Summary Lecture 1 (glossery: see App. B, SG)

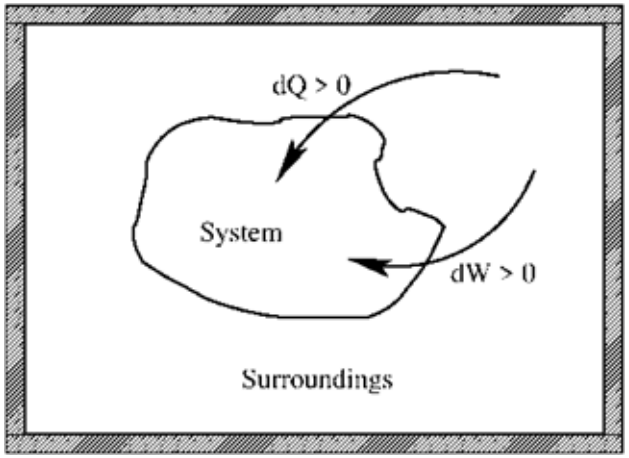
- **First law: conservation of energy**

$$dU = dW + dQ$$

$$\Delta U = \int dU = W + Q$$

$$\oint dU = 0$$

U is a state function



Reversible process

- Mechanical work

$$W = -\int P_{\text{ext}}\, dV \overset{=}{} -\int P dV$$

- Perfect gas

$$PV = nRT$$

Equation of state

- Perfect atomic gas

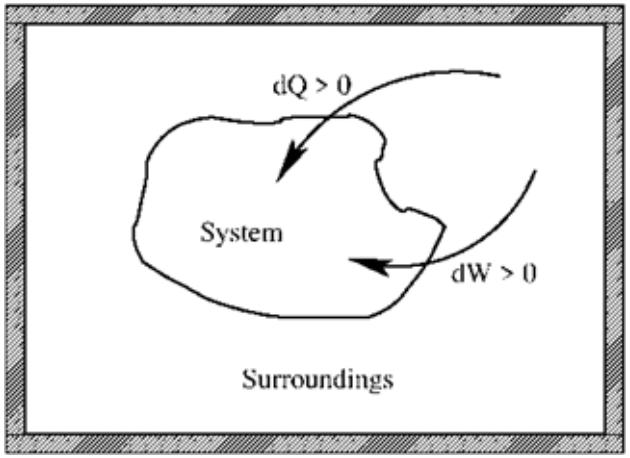
$$U = \frac{3}{2} nRT = \frac{3}{2} PV$$

Summary Lecture 2 (second law and entropy)

Second law:
for any spontaneous process

$$dS_{tot} = dS + dS_{sur} \geq 0$$

$$dS \equiv \frac{dQ^{rev}}{T}$$



S is a state function, so independent of path

Alternative form: Clausius inequality:

$$dQ \leq TdS$$

$$dQ^{rev} = TdS$$ **Reversible process**

$$dQ^{irr} < TdS$$ **Irreversible process**

Summary Lecture 2 (alternative energy functions)

Internal energy U

Enthalpy $H \equiv U + PV$

Helmholtz free energy $A \equiv U - TS$

Gibbs free energy $G \equiv H - TS$

State functions

(alternative) reversible processes

$dU = TdS - PdV \Rightarrow dU\big|_V = TdS$

$dH = TdS + VdP \Rightarrow dH\big|_P = TdS$

$dA = -SdT - PdV \Rightarrow dA\big|_{T,V} = 0$

$dG = -SdT + VdP \Rightarrow dG\big|_{T,P} = 0$

Heat capacities

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)\Big|_V \qquad C_P \equiv \left(\frac{\partial H}{\partial T}\right)\Big|_P$$

Lecture 3: Chemical reaction equilibria

Lecture 3: Chemical reaction equilibria

Dissociation reaction of a weak acid:

$$CH_3COOH + H_2O \longleftrightarrow CH_3COO^-(aq) + H_3O^+(aq)$$

Chemical equilibrium reaction

Where is the equilibrium state?

Chemical reaction equilibria

Dissociation reaction of a weak acid:

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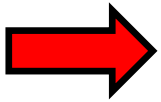
Chemical equilibrium reaction

Where is the equilibrium state?



Depends on P, T, V and n

Depends on equation of state of the system

Chemical reaction equilibria

Dissociation reaction of a weak acid:

$$CH_3COOH + H_2O \longleftrightarrow CH_3COO^-(aq) + H_3O^+(aq)$$

Chemical equilibrium reaction

Where is the equilibrium state?

Depends on P, T, V and n

Depends on equation of state of the system

Equation of state of an ionic solution:

probably very difficult

Chemical reaction equilibria

More simple system: equilibrium between perfect gases

$$2\mathrm{H}_2(g) + \mathrm{O}_2(g) \longleftrightarrow 2\mathrm{H}_2\mathrm{O}(\mathrm{g})$$

equation of state $PV = nRT$ **(perfect gas)**

However: we have a mixture of 3 different perfect gases!

Chemical reaction equilibria

More simple system: equilibrium between perfect gases

$$2\mathrm{H}_2(g) + \mathrm{O}_2(g) \longleftrightarrow 2\mathrm{H}_2\mathrm{O}(g)$$

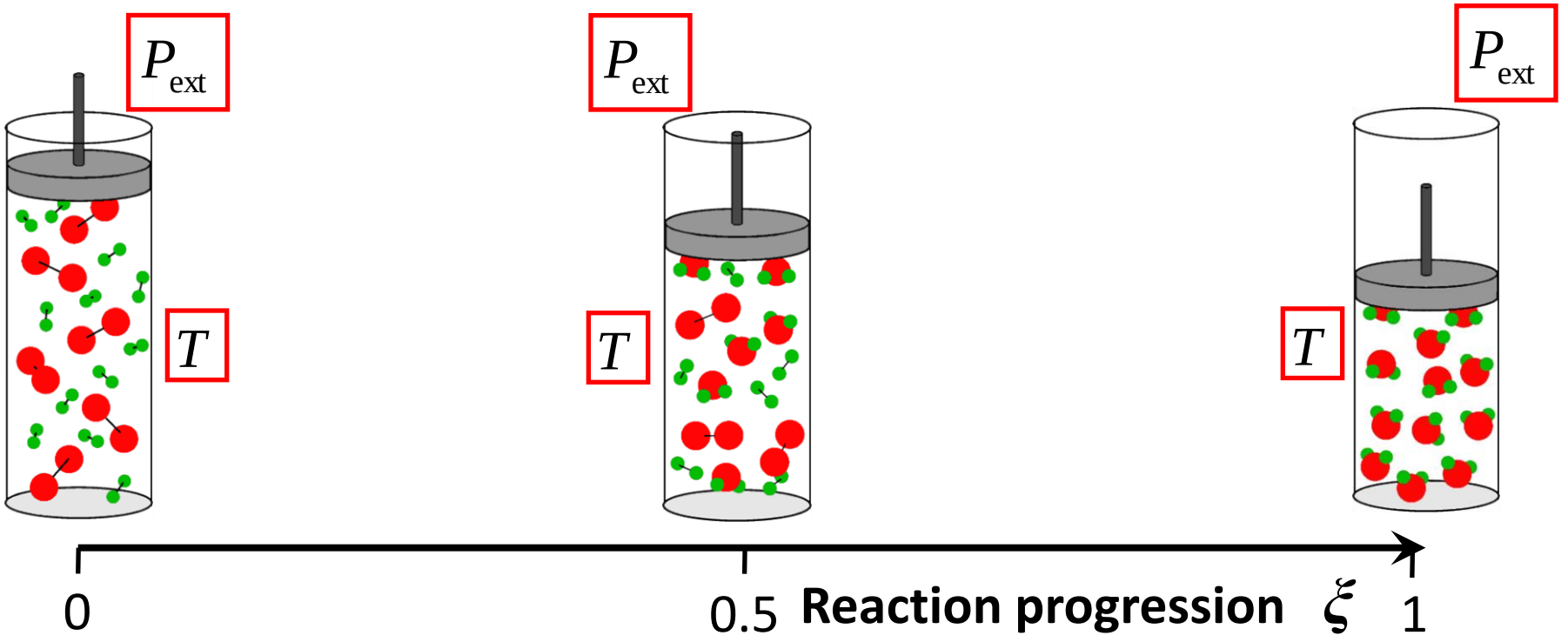
equation of state $PV = nRT$ **(perfect gas)**

However: we have a mixture of 3 different perfect gases!

- **In equilibrium T, V are the same for all 3 components**
  (although V will change during progression of the reaction)
- **Let us choose P_{ext}, T to be constant**

Chemical reaction equilibria

$$2\mathrm{H}_2(\mathrm{g}) + \mathrm{O}_2(g) \leftrightarrow 2\mathrm{H}_2\mathrm{O}(g)$$



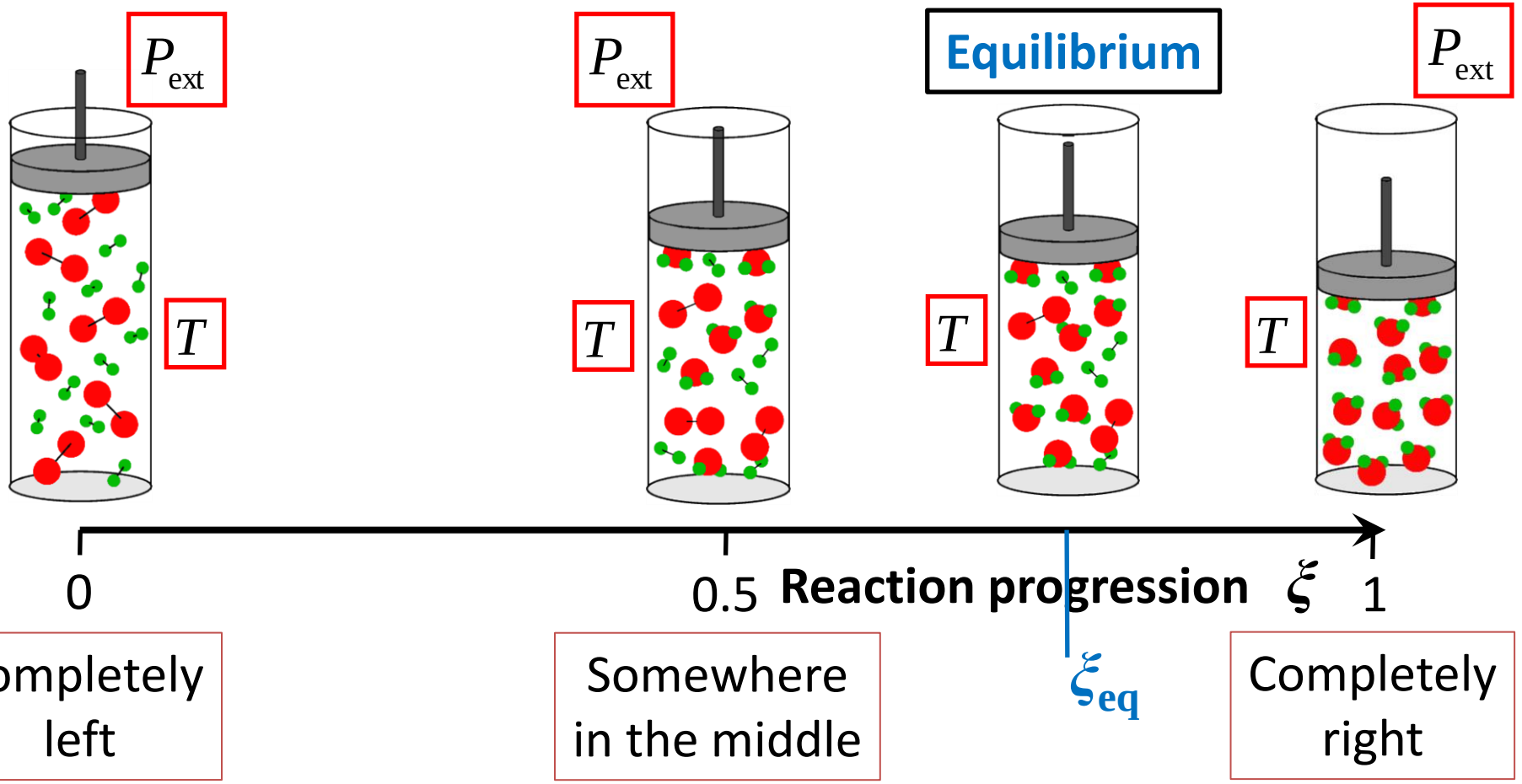
Completely left

Somewhere in the middle

Completely right

Chemical reaction equilibria

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$$



Chemical reaction equilibria

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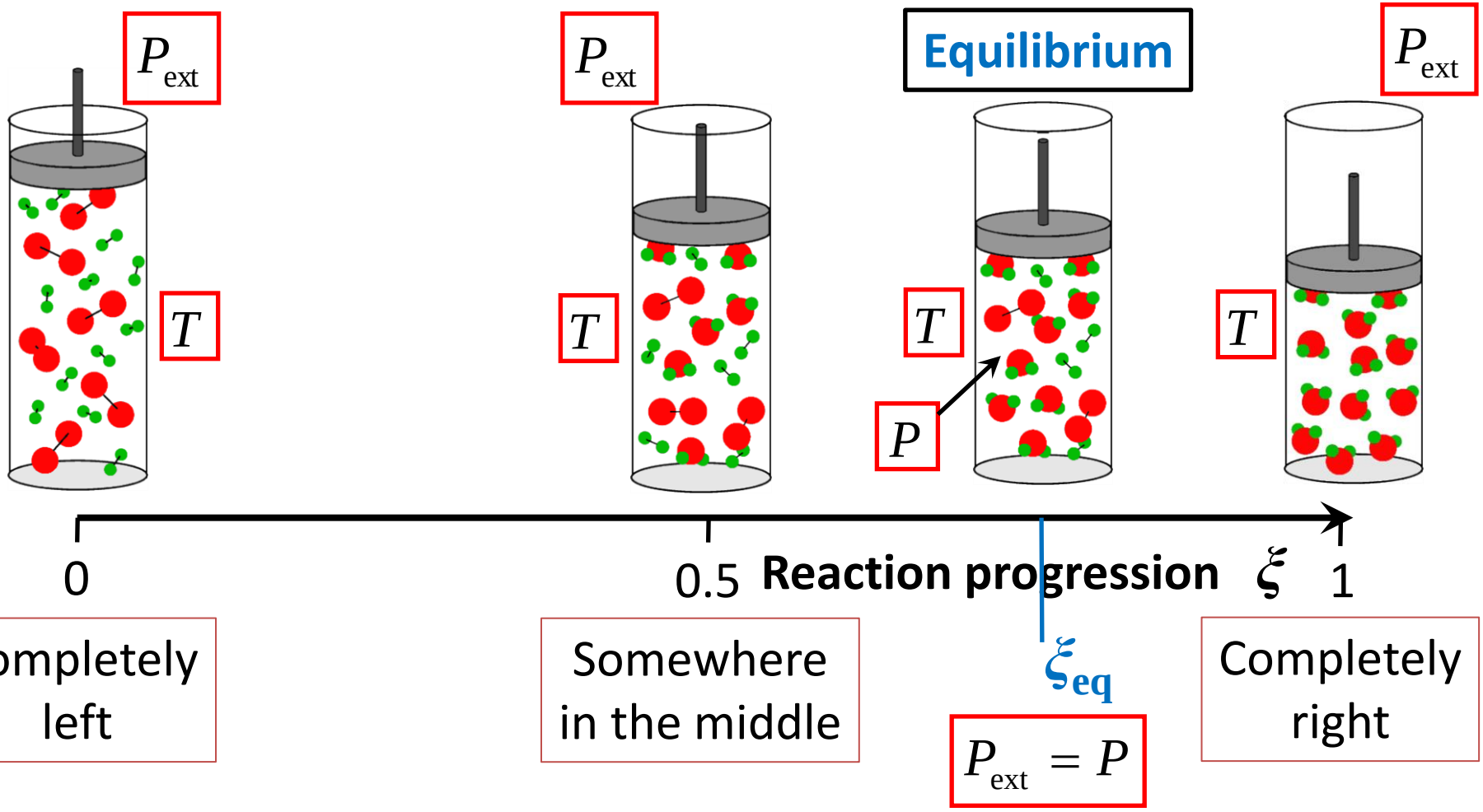

