – true not only for small δn.

Note that $\delta Q_p > 0$ – endothermic then $\frac{\partial \log K}{\partial T} < 0$.

– " – $\delta Q_p < 0$ – exothermic – " – $\frac{\partial \log K}{\partial T} > 0$.

Increase of K (as we said previously) implies that the equil. is shifted to reformation of original substance (i.e opposite reactions happen to get there).

Decrease K – forward reactions to get to equil.

Deduce the rule:

Heating the system: for an endothermic process $\frac{\partial \log K}{\partial T} < 0$

K is decreased → shift to more endothermic process.

An exothermic proc. $\frac{\partial \log K}{\partial T} > 0$ → opposite process "dominate" = = endothermic.

For cooling K changes according to $-\frac{\partial \log K}{\partial T}$ and get a shift to exothernic process.

La chatelier's principle (consistant with)

Heat of reaction at constant volume:

at constant volume δQ_V = Change in energy

$\Rightarrow \delta Q_V = \delta Q_p - \delta(PV)$, $PV = T\sum N_i$, $\delta N_i = -\nu_i \delta n$

$\Rightarrow \delta Q_V = \delta Q_p + T\delta n \sum_i \nu_i$

Change in volume as a result of a reaction at $P = \text{const}$

$$\delta V = \frac{T}{P}\delta N = -\frac{T}{P}\delta n \sum_i \nu_i$$

$\delta V = 0$ for $\sum_i \nu_i = 0$ (tot. no. of particles unchanged).

Ionisation Equilibrium

At high enough T collisions $\Rightarrow$ ionisation.

$\Rightarrow$ establishment of equil. with certain fractions of gas particles at certain stages of ionization.

Take monoatomic gas (no chemical compounds at such temps)

Can write: $A_0 = A_1 + e^-$, $A_1 = A_2 + e^-$, ...

A_0 = neutral atom, $A_1, A_2, \ldots$ singly, doubly etc. ionised atoms.

e^- - electron.

~~chemical~~ ionisation equil. — special case of chemical equil.

Use law of mass action we derived:

$$\frac{C_{n-1}}{C\,C_n} = P K_p^{(n)}(T) \qquad (n = 1, 2, \ldots)$$

C_0 - concentration of neutral atoms

C_1, C_2 - " - of ions

each reaction: $\nu_{C_{n-1}} = 1$, $\nu_{C_n} = -1$, $\nu_C = -1$

$\sum \nu_i = -1$

Add equation for neutrality of gas:

$$C = C_1 + 2C_2 + 3C_3 + \dots$$

⇒ determine concentrations C_i @ equil.

Calculate $K_p(T)$:

We assumed monoatomic gas → all "gasses" (ions, electrons, atoms) are monoatomic have constant specific heat $c_p = \frac{3}{2} + 1 = \frac{5}{2}$

Chemical constant: $\zeta = \ln\left[g\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\right]$

g – statistical weight of ground state

electrons: $g=2$, atoms & ions $g = (2L+1)(2S+1)$

L – orbital, S – spin

m – mass of gas particle

Use the formula

$$K_p(T) = e^{-\sum \nu_i \varepsilon_{0i}/T}\, T^{(\sum c_{pi}\nu_i)}\, e^{\sum \nu_i \zeta_i}$$

$$\frac{\sum \nu_i \varepsilon_{0i}}{T} = \frac{\varepsilon_{0,n-1} - \varepsilon_{0,n}}{T} = -\frac{I_n}{T}$$

I_n – ~~ion~~ nth ionisation energy

$$\sum c_{pi}\nu_i = -\frac{5}{2}$$

$$\sum \nu_i \zeta_i = \ln g_{n-1} - \ln g_n - \ln 2 - \ln\left(\frac{1}{2\pi\hbar^2}\right)^{3/2} + \underbrace{\ln m_{n-1}^{3/2} - \ln m_n^{3/2} - \ln m_e^{3/2}}_{\ln\left[\left(\frac{m_{n-1}}{m_n m_e}\right)^{3/2}\right] \approx \ln\left(\frac{1}{m_e^{3/2}}\right)}$$

$$= \ln\left(\frac{g_{n-1}}{2g_n}\right) + \ln\left(\left(\frac{2\pi\hbar^2}{m_e}\right)^{3/2}\right)$$

$$\Rightarrow \boxed{K_p^{(n)}(T) = \frac{g_{n-1}}{2g_n}\left(\frac{2\pi}{m_e}\right)^{3/2}\frac{\hbar^3}{T^{5/2}}\, e^{I_n/T}}$$

since $K_p^{(n)}(T) \propto \frac{C_{n-1}}{C_n}$ and $K_p^{(n)}(T)$ decreases with increasing temp. the ionisation becomes $O(1)$ with increasing T.

Inspite the exponential dependence of $k_p^{(n)}(T)$ on T the stage of $O(1)$ ionisation is reached for $T \ll I_n$.

This is so because of prefactor: $\frac{P}{T}\left(\frac{2\pi\hbar^2}{mT}\right)^{3/2} = \frac{N}{V}\lambda_T^3$

which is very small: $n\lambda_T^3 \ll 1$

(order of ratio of atomic volume to volume per atom $\frac{V}{N}$ at $T \sim I$)

$\Rightarrow$ Gas ionised for $T < I_n$ $\rightarrow$ no. of excited atoms small since $\mathcal{E}_{\text{excitation}} \sim I$ (that's why we took ground state).

* At $T \sim$ binding energy of last electron in atom the gas may be considered as electrons & bare nuclei only.

* Usually binding energy of the first electron, $I_1 \ll I_n$ for n-subsequent elect.

$\Rightarrow$ range of temps in which only neutral atoms + singly charged ions.

Define α - degree of ionisation $= \frac{\text{No. of ionized atoms}}{N_{\text{tot atoms}}}$

$$c = c_1 = \frac{\alpha}{1+\alpha}\left(= \frac{N_I}{N_I + N_{\text{tot at.}}}\right)$$

$$c_0 = \frac{1-\alpha}{1+\alpha}\left(= 1 - \frac{\alpha}{1+\alpha}\right)$$

$$\Rightarrow \; P K_p^{(1)} = \frac{1-\alpha^2}{\alpha^2}\left(= \frac{c_0}{c \cdot c_1}\right) \;\Rightarrow\; \alpha = \frac{1}{\sqrt{1 + P K_p^{(n)}(T)}}$$

$\rightarrow$ determine degree of ionisation in terms of P, T for this range.