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Chemical reaction equilibria

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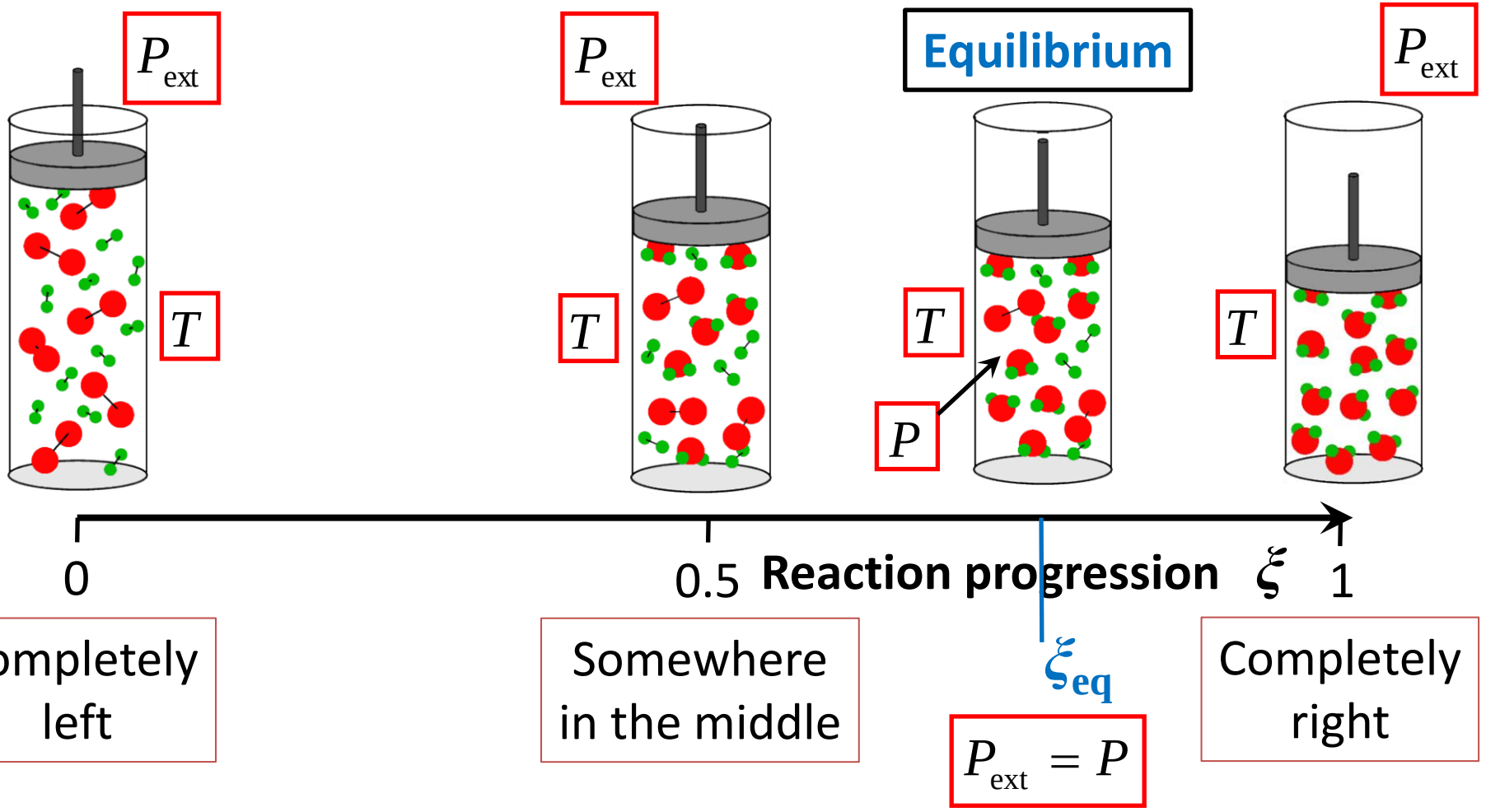

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Somewhere in the middle

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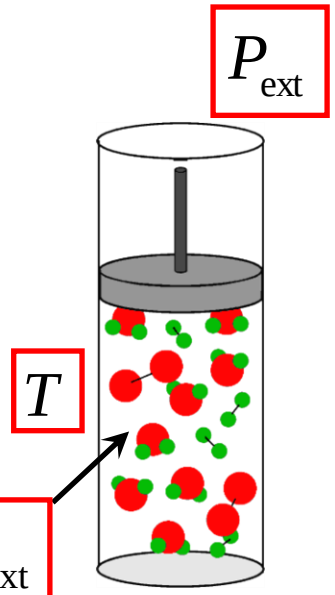
What drives the reaction to the equilibrium state?

Chemical reaction equilibria

$$2\mathrm{H}_2(\mathrm{g}) + \mathrm{O}_2(g) \leftrightarrow 2\mathrm{H}_2\mathrm{O}(g)$$

What drives the reaction to the equilibrium state?

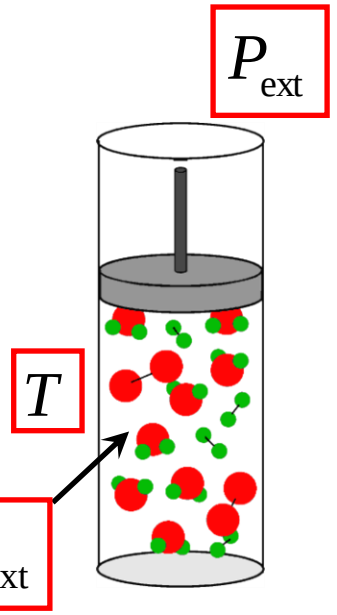
equilibrium state ⇒ $P = P_{\text{ext}}$



Equilibrium ξ_{eq}

Chemical reaction equilibria

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$$



What drives the reaction to the equilibrium state?

equilibrium state ➡ $P = P_{ext}$

Equilibrium ξ_{eq}

We chose P and T to be constant

➡ **The Gibbs free energy is the most convenient choice:**

$$G \equiv H - TS \Rightarrow dG = -SdT + VdP \Rightarrow dG\big|_{T,P} = 0$$

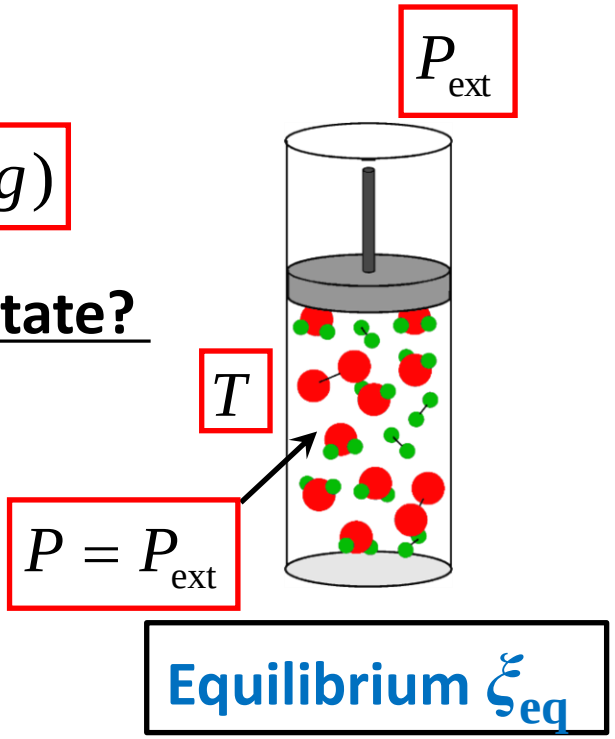
But the second law gives even more information

Chemical reaction equilibria

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$$

What drives the reaction to the equilibrium state?

$$dG = -SdT + VdP \Rightarrow dG\big|_{T,P} = 0$$



Always, so also in non-equilibrium:

$$G \equiv H - TS \Rightarrow dG = dH - d(TS) = dH - TdS - SdT$$

second law: **for a spontaneous process** $dQ^{irr} < TdS$?

Intermezzo: dG in non-equilibrium

Always, so also in non-equilibrium:

$G \equiv H - TS$ ⇒ $dG = dH - d(TS) = dH - TdS - SdT$

$H \equiv U + PV$ ⇒ **at constant pressure:**

$$dH\big|_P \equiv dU\big|_P + d(PV)_P = dU\big|_P + PdV\big|_P + VdP\big|_P$$
$$= dU\big|_P + PdV\big|_P = dQ\big|_P - PdV\big|_P + PdV\big|_P = dQ\big|_P$$

$dP = 0$

second law: **for a spontaneous process** $dQ^{\text{irr}} < TdS$

⇒ **In non-equilibrium:** $dH\big|_P < TdS$ **(SG: eq. 46)**

Intermezzo: dG in non-equilibrium

Always, so also in non-equilibrium:

$G \equiv H - TS$ ⇒ $dG = dH - d(TS) = dH - TdS - SdT$

In non-equilibrium: $dH\big|_P < TdS$

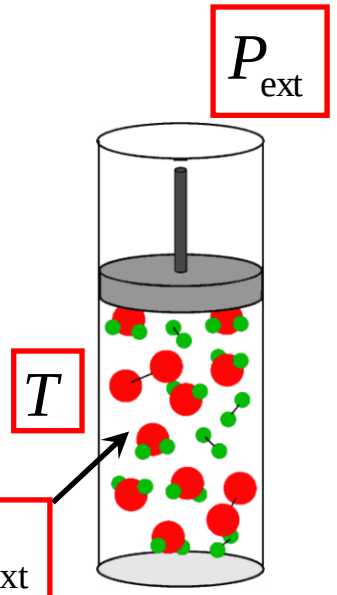
⇒ **In non-equilibrium:** $dG\big|_P < -SdT$ **(SG: eq. 58)**

⇒ **In non-equilibrium:** $dG\big|_{P,T} < 0$ **(SG: eq. 59)**

Chemical reaction equilibria

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$$

What drives the reaction to the equilibrium state?



equilibrium state ⇒ $P = P_{ext}$

Equilibrium ξ_{eq}

⇒

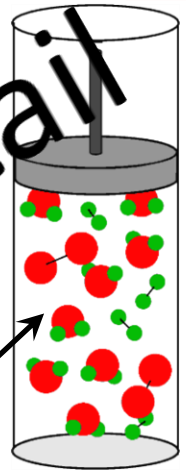
In equilibrium: $dG\big|_{P,T} = 0$

In non-equilibrium: $dG\big|_{P,T} < 0$

Chemical reaction equilibria

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$$

What drives the reaction to the equilibrium state?



equilibrium state ⇒ $P = P_{ext}$

Equilibrium ξ_{eq}

Let's work this out in detail

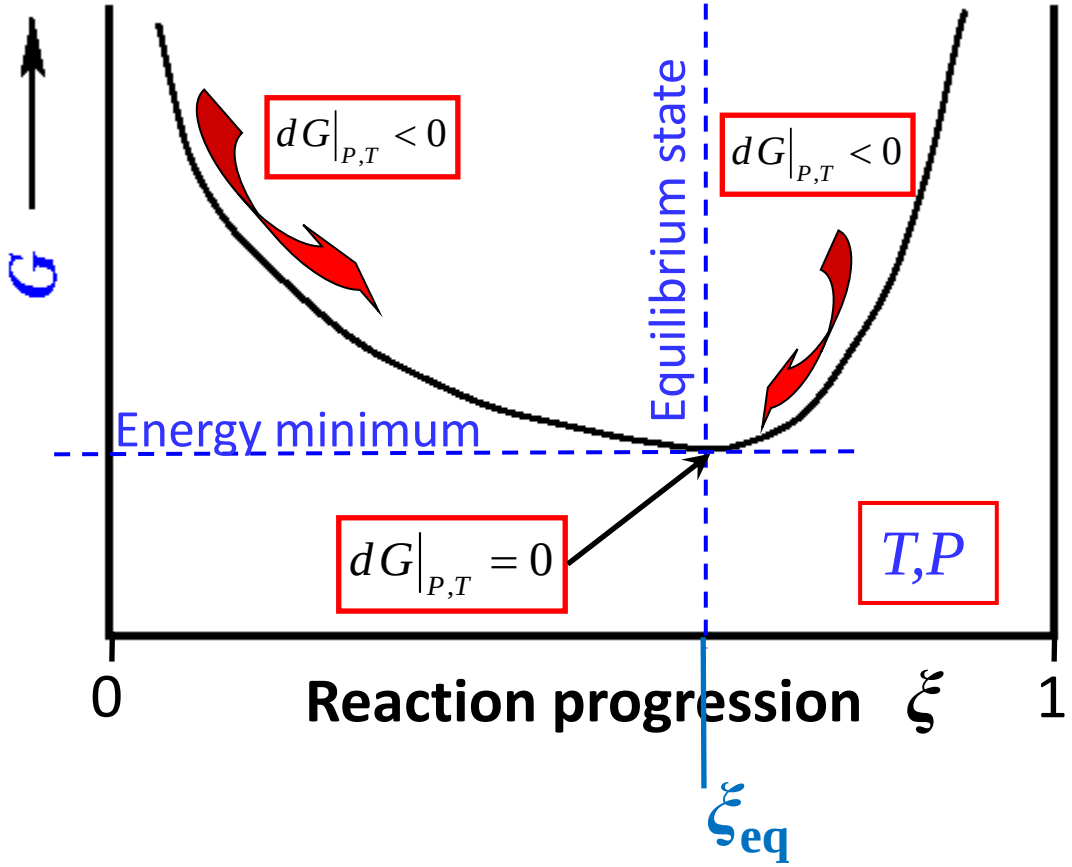
In equilibrium: $dG\big|_{P,T} = 0$

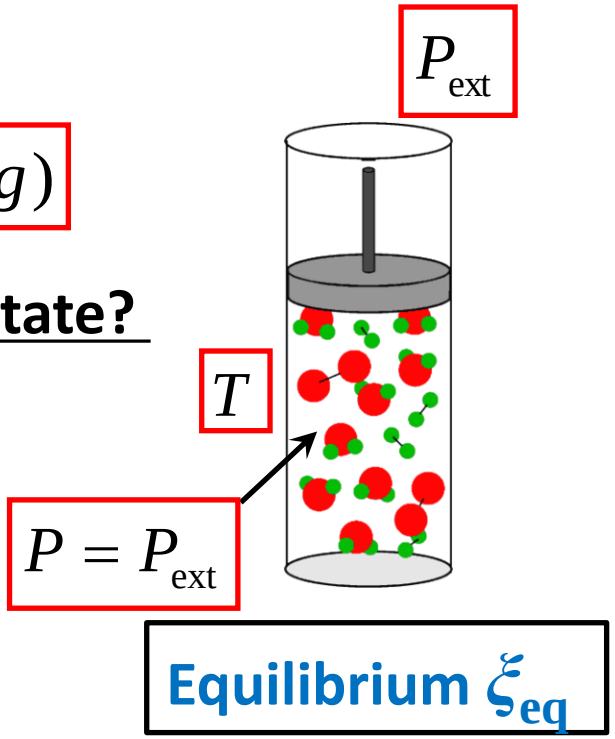
In non-equilibrium: $dG\big|_{P,T} < 0$

Chemical reaction equilibria

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$$

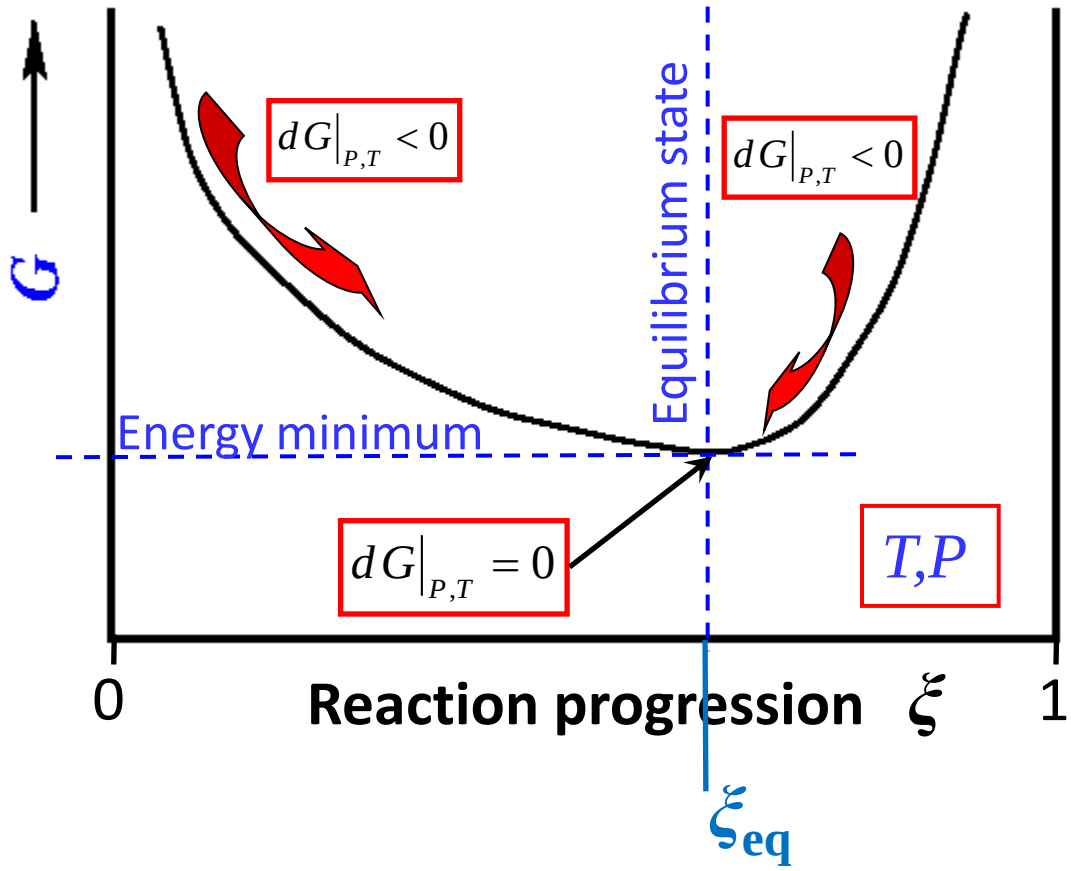
What drives the reaction to the equilibrium state?

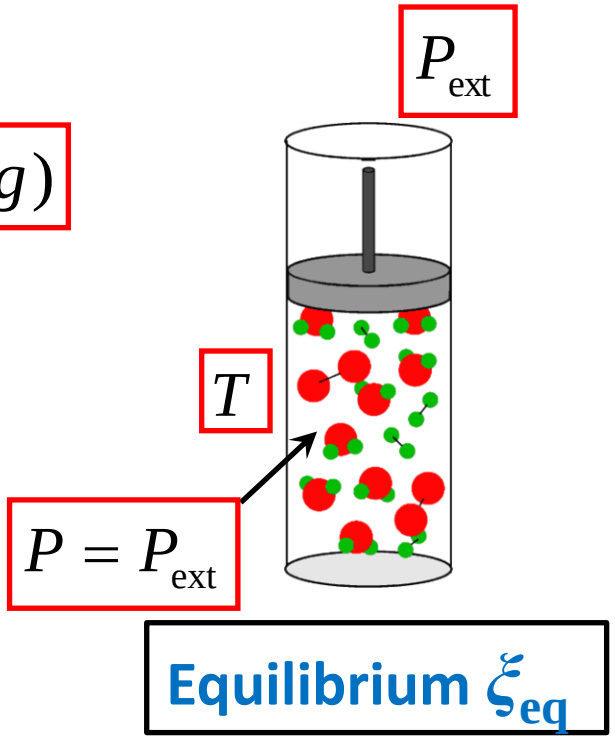




Chemical reaction equilibria

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$$

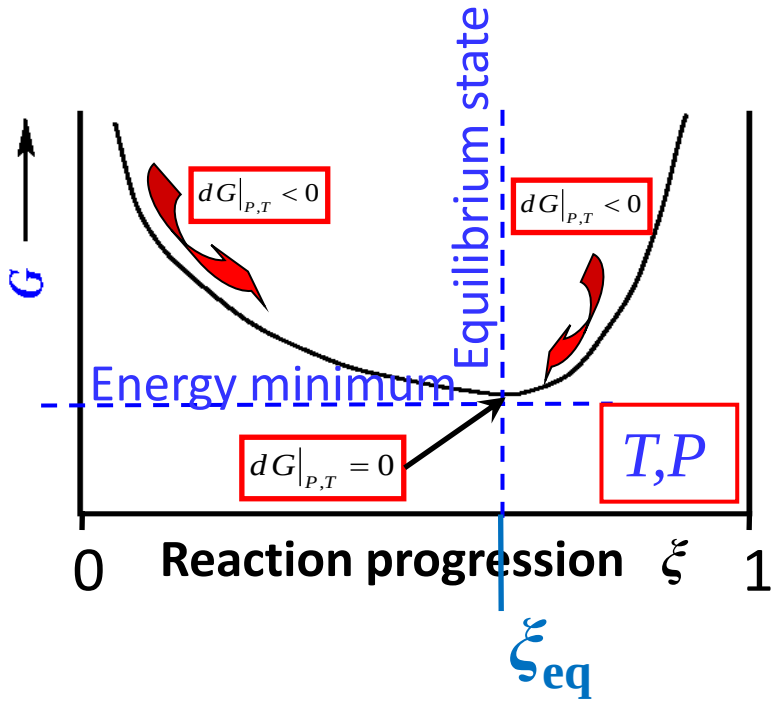


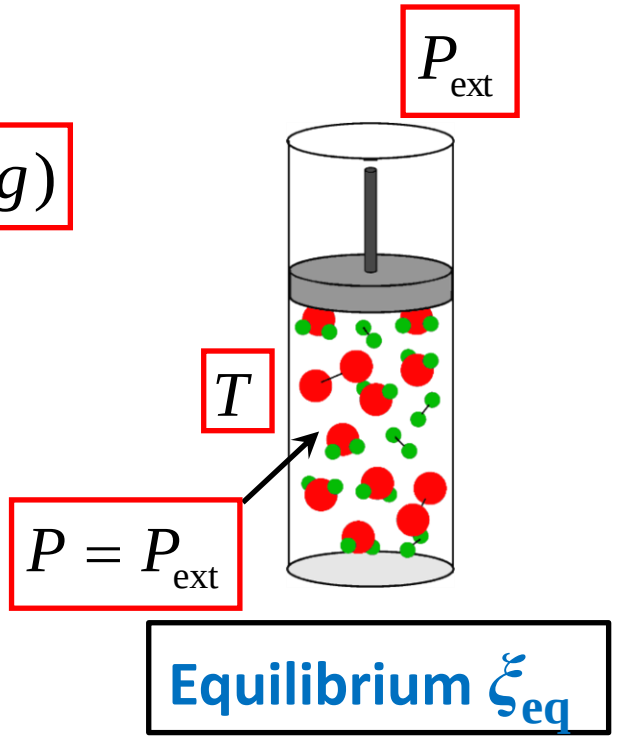


so the second law (entropy) drives the reaction to the equilibrium state

Chemical reaction equilibria

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$$





We have overlooked, however, one detail:

$$n \rightarrow n_{H_2}, n_{O_2}, n_{H_2O}$$

Chemical reaction equilibria

$$2\mathrm{H}_2(\mathrm{g}) + \mathrm{O}_2(g) \leftrightarrow 2\mathrm{H}_2\mathrm{O}(g)$$

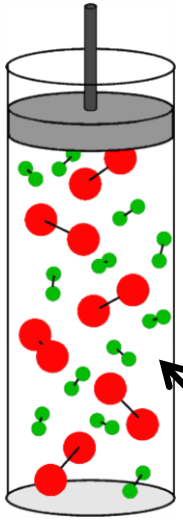
Some new definitions:

- Partial pressure P_i in a mixture of *perfect* (*or real*) gases:

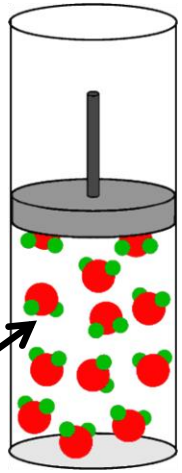
$$P_i \equiv x_i P$$

- Mole fraction x_i of component i :

$$x_i \equiv \frac{n_i}{n} = \frac{n_i}{\sum_j n_j}$$



ξ =0 state



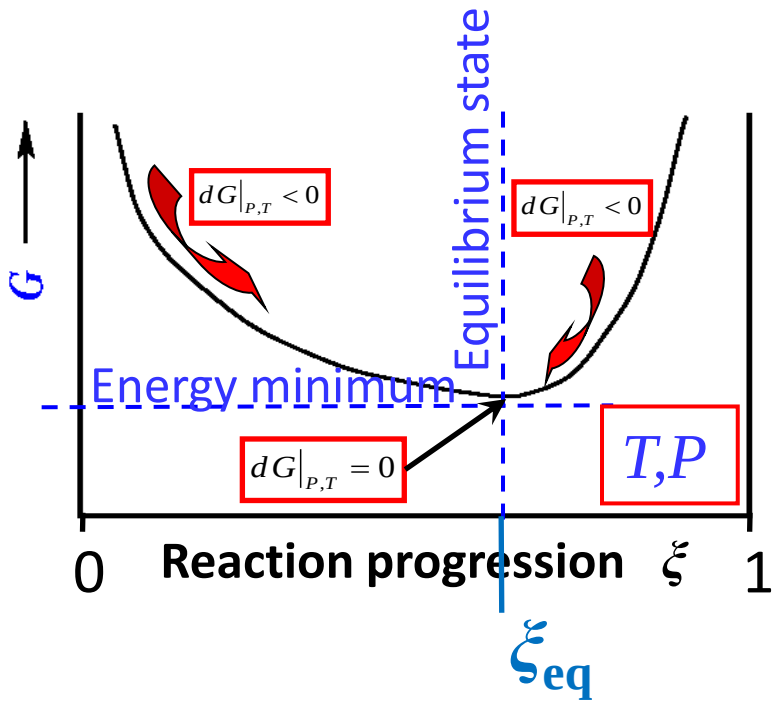
ξ =1 state

$$x_{\mathrm{H}_2} = \frac{n_{\mathrm{H}_2}}{n} = \frac{n_{\mathrm{H}_2}}{n_{\mathrm{H}_2} + n_{\mathrm{O}_2}} = \frac{2}{3}$$

$$x_{\mathrm{H}_2\mathrm{O}} = \frac{n_{\mathrm{H}_2\mathrm{O}}}{n} = \frac{n_{\mathrm{H}_2\mathrm{O}}}{n_{\mathrm{H}_2\mathrm{O}}} = 1$$

Chemical reaction equilibria

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$$

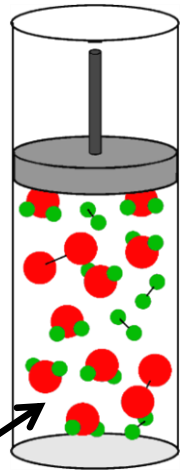


Partial pressure

$$P_i \equiv x_i P$$

Mole fraction

$$x_i = \frac{n_i}{n} = \frac{n_i}{\sum_j n_j}$$



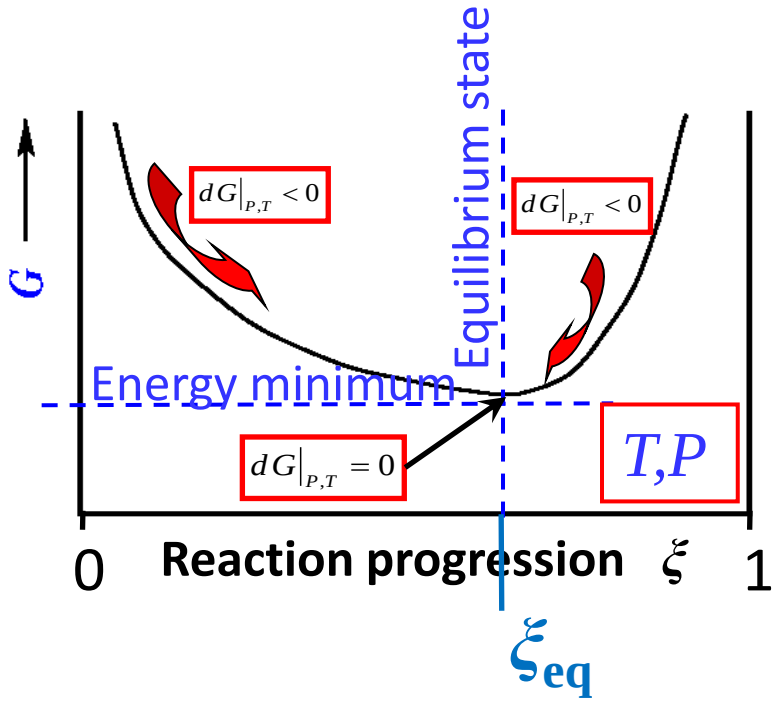
$0 < \xi < 1$ state

$$x_{O_2} = \frac{n_{O_2}}{n} = \frac{n_{O_2}}{n_{H_2} + n_{O_2} + n_{H_2O}} = x_{O_2}(\xi)$$

with $n_i = n_i(\xi)$

Chemical reaction equilibria

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$$



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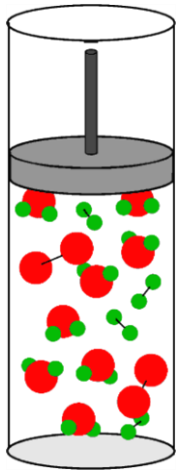


We have additional variables

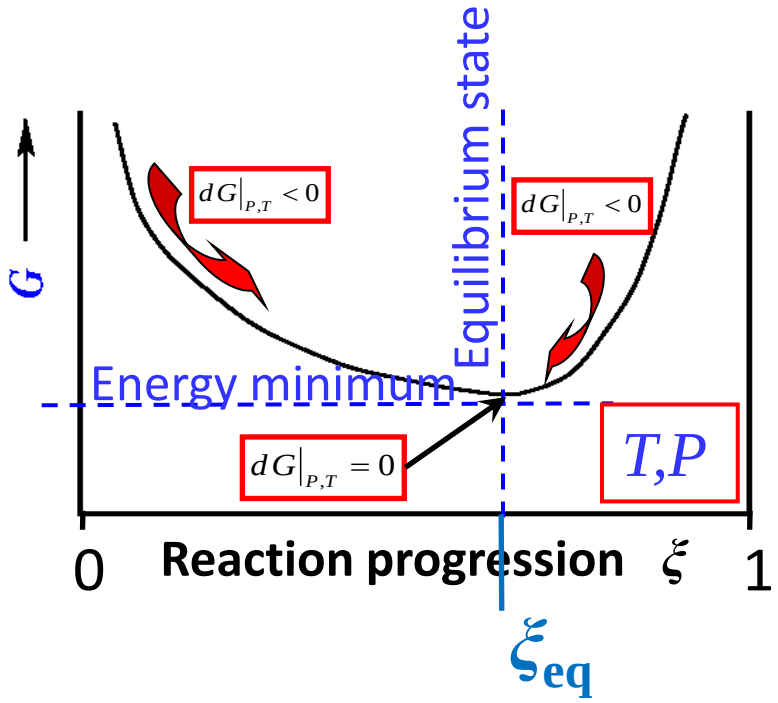
$$n_{O_2} = n_{O_2}(\xi)$$

$$n_{H_2} = n_{H_2}(\xi)$$

$$n_{H_2O} = n_{H_2O}(\xi)$$

Chemical reaction equilibria

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$$



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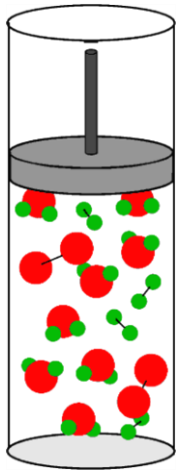
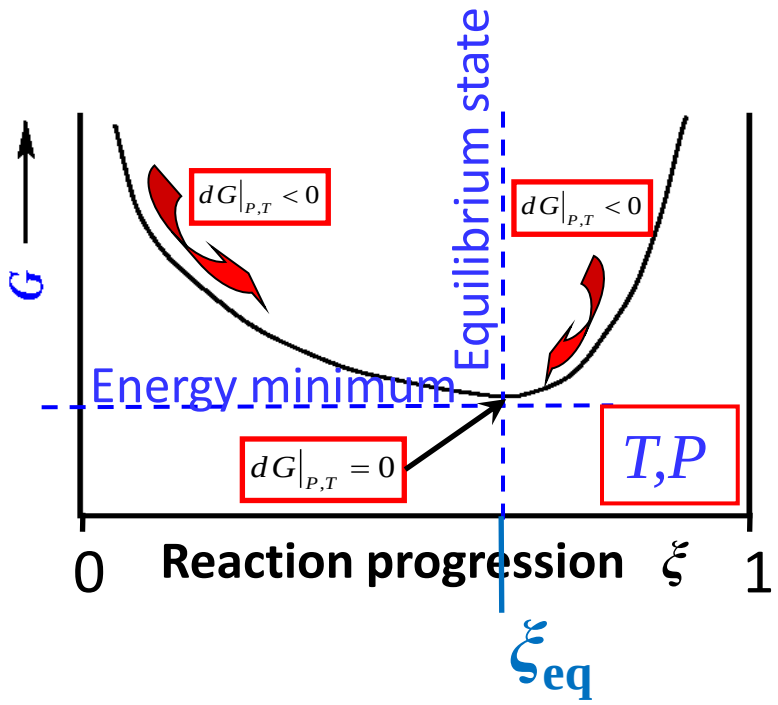


$$dG = -SdT + VdP + \mu_{H_2} dn_{H_2} + \mu_{O_2} dn_{O_2} + \mu_{H_2O} dn_{H_2O}$$

Chemical reaction equilibria

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$$



Partial pressure

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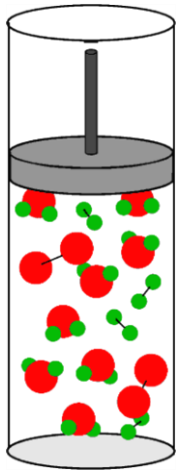


$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

μ_i : The chemical potential of component *i* in the mixture

Chemical reaction equilibria: in general

$$\nu_A A + \nu_B B + \cdots \leftrightarrow \nu_C C + \nu_D D + \cdots$$

reactants **products**

ν_i : stoichiometric constant of component i in the reaction equation

Chemical reaction equilibria: in general

$$\nu_A A + \nu_B B + \cdots \leftrightarrow \nu_C C + \nu_D D + \cdots$$

reactants **products**

$$-\left(\nu_C C + \nu_D D + \cdots\right) + \left(\nu_A A + \nu_B B + \cdots\right) \leftrightarrow 0$$

products **reactants**

Chemical reaction equilibria: in general

$$\nu_A A + \nu_B B + \cdots \leftrightarrow \nu_C C + \nu_D D + \cdots$$

reactants **products**

$$-\left(\nu_C C + \nu_D D + \cdots\right) + \left(\nu_A A + \nu_B B + \cdots\right) \leftrightarrow 0$$

products **reactants**

$$\left(\nu_C C + \nu_D D + \cdots\right) - \left(\nu_A A + \nu_B B + \cdots\right) \leftrightarrow 0$$

products **reactants**

Chemical reaction equilibria: in general

$$\left(\nu_{\mathrm{C}}\mathrm{C} + \nu_{\mathrm{D}}\mathrm{D} + \cdots\right) - \left(\nu_{\mathrm{A}}\mathrm{A} + \nu_{\mathrm{B}}\mathrm{B} + \cdots\right) \leftrightarrow 0$$

products **reactants**

example $2\mathrm{H}_2(\mathrm{g}) + \mathrm{O}_2(g) \leftrightarrow 2\mathrm{H}_2\mathrm{O}(g)$

rewritten: $2\mathrm{H}_2\mathrm{O}(g) - 2\mathrm{H}_2(\mathrm{g}) - \mathrm{O}_2(g) \leftrightarrow 0$

product **reactants**

$\nu_{\mathrm{H_2O}} = 2$ $\nu_{\mathrm{H_2}} = -2$ $\nu_{\mathrm{O_2}} = -1$

Chemical reaction equilibria: in general

$$\nu_A A + \nu_B B + \cdots \leftrightarrow \nu_C C + \nu_D D + \cdots$$

reactants **products**

$$(\nu_C C\ \nu_D D + \cdots) + (-\nu_A A\ -\nu_B B + \cdots) \leftrightarrow 0$$

products **reactants**

$$\sum_i \nu_i I \leftrightarrow 0$$

Products: $\nu_i > 0$

Reactants: $\nu_i < 0$

Chemical reaction equilibria: in general

$$\nu_A A + \nu_B B + \cdots \leftrightarrow \nu_C C + \nu_D D + \cdots$$

$$\sum_i \nu_i I \leftrightarrow 0$$

Products: $\nu_i > 0$

Reactants: $\nu_i < 0$

Chemical reaction equilibria: in general

$$\nu_A A + \nu_B B + \cdots \leftrightarrow \nu_C C + \nu_D D + \cdots$$

$$\sum_i \nu_i I \leftrightarrow 0$$

Products: $\nu_i > 0$

Reactants: $\nu_i < 0$

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

μ_i : The chemical potential of component *i*

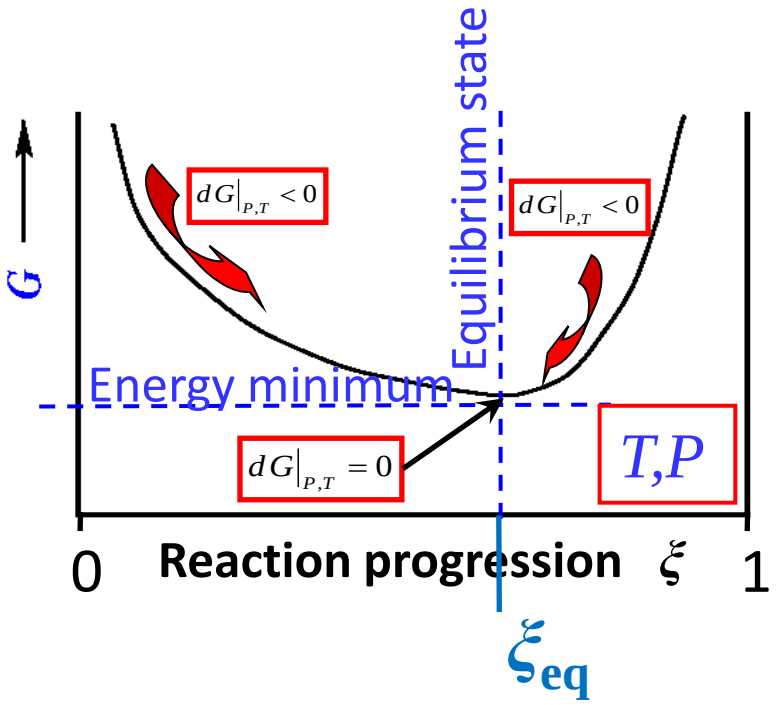
Chemical reaction equilibria: in general

$$\nu_A A + \nu_B B + \cdots \leftrightarrow \nu_C C + \nu_D D + \cdots$$

$$\sum_i \nu_i I \leftrightarrow 0$$

Products: $\nu_i > 0$

Reactants: $\nu_i < 0$



$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

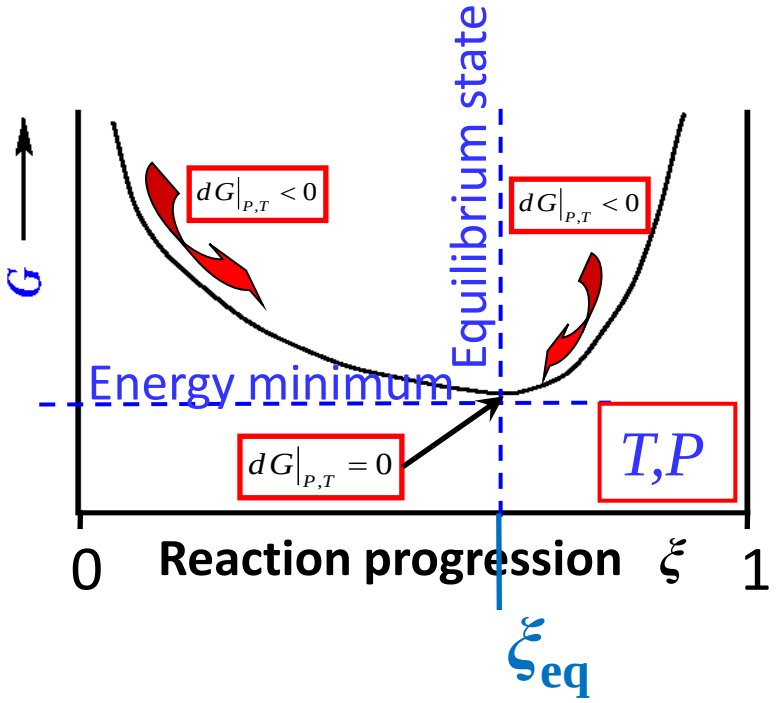
Chemical reaction equilibria: in general

$$\nu_A A + \nu_B B + \cdots \leftrightarrow \nu_C C + \nu_D D + \cdots$$

$$\sum_i \nu_i I \leftrightarrow 0$$

Products: $\nu_i > 0$

Reactants: $\nu_i < 0$



$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

So, where is the minimum of G at the chosen T,P ?

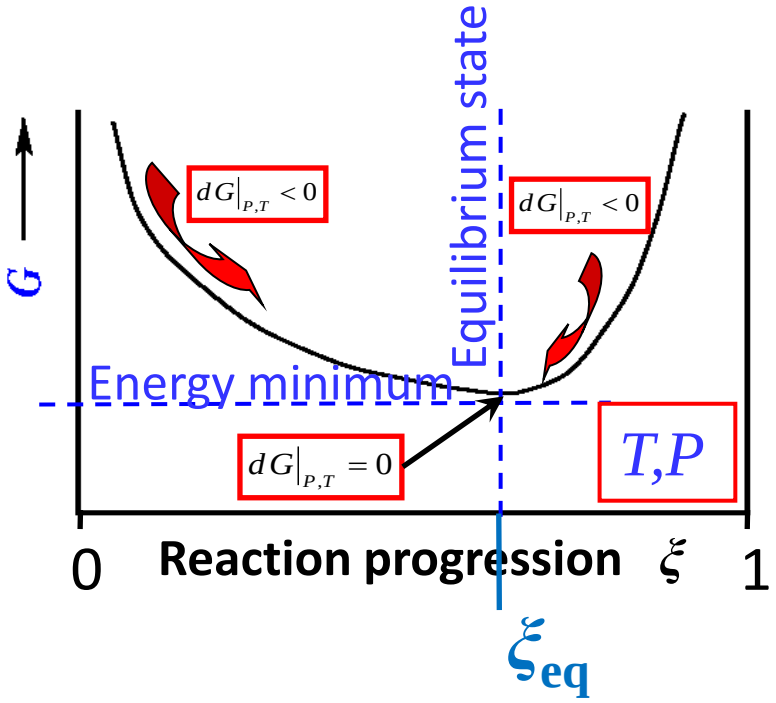
Chemical reaction equilibria: in general

$$\nu_A A + \nu_B B + \cdots \leftrightarrow \nu_C C + \nu_D D + \cdots$$

$$\sum_i \nu_i I \leftrightarrow 0$$

Products: $\nu_i > 0$

Reactants: $\nu_i < 0$



$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

So, where is the minimum of G at the chosen T,P ?

$$dG\big|_{T,P} = \sum_i \mu_i dn_i = 0$$

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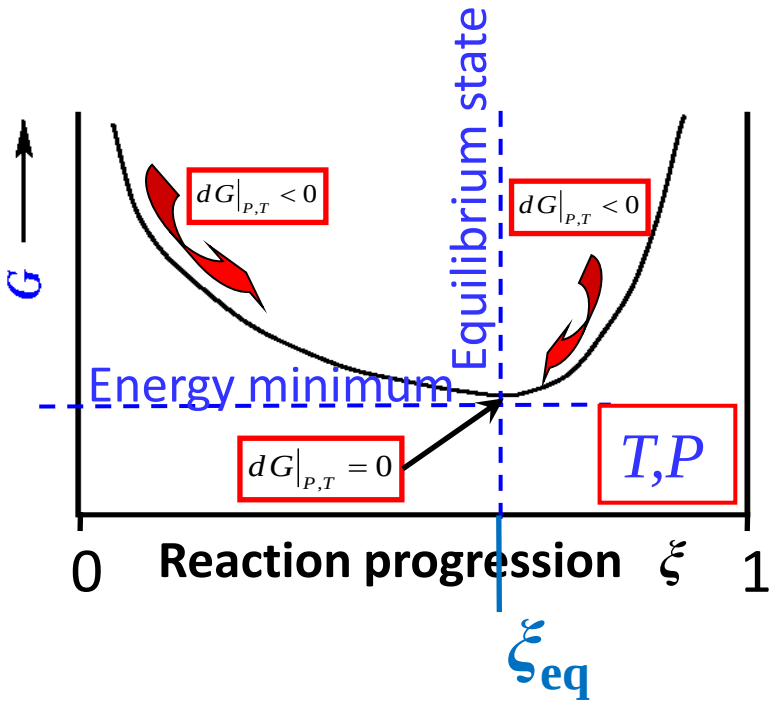
$$\nu_A A + \nu_B B + \cdots \leftrightarrow \nu_C C + \nu_D D + \cdots$$

Equilibrium: ⇒ $dG\big|_{T,P} = \sum_i \mu_i dn_i = 0$



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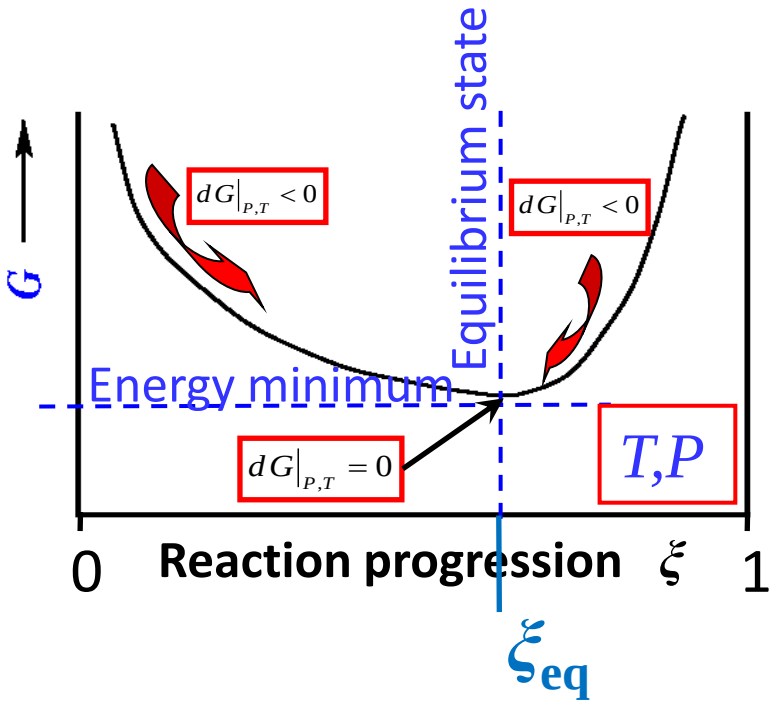

$dn_i = \nu_i d\xi$

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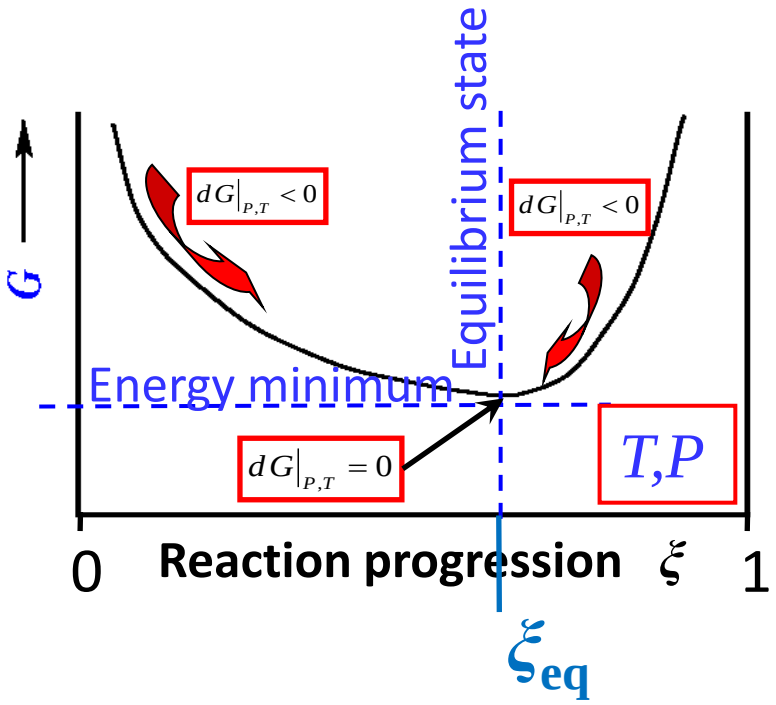

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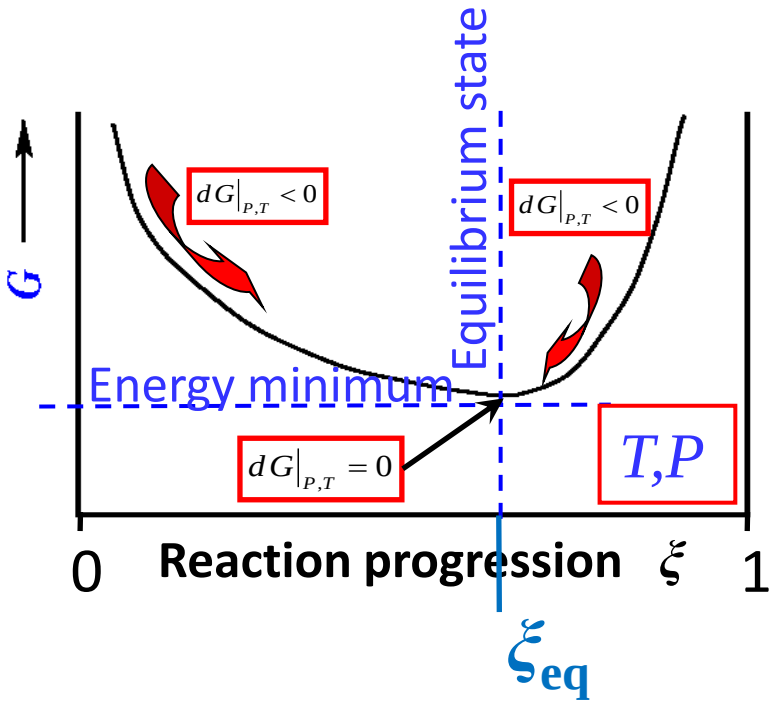

⇒ $$\Delta_r G \equiv \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_i \mu_i \nu_i$$

The reaction Gibbs free energy

Chemical reaction equilibria: in general

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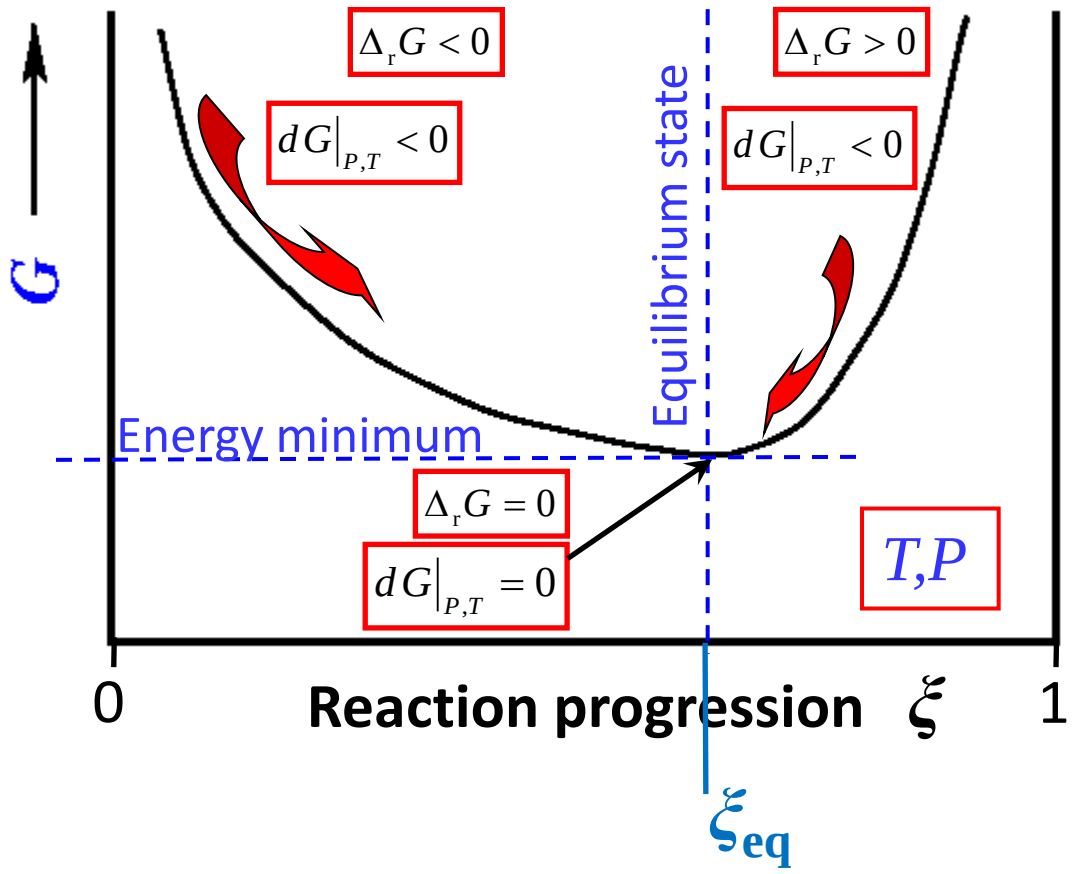

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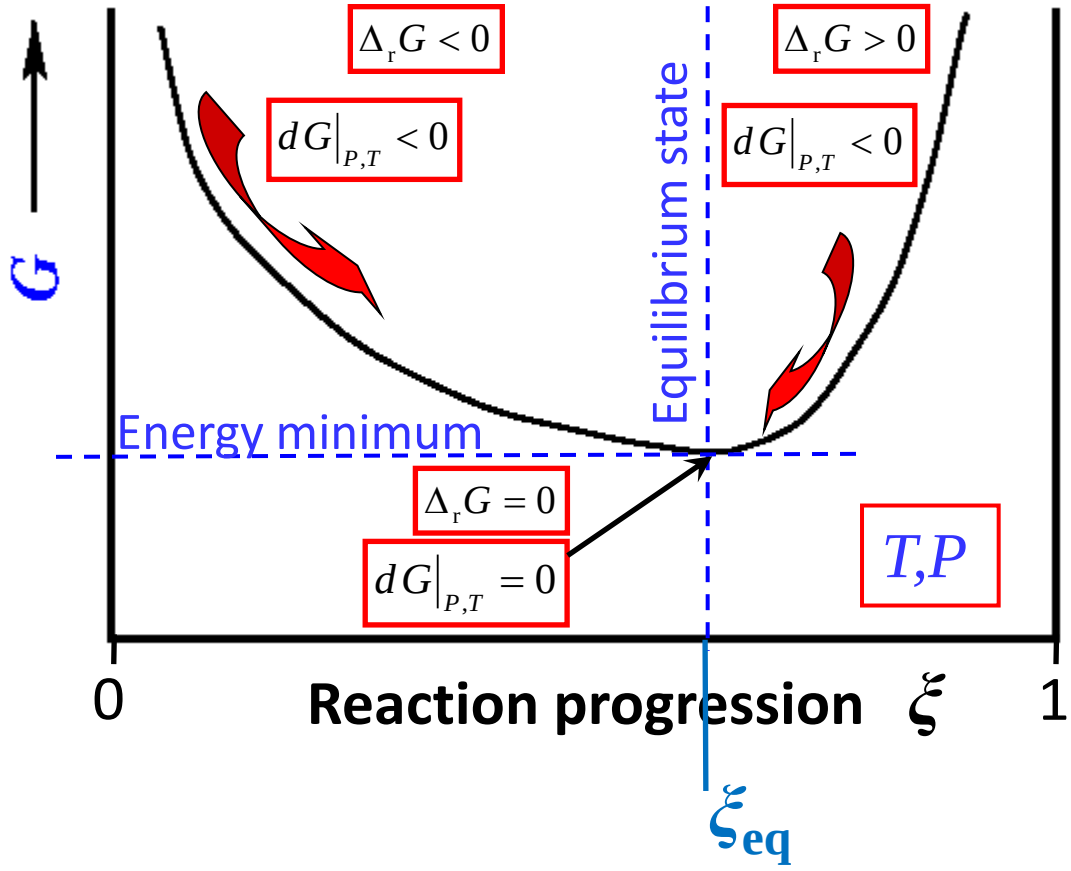

$\Delta_r G$	reaction
$\Delta_r G < 0$	→
$\Delta_r G > 0$	←
$\Delta_r G = 0$	↔ equilibrium

Chemical reaction equilibria: in general

$$\nu_A A + \nu_B B + \cdots \leftrightarrow \nu_C C + \nu_D D + \cdots$$

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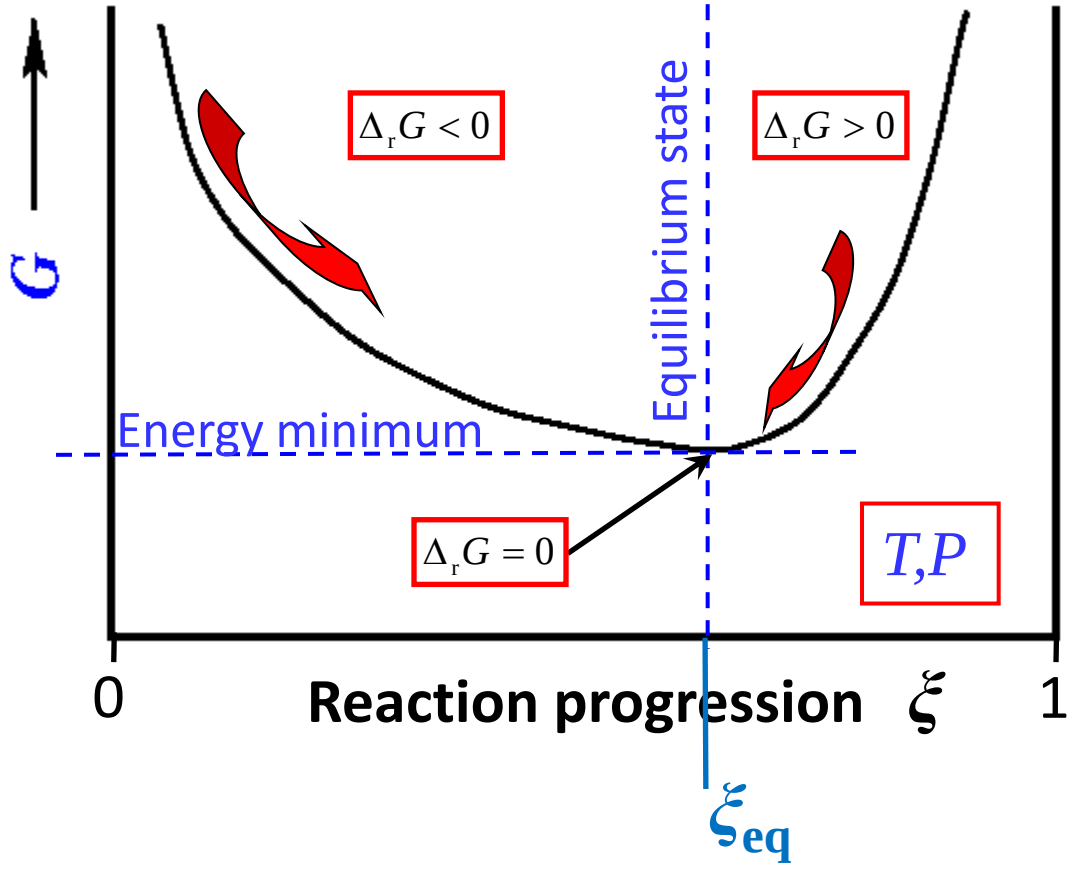

$\Delta_r G$	reaction
$\Delta_r G < 0$	→
$\Delta_r G > 0$	←
$\Delta_r G = 0$	↔ equilibrium

$\mu_i = ?$

Chemical reaction equilibria: perfect gases

$$\nu_A A(g) + \nu_B B(g) + \cdots \leftrightarrow \nu_C C(g) + \nu_D D(g) + \cdots$$

perfect gases ⇒ **The components are mutually independent**

⇒ $G = \sum_i G_i$

$dG = -SdT + VdP + \sum_i \mu_i dn_i$

⇒ $\left(G_{m,i} \equiv \frac{G_i}{n_i} \right)$

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

NB: Only for a mixture of perfect gases

Chemical reaction equilibria: perfect gases

$$\nu_{\mathrm{A}}\mathrm{A}(g)+\nu_{\mathrm{B}}\mathrm{B}(g)+\cdots \leftrightarrow \nu_{\mathrm{C}}\mathrm{C}(g)+\nu_{\mathrm{D}}\mathrm{D}(g)+\cdots$$

Perfect gases → **The components are mutually independent** $\mu_i = G_{\mathrm{m},i}$

→ $\mu_i = G_{\mathrm{m},i} = G_{\mathrm{m},i}(T, P_i)$ **partial pressure for each component**

$$\mu_i\big|_T = G_{\mathrm{m},i}(P_i)\big|_T = \left[\mu_i^{\Theta} + \int_{P^{\Theta}}^{P_i} dG_{\mathrm{m},i}(P)\right]_T = \left[\mu_i^{\Theta} + \int_{P^{\Theta}}^{P_i} V_{\mathrm{m},i}\,dP\right]_T$$

$P^{\Theta} \equiv 1\,\mathrm{bar}$

$dG_{\mathrm{m},i} = -S_{\mathrm{m},i}dT + V_{\mathrm{m},i}dP$

Chemical reaction equilibria: perfect gases

$$\nu_{\mathrm{A}}\mathrm{A}(g) + \nu_{\mathrm{B}}\mathrm{B}(g) + \cdots \leftrightarrow \nu_{\mathrm{C}}\mathrm{C}(g) + \nu_{\mathrm{D}}\mathrm{D}(g) + \cdots$$

Perfect gases ⇒ **The components are mutually independent**

$$\mu_i = G_{\mathrm{m},i}$$

$$\mu_i\big|_T = G_{\mathrm{m},i}(P_i)\big|_T = \left[\mu_i^{\Theta} + \int_{P^{\Theta}}^{P_i} V_{\mathrm{m},i}\,dP\right]_T = \left[\mu_i^{\Theta} + RT\int_{P^{\Theta}}^{P_i}\frac{dP}{P}\right]_T$$

$$PV_{\mathrm{m}} = RT$$

$$\mu_i\big|_T = G_{\mathrm{m},i}(P_i)\big|_T = \left[\mu_i^{\Theta} + RT\ln\frac{P_i}{P^{\Theta}}\right]_T$$

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Perfect gases ➡ **The components are mutually independent**

$$\mu_i = \mu_i^{\Theta} + RT \ln \frac{P_i}{P^{\Theta}}$$

The chemical potential of a component *i* with partial pressure P_i in a perfect gas mixture @ T

Θ {
- $P = P^{\Theta} \equiv 1$ bar (standard pressure)
- component *i* is pure (as if it is not in a mixture)

➡ $\mu_i^{\Theta} = \mu_i^{\Theta}(T)$

Chemical reaction equilibria: perfect gases

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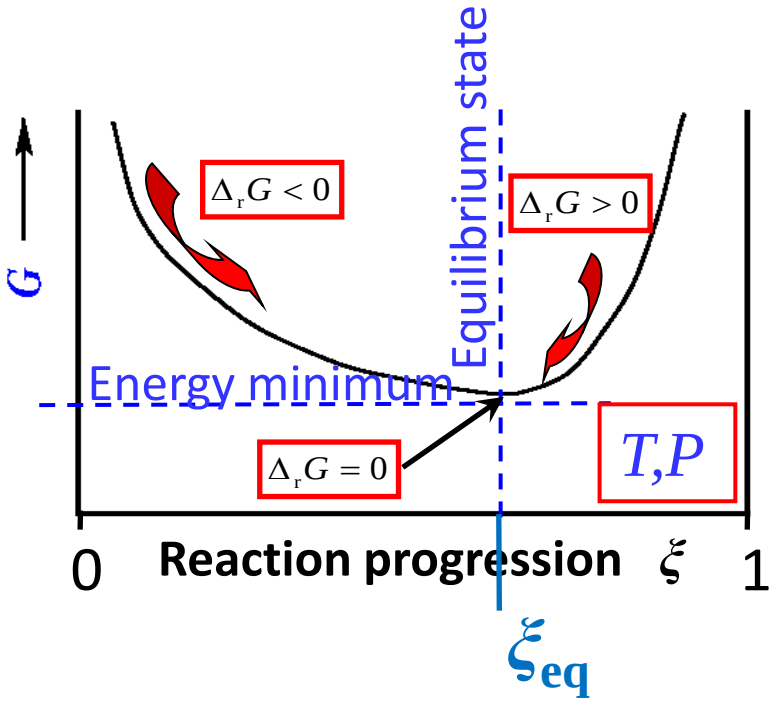

$$\Delta_r G \equiv \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_i \mu_i \nu_i$$

The reaction Gibbs free energy

$$\mu_i = \mu_i^{\Theta} + RT \ln \frac{P_i}{P^{\Theta}}$$

The chemical potential of a perfect gas component *i*

Chemical reaction equilibria: perfect gases

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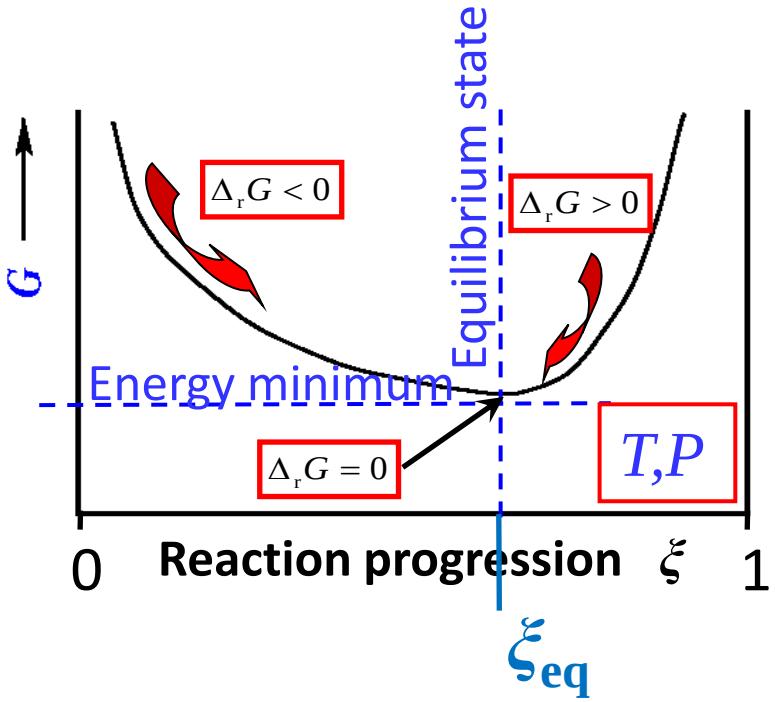

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The reaction Gibbs free energy

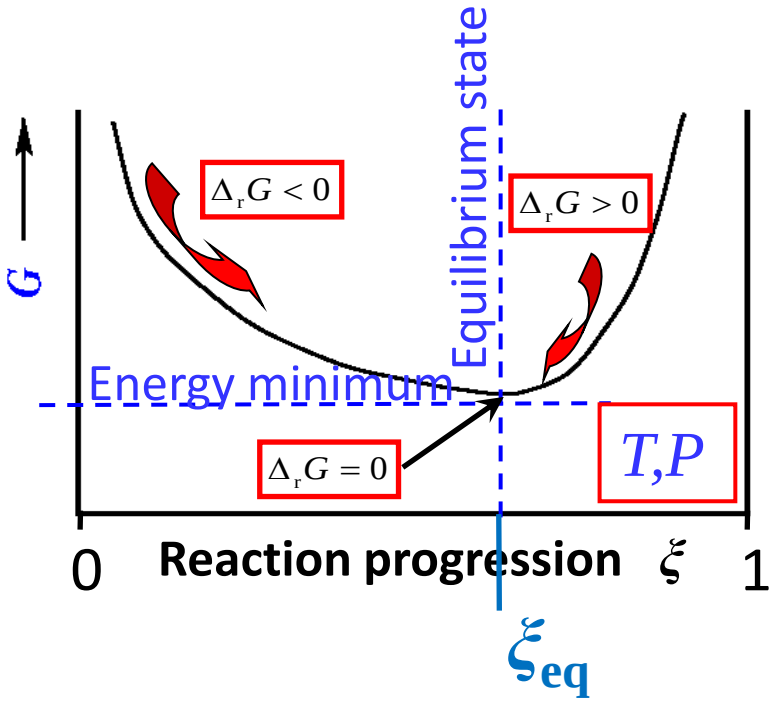
$$\mu_i = \mu_i^{\Theta} + RT \ln \frac{P_i}{P^{\Theta}}$$

The chemical potential of perfect gas component *i*

$$\Delta_r G = \sum_i \mu_i \nu_i = \sum_i \nu_i \mu_i^{\Theta} + \sum_i \nu_i RT \ln \frac{P_i}{P^{\Theta}}$$

Chemical reaction equilibria: perfect gases

$$\nu_A A(g) + \nu_B B(g) + \cdots \leftrightarrow \nu_C C(g) + \nu_D D(g) + \cdots$$



$$\Delta_r G = \sum_i \nu_i \mu_i^{\Theta} + RT \sum_i \nu_i \ln \frac{P_i}{P^{\Theta}}$$

$$\equiv \Delta_r G^{\Theta} \qquad \equiv RT \ln Q$$

Reaction quotient for perfect gases

$$Q \equiv \prod_i \left(\frac{P_i}{P^{\Theta}} \right)^{\nu_i}$$

$$\Delta_r G = \Delta_r G^{\Theta} + RT \ln Q$$

Chemical reaction equilibria: perfect gases

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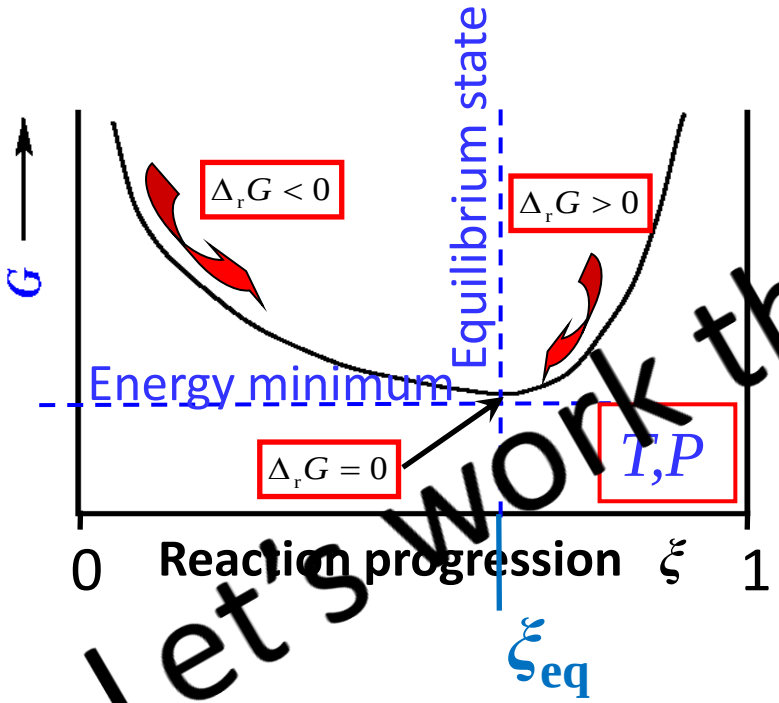

$$\Delta_r G = \sum_i \nu_i \mu_i + RT \sum_i \nu_i \ln \frac{P_i}{P^\Theta}$$

$$\equiv \Delta_r G^\Theta \qquad \equiv RT \ln Q$$

Let's work this out in detail

Reaction quotient for perfect gases

$$Q \equiv \prod_i \left(\frac{P_i}{P^\Theta} \right)^{\nu_i}$$

$$\Delta_r G = \Delta_r G^\Theta + RT \ln Q$$

Chemical reaction equilibria: perfect gases

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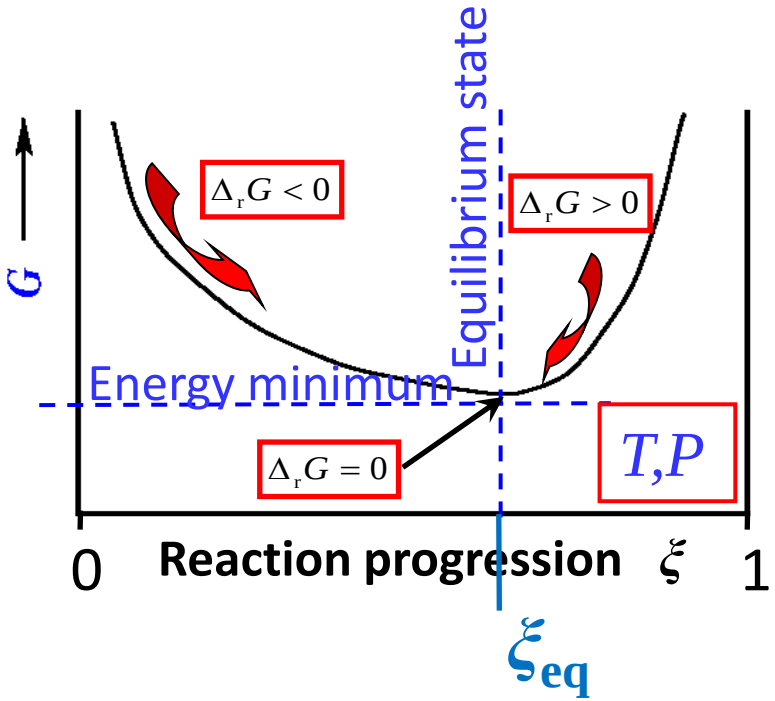

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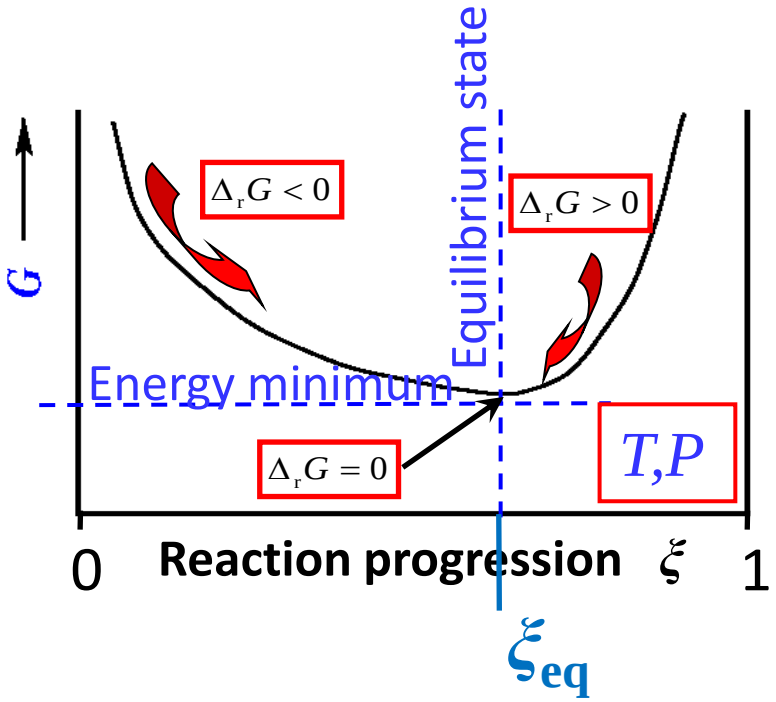


$$\Delta_r G = \Delta_r G^{\Theta} + RT \ln Q$$

Reaction quotient for perfect gases

$$Q \equiv \prod_i \left(\frac{P_i}{P^{\Theta}} \right)^{\nu_i}$$

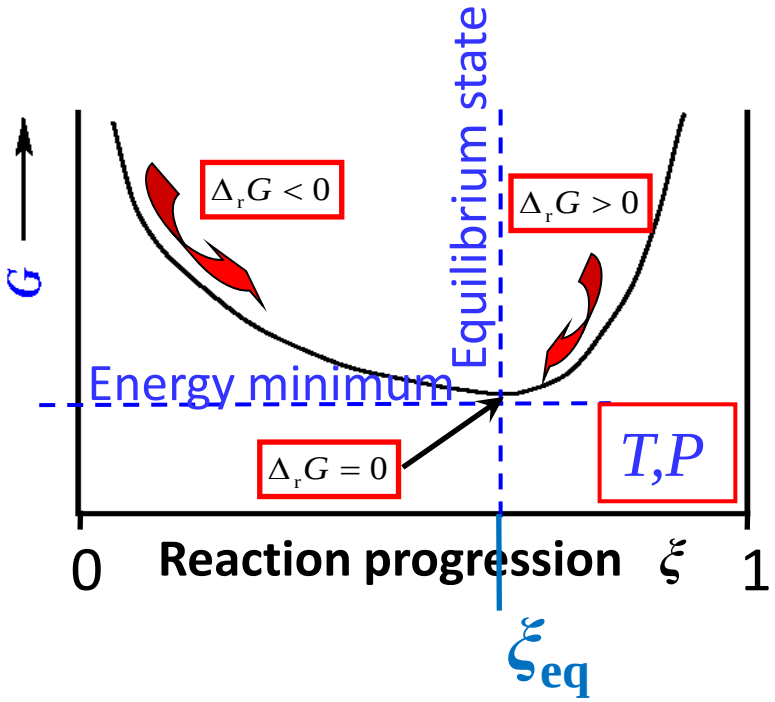
$$\Delta_r G = 0 \quad \Rightarrow \quad \Delta_r G^{\Theta} = -RT \ln Q_{eq} \equiv -RT \ln K$$

Equilibrium ξ_{eq}

Equilibrium constant: K

Chemical reaction equilibria: perfect gases

$$\nu_A A(g) + \nu_B B(g) + \cdots \leftrightarrow \nu_C C(g) + \nu_D D(g) + \cdots$$



$$\Delta_r G = \Delta_r G^{\Theta} + RT \ln Q$$

Reaction quotient for perfect gases

$$Q \equiv \prod_i \left(\frac{P_i}{P^{\Theta}} \right)^{\nu_i}$$

Non-equilibrium ξ

$$\Delta_r G = 0 \quad \Rightarrow \quad \Delta_r G^{\Theta} = -RT \ln Q_{eq} \equiv -RT \ln K$$

Equilibrium ξ_{eq}

Equilibrium constant: K

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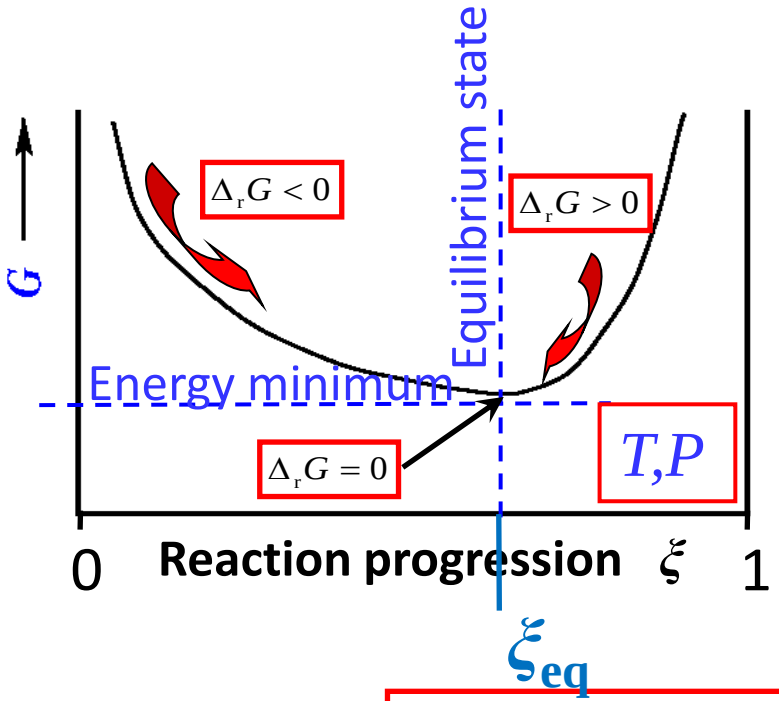


$$-RT \ln Q_{eq} \equiv -RT \ln K = \Delta_r G^{\Theta}$$

Equilibrium constant: K

equilibrium reaction quotient for perfect gases

$$K \equiv \prod_i \left(\frac{P_i}{P^{\Theta}} \right)_{eq}^{\nu_i}$$

$$\Delta_r G^{\Theta} = \sum_i \nu_i \mu_i^{\Theta} = \sum_i \nu_i G_{m,i}^{\Theta} = \sum_i \nu_i \Delta_f G_{m,i}^{\Theta}$$

Θ : pure component i

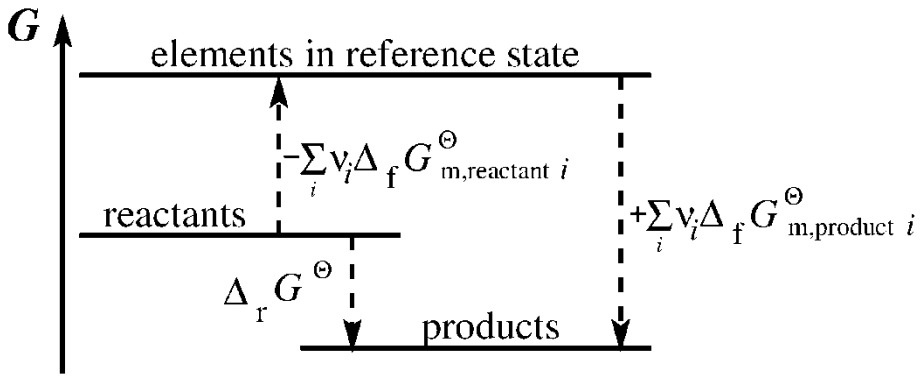
G is state function

Chemical reaction equilibria: perfect gases

$$\nu_A A(g) + \nu_B B(g) + \cdots \leftrightarrow \nu_C C(g) + \nu_D D(g) + \cdots$$

$$-RT \ln K = \Delta_r G^\Theta \quad \textbf{with} \quad \Delta_r G^\Theta = \sum_i \nu_i G^\Theta_{m,i} = \sum_i \nu_i \Delta_f G^\Theta_{m,i}$$

Standard formation molar Gibbs free energy $\Delta_f G^\Theta_{m,i}$



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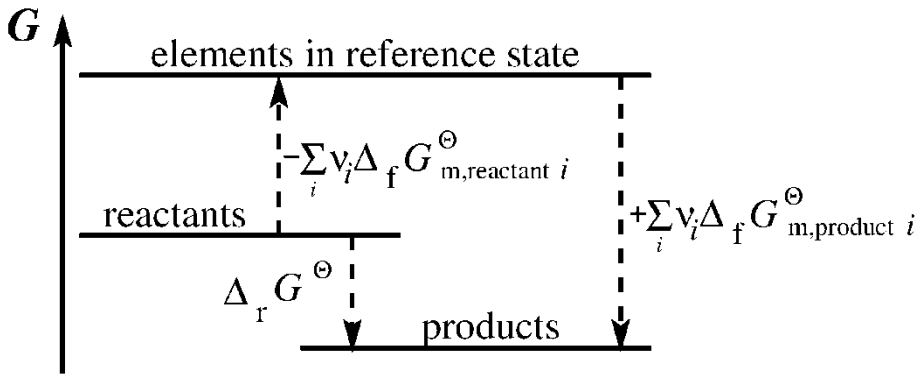

$$K = \exp\left[-\frac{\Delta_r G^\Theta}{RT}\right]$$

Chemical reaction equilibria: perfect gases

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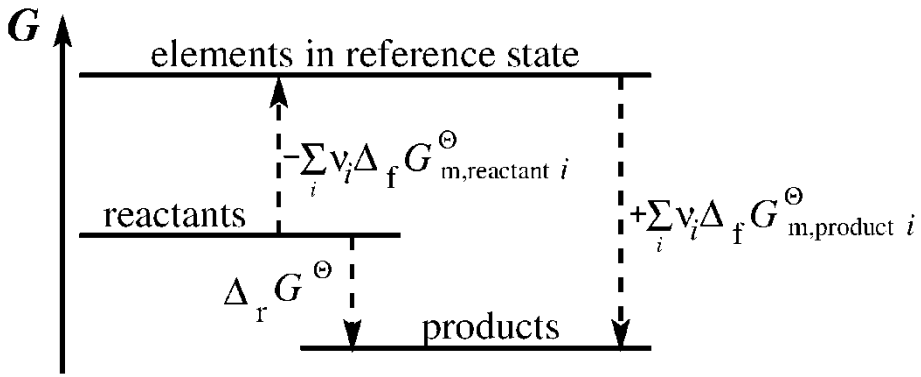


Reference states (T):

$H_2O(400\,K) : H_2O(g)$

$H_2O(300\,K) : H_2O(l)$

$H(400\,K) : H_2(g)$

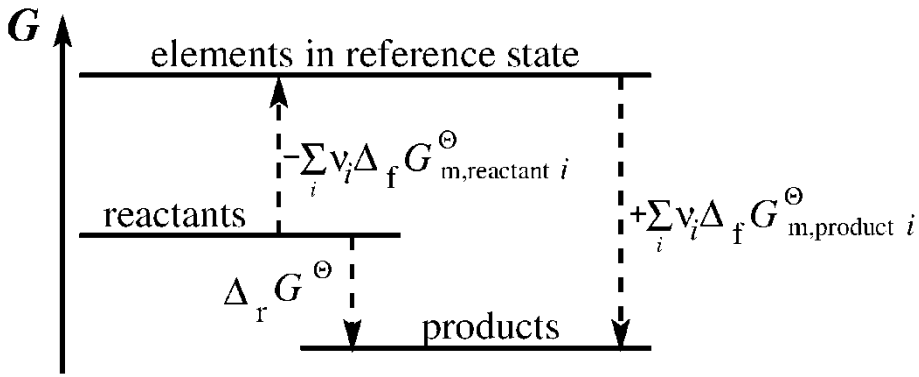
$C(400\,K) : C(s)$

Chemical reaction equilibria: perfect gases

$$\nu_A A(g) + \nu_B B(g) + \cdots \leftrightarrow \nu_C C(g) + \nu_D D(g) + \cdots$$

$$K = \exp\left[-\frac{\Delta_r G^\Theta}{RT}\right] \quad \textbf{with} \quad \Delta_r G^\Theta = \sum_i \nu_i G^\Theta_{m,i} = \sum_i \nu_i \Delta_f G^\Theta_{m,i}$$

Standard formation molar Gibbs free energy $\Delta_f G^\Theta_{m,i}$



Reference states (T):

$$\Delta_f G^\Theta_{m,H_2O}(400\,\text{K}, g) \neq 0$$

$$\Delta_f G^\Theta_{m,H_2O}(300\,\text{K}, l) \neq 0$$

$$\Delta_f G^\Theta_{m,H_2}(400\,\text{K}, g) \equiv 0$$

$$\Delta_f G^\Theta_{m,C}(400\,\text{K}, s) \equiv 0$$

Chemical reaction equilibria: perfect gases

	M/(g mol^{-1})	$\Delta_f H^\ominus$/(kJ mol^{-1})	$\Delta_f G^\ominus$/(kJ mol^{-1})	$S_m^\ominus$/(J K^{-1} mol^{-1})†	$C_{p,m}^\ominus$/(J K^{-1} mol^{-1}
Fluorine					
F_2(g)	38.00	0	0	202.78	31.30
F(g)	19.00	+78.99	+61.91	158.75	22.74
F^-(aq)	19.00	−332.63	−278.79	−13.8	−106.7
HF(g)	20.01	−271.1	−273.2	173.78	29.13
Gold					
Au(s)	196.97	0	0	47.40	25.42
Au(g)	196.97	+366.1	+326.3	180.50	20.79
Helium					
He(g)	4.003	0	0	126.15	20.786
Hydrogen (see also deuterium)					
H_2(g)	2.016	0	0	130.684	28.824
H(g)	1.008	+217.97	+203.25	114.71	20.784
H^+(aq)	1.008	0	0	0	0
H^+(g)	1.008	+1536.20			
H_2O(s)	18.015			37.99	
H_2O(l)	18.015	−285.83	−237.13	69.91	75.291
H_2O(g)	18.015	−241.82	−228.57	188.83	33.58
H_2O_2(l)	34.015	−187.78	−120.35	109.6	89.1
Iodine					
I_2(s)	253.81	0	0	116.135	54.44
I_2(g)	253.81	+62.44	+19.33	260.69	36.90
I(g)	126.90	+106.84	+70.25	180.79	20.786
I^-(aq)	126.90	−55.19	−51.57	+111.3	−142.3
HI(g)	127.91	+26.48	+1.70	206.59	29.158
Iron					
Fe(s)	55.85	0	0	27.28	25.10
Fe(g)	55.85	+416.3	+370.7	180.49	25.68
Fe^{2+}(aq)	55.85	−89.1	−78.90	−137.7	
Fe^{3+}(aq)	55.85	−48.5	−4.7	−315.9	
Fe_3O_4(s) (magnetite)	231.54	−1118.4	−1015.4	146.4	143.43
Fe_2O_3(s) (haematite)	159.69	−824.2	−742.2	87.40	103.85
FeS(s, α)	87.91	−100.0	−100.4	60.29	50.54
FeS_2(s)	119.98	−178.2	−166.9	52.93	62.17
Krypton					
Kr(g)	83.80	0	0	164.08	20.786
Lead					
Pb(s)	207.19	0	0	64.81	26.44
Pb(g)	207.19	+195.0	+161.9	175.37	20.79
Pb^{2+}(aq)	207.19	−1.7	−24.43	+10.5	
PbO(s, yellow)	223.19	−217.32	−187.89	68.70	45.77
PbO(s, red)	223.19	−218.99	−188.93	66.5	45.81
PbO_2(s)	239.19	−277.4	−217.33	68.6	64.64

← **specified @ 298 K**

← $\Delta_f G_m^\Theta \equiv 0 \,@\, T(\mathrm{H_2(g)})$

← $\Delta_f G_m^\Theta(\mathrm{H_2O}(l)) \neq 0$

← $\Delta_f G_m^\Theta \equiv 0 \,@\, T(\mathrm{Fe}(s))$

Chemical reaction equilibria: perfect gases

	M/(g mol^{-1})	$\Delta_f H^\circ$/(kJ mol^{-1})	$\Delta_f G^\circ$/(kJ mol^{-1})	S_m°/(J K^{-1} mol^{-1})†	$C_{p,m}^\circ$/(J K^{-1} mol^{-1}
Fluorine					
F_2(g)	38.00	0	0	202.78	31.30
F(g)	19.00	+78.99	+61.91	158.75	22.74
F^-(aq)	19.00	−332.63	−278.79	−13.8	−106.7
HF(g)	20.01	−271.1	−273.2	173.78	29.13
Gold					
Au(s)	196.97	0	0	47.40	25.42
Au(g)	196.97	+366.1	+326.3	180.50	20.79
Helium					
He(g)	4.003	0	0	126.15	20.786
Hydrogen (see also deuterium)					
H_2(g)	2.016	0	0	130.684	28.824
H(g)	1.008	+217.97	+203.25	114.71	20.784
H^+(aq)	1.008	0	0	0	0
H^+(g)	1.008	+1536.20			
H_2O(s)	18.015			37.99	
H_2O(l)	18.015	−285.83	−237.13	69.91	75.291
H_2O(g)	18.015	−241.82	−228.57	188.83	33.58
H_2O_2(l)	34.015	−187.78	−120.35	109.6	89.1
Iodine					
I_2(s)	253.81	0	0	116.135	54.44
I_2(g)	253.81	+62.44	+19.33	260.69	36.90
I(g)	126.90	+106.84	+70.25	180.79	20.786
I^-(aq)	126.90	−55.19	−51.57	+111.3	−142.3
HI(g)	127.91	+26.48	+1.70	206.59	29.158
Iron					
Fe(s)	55.85	0	0	27.28	25.10
Fe(g)	55.85	+416.3	+370.7	180.49	25.68
Fe^{2+}(aq)	55.85	−89.1	−78.90	−137.7	
Fe^{3+}(aq)	55.85	−48.5	−4.7	−315.9	
Fe_3O_4(s) (magnetite)	231.54	−1118.4	−1015.4	146.4	143.43
Fe_2O_3(s) (haematite)	159.69	−824.2	−742.2	87.40	103.85
FeS(s, α)	87.91	−100.0	−100.4	60.29	50.54
FeS_2(s)	119.98	−178.2	−166.9	52.93	62.17
Krypton					
Kr(g)	83.80	0	0	164.08	20.786
Lead					
Pb(s)	207.19	0	0	64.81	26.44
Pb(g)	207.19	+195.0	+161.9	175.37	20.79
Pb^{2+}(aq)	207.19	−1.7	−24.43	+10.5	
PbO(s, yellow)	223.19	−217.32	−187.89	68.70	45.77
PbO(s, red)	223.19	−218.99	−188.93	66.5	45.81
PbO_2(s)	239.19	−277.4	−217.33	68.6	64.64

← **specified @ 298 K**

← $\Delta_f H_m^\Theta \equiv 0 \,@\, T(\mathrm{H_2(g)})$

← $\Delta_f H_m^\Theta(\mathrm{H_2O}(l)) \neq 0$

← $\Delta_f H_m^\Theta \equiv 0 \,@\, T(\mathrm{Fe}(s))$

Chemical reaction equilibria: example

$$2\mathrm{H}_2(\mathrm{g}) + \mathrm{O}_2(g) \leftrightarrow 2\mathrm{H}_2\mathrm{O}(l)$$

298 K

Elements in reference states (*T*)

$$\Delta_\mathrm{f} G^{\Theta}_{\mathrm{m},\mathrm{H}_2}(298\,\mathrm{K}, g) \equiv 0$$

$$\Delta_\mathrm{f} G^{\Theta}_{\mathrm{m},\mathrm{O}_2}(298\,\mathrm{K}, g) \equiv 0$$

$$\Delta_\mathrm{f} G^{\Theta}_{\mathrm{m},\mathrm{H}_2\mathrm{O}}(298\,\mathrm{K}, l) = -237.13\,\mathrm{kJ/mol}$$

$$\Delta_\mathrm{r} G^{\Theta} = \sum_i \nu_i \Delta_\mathrm{f} G^{\Theta}_{\mathrm{m},i} = +2\cdot(-237.15) - 2\cdot 0 - 1\cdot 0 = -474.30\,\mathrm{kJ/mol}$$

product **reactants**

$$K = \exp\left[-\frac{\Delta_\mathrm{r} G^{\Theta}}{RT}\right] = \exp\left[-\frac{-474.30\cdot 10^3}{8.314\cdot 298}\right] = 1.4\cdot 10^{83}$$

As expected: completely on the right hand side

Chemical reaction equilibria: perfect gases

$$2\mathrm{H_2(g)} + \mathrm{O_2}(g) \leftrightarrow 2\mathrm{H_2O}(l)$$

$$323\,\mathrm{K}$$

$$(50\,^{\circ}\mathrm{C})$$

Elements in reference states (*T*)

$$\Delta_f G^{\Theta}_{m,H_2}(323\mathrm{K}, g) \equiv 0$$

$$\Delta_f G^{\Theta}_{m,O_2}(323\mathrm{K}, g) \equiv 0$$

$$\Delta_f G^{\Theta}_{m,H_2O}(323\mathrm{K}, l) = ?$$

(tables refer to 298 K)

$$\Delta_f G^{\Theta}_{m,i} = \Delta_f H^{\Theta}_{m,i} - T\Delta_f S^{\Theta}_{m,i}$$

at constant, chosen *T*

and assume that $\Delta_f H^{\Theta}_{m,i}$ and $\Delta_f S^{\Theta}_{m,i}$ **are weakly dependent on *T***

$$\Delta_f G^{\Theta}_{m,i}(323K) \approx \Delta_f H^{\Theta}_{m,i}(298K) - 323K \cdot \Delta_f S^{\Theta}_{m,i}(298K)$$

Chemical reaction equilibria: perfect gases

$$2\mathrm{H_2(g)} + \mathrm{O_2}(g) \leftrightarrow 2\mathrm{H_2O}(l)$$

$$323\,\mathrm{K} \quad (50\,^{\circ}\mathrm{C})$$

Elements in reference states (*T*)

$$\Delta_f G^{\Theta}_{\mathrm{m},\mathrm{H_2}}(323\,\mathrm{K}, g) \equiv 0$$

$$\Delta_f G^{\Theta}_{\mathrm{m},\mathrm{O_2}}(323\,\mathrm{K}, g) \equiv 0$$

$$\Delta_f H^{\Theta}_{\mathrm{m},\mathrm{H_2O}}(298\,\mathrm{K}, l) = -285.83\,\mathrm{kJ/mol}$$

$$\Delta_f S^{\Theta}_{\mathrm{m},\mathrm{H_2O}}(298\,\mathrm{K}, l) = ?$$

(tables: $S^{\Theta}_{\mathrm{m},\mathrm{H_2O}}(298\,\mathrm{K}, l)$)

$$\Delta_f G^{\Theta}_{\mathrm{m},\mathrm{H_2O}}(298\,\mathrm{K}, l) = -237.13\,\mathrm{kJ/mol}$$

assume that $\Delta_f H^{\Theta}_{\mathrm{m},i}$ and $\Delta_f S^{\Theta}_{\mathrm{m},i}$ **are weakly dependent on** T

$$\Delta_f G^{\Theta}_{\mathrm{m},i}(323\,K) \approx \Delta_f H^{\Theta}_{\mathrm{m},i}(298\,K) - 323\,K \cdot \Delta_f S^{\Theta}_{\mathrm{m},i}(298\,K)$$

Chemical reaction equilibria: perfect gases

$$2\mathrm{H_2(g)} + \mathrm{O_2}(g) \leftrightarrow 2\mathrm{H_2O}(l)$$

$$323\,\mathrm{K} \quad (50\,^{\circ}\mathrm{C})$$

Elements in reference states (*T*)

$$\Delta_f G^{\Theta}_{m,H_2}(323\,\mathrm{K}, g) \equiv 0$$

$$\Delta_f G^{\Theta}_{m,O_2}(323\,\mathrm{K}, g) \equiv 0$$

$$\Delta_f H^{\Theta}_{m,H_2O}(298\,\mathrm{K}, l) = -285.83\,\mathrm{kJ/mol}$$

$$\Delta_f S^{\Theta}_{m,H_2O}(298\,\mathrm{K}, l) = ?$$

$$\Delta_f G^{\Theta}_{m,H_2O}(298\,\mathrm{K}, l) = -237.13\,\mathrm{kJ/mol}$$

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

At constant, chosen T

$$\Delta_f S^{\Theta}_{m,H_2O}(298\,\mathrm{K}, l) = \frac{\Delta_f H^{\Theta}_{m,H_2O}(298\,\mathrm{K}, l) - \Delta_f G^{\Theta}_{m,H_2O}(298\,\mathrm{K}, l)}{298\,\mathrm{K}}$$

$$\Delta_f S^{\Theta}_{m,H_2O}(298\,\mathrm{K}, l) = -163\,\mathrm{J/mol\ K}$$

Chemical reaction equilibria: perfect gases

$$2\mathrm{H_2(g)} + \mathrm{O_2}(g) \leftrightarrow 2\mathrm{H_2O}(l)$$

$$323\,\mathrm{K} \quad (50\,^{\circ}\mathrm{C})$$

Elements in reference states (*T*)

$$\Delta_f G^{\Theta}_{m,H_2}(323\,\mathrm{K}, g) \equiv 0$$

$$\Delta_f G^{\Theta}_{m,O_2}(323\,\mathrm{K}, g) \equiv 0$$

$$\Delta_f H^{\Theta}_{m,H_2O}(298\,\mathrm{K}, l) = -285.83\,\mathrm{kJ/mol}$$

$$\Delta_f S^{\Theta}_{m,H_2O}(298\,\mathrm{K}, l) = -163\,\mathrm{J/mol\,K}$$

$$\Delta_f G^{\Theta}_{m,H_2O}(298\,\mathrm{K}, l) = -237.13\,\mathrm{kJ/mol}$$

assume that $\Delta_f H^{\Theta}_{m,i}$ and $\Delta_f S^{\Theta}_{m,i}$ **are weakly dependent on** T

$$\Delta_f G^{\Theta}_{m,i}(323\,K) \approx \Delta_f H^{\Theta}_{m,i}(298\,K) - 323\,K \cdot \Delta_f S^{\Theta}_{m,i}(298\,K)$$

$$\Delta_f G^{\Theta}_{m,H_2O}(323\,\mathrm{K}, l) \approx -233.2\,\mathrm{kJ/mol}$$

Chemical reaction equilibria: example

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(l)$$ 298 K

$$K = \exp\left[-\frac{\Delta_r G^\Theta}{RT}\right] = \exp\left[-\frac{-474.30 \cdot 10^3}{8.314 \cdot 298}\right] = 1.4 \cdot 10^{83}$$

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O(l)$$ 323 K

$$\Delta_r G^\Theta = \sum_i \nu_i \Delta_f G^\Theta_{m,i} = +2 \cdot (-233.2) - 2 \cdot 0 - 1 \cdot 0 = -466.4\ \text{kJ/mol}$$

product **reactants**

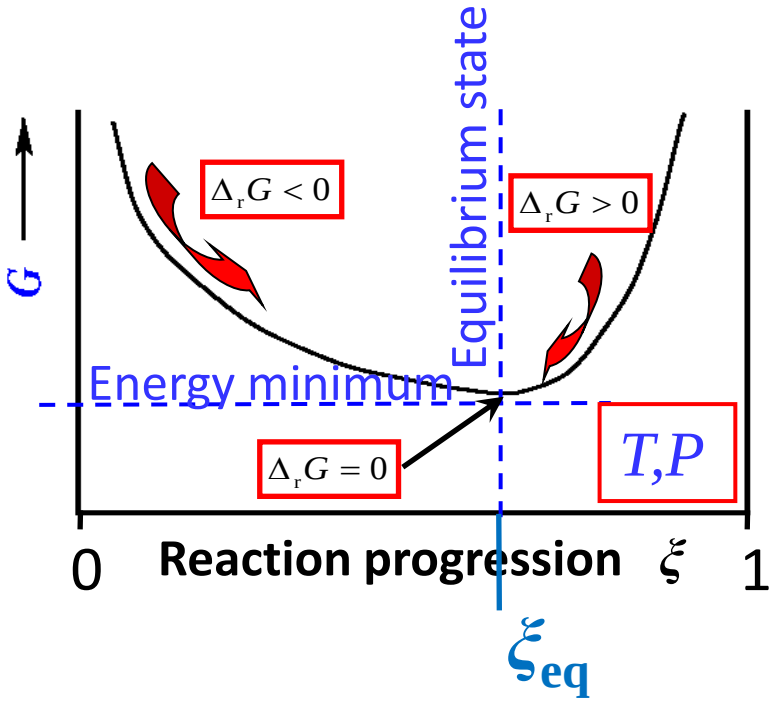
$$K = \exp\left[-\frac{\Delta_r G^\Theta}{RT}\right] = \exp\left[-\frac{-466.4 \cdot 10^3}{8.314 \cdot 323}\right] = 2.7 \cdot 10^{75}$$

A little bit less "completely on the right hand side"

Summary Lecture 3 (chemical equilibria)

Summary Lecture 3 (chemical equilibria)

Second law→ $dG\big|_{P,T} \leq 0$



$\Delta_r G$	reaction
$\Delta_r G < 0$	→
$\Delta_r G > 0$	←
$\Delta_r G = 0$	↔

$$\Delta_r G = \Delta_r G^{\Theta} + RT \ln Q$$

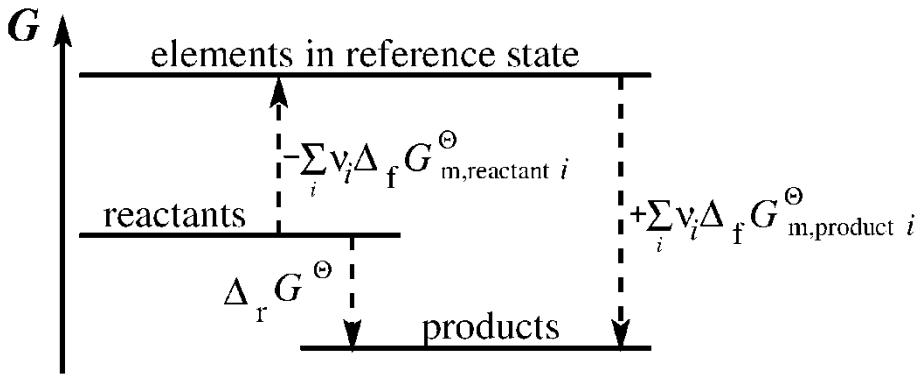
$$\Delta_r G^{\Theta} = \sum_i \nu_i \Delta_f G^{\Theta}_{m,i}$$

$$P^{\Theta} \equiv 1\,\text{bar}$$

$$K = \exp\left[-\frac{\Delta_r G^{\Theta}}{RT}\right]$$

Equilibrium constant

Summary Lecture 3 (formation energies)



$$\Delta_f G^{\Theta}_{m,i} = \Delta_f H^{\Theta}_{m,i} - T\Delta_f S^{\Theta}_{m,i}$$

At constant, chosen T

For all ellements in their reference states at T $\Delta_f G^{\Theta}_{m,i} \equiv 0$

For all ellements in their reference states at T $\Delta_f H^{\Theta}_{m,i} \equiv 0$

For gaseous mixtures

Partial pressure

$$P_i \equiv x_i P$$

Mole fraction

$$x_i \equiv \frac{n_i}{n} = \frac{n_i}{\sum_j n_j}$$

For perfect gas mixtures

$$Q = \prod_i \left(\frac{P_i}{P^{\Theta}} \right)^{\nu_i}$$