T-Abhängigkeit von K

Regeln: 1) exoth. Reaktion

$\Delta_R H^{\circ} < 0 \longrightarrow \left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta_R H^{\circ}}{RT^2} < 0$

GG: $\longleftarrow$

z.B. $H_2O\,(g) \rightleftharpoons H_2O\,(fl)$

$C\,(f) + O_2\,(g) \rightleftharpoons CO_2\,(g)$

2) endoth. Reaktion

$\Delta_R H^{\circ} > 0 \longrightarrow \left(\frac{\partial \ln K}{\partial T}\right)_p > 0$

GG: $\longrightarrow$

z.B. $H_2O\,(fl) \rightleftharpoons H_2O\,(g)$

$CO_2\,(g) \rightleftharpoons C\,(f) + O_2\,(g)$

12.3 Druckabh. von GG

$\Delta_R G^{\circ} = -RT \ln K$

$R \ln K = -\Delta_R G^{\circ}/T$

$R\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\partial\left(\frac{\Delta_R G^{\circ}}{T}\right)_T}{\partial p} = -\frac{1}{T}\left(\frac{\partial \Delta_R G^{\circ}}{\partial p}\right)_T$

$dG = Vdp - SdT$

$T = \text{const.}: \left(\frac{\partial G}{\partial p}\right)_T = V \longrightarrow \left(\frac{\partial \Delta G}{\partial p}\right)_T = \Delta V$

$R \cdot \left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{1}{T}\Delta_R V^{\circ}$

$$\boxed{\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta_R V^{\circ}}{RT}}$$

T-Abhängigkeit von K

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z.B $H_2O\,(g) \rightleftharpoons H_2O\,(fl.)$

$C\,(f) + O_2\,(g) \rightleftharpoons CO_2\,(g)$

2) endoth. Reaktion

$\Delta_R H^\circ > 0 \longrightarrow \left(\frac{\partial \ln K}{\partial T}\right)_p > 0$

GG. $\longrightarrow$

z.B $H_2O\,(fl.) \rightleftharpoons H_2O\,(g)$

$CO_2\,(g) \rightleftharpoons C\,(f) + O_2\,(g)$

12.3 Druckabh. von GG

$\Delta_R G^\circ = -RT\ln K$

$R\ln K = -\Delta_R G^\circ / T$

$R\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\partial\left(\frac{\Delta_R G^\circ}{T}\right)_T}{\partial p} = -\frac{1}{T}\left(\frac{\partial \Delta_R G^\circ}{\partial p}\right)_T$

$dG = Vdp - SdT$

T = const. $\left(\frac{\partial G}{\partial p}\right)_T = V \longrightarrow \left(\frac{\partial \Delta G}{\partial p}\right)_T = \Delta V$

$R\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{1}{T}\Delta_R V^\circ$

$$\boxed{\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta_R V^\circ}{RT}}$$

Regeln: 1) Vol. zunahme bei Rxn

$$\Delta_R V^{\ominus} > 0 \longrightarrow \left(\frac{\partial \ln K}{\partial p}\right)_T < 0$$

GG: $\longleftarrow$

z.B. $H_2O\,(fl.) \rightleftharpoons H_2O\,(f)$

2) Vol. abnahme bei Rxn

$$\Delta_R V^{\ominus} < 0 \longrightarrow \left(\frac{\partial \ln K}{\partial p}\right)_T > 0$$

GG: $\longrightarrow$

z.B. $H_2O\,(g) \rightleftharpoons H_2O\,(fl.)$

↳ vgl. mit Prinzip von le Chatelier

Merke: ΔV ist typischerweise sehr klein!

↳ Druckeinfluss nur bei großen Druckänderungen

z.B. Diamantsynthese

c (Graphit) $\rightleftharpoons$ c (Diamant)

PHASENDIAGRAMM KOHLENSTOFF

Druckabh. von Rxn mit Gasen

z.B. $N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$

$$K_p = \frac{(p(NO_2)/p^\circ)^2}{(p(N_2O_4)/p^\circ)}$$

Abh. vom Gesamtdruck?

$p_i = x_i\,p$ (ideal)

$$\hookrightarrow \quad K_p = \frac{x_{NO_2}^2 \cdot \left(\frac{p}{p^\circ}\right)^2}{x_{N_2O_4}\left(\frac{p}{p^\circ}\right)} = \underbrace{\frac{x_{NO_2}^2}{x_{N_2O_4}}}_{K_x}\ \frac{p}{p^\circ}$$

moderate Drücke: ~200 bar $\longrightarrow K_p \approx$ const.

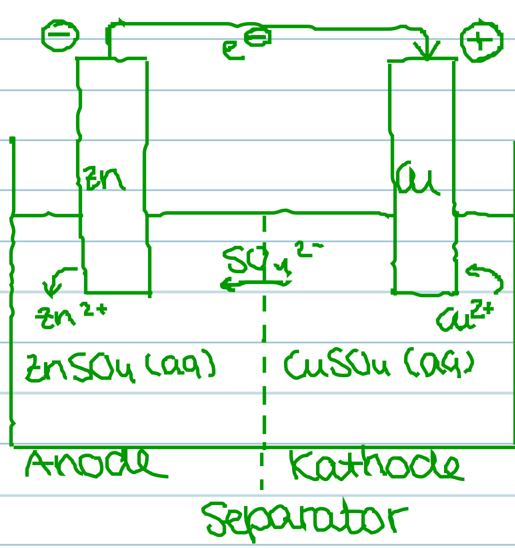
$K_p \approx$ const: $p\uparrow \quad K_x \downarrow$

z.B. Ammoniak-Synthese: $3H_2 + N_2 \rightleftharpoons 2NH_3$

13. Elektrochemie im GG

13.1 Elektrochem. Zelle

z.B. Daniell-Element



$Zn(s)\,|\,ZnSO_4(aq)\,\vdots\,CuSO_4(aq)\,|\,Cu(s)$

A: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ Ox

K: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ Red

Σ $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

13.2 Zellspannung

= Potentialdiff. zw. Elektroden [V]

bewegte Ladung
pro Formelumsatz $= -z e N_L \, d\xi = -z F \, d\xi$

z: Ladungszahl; e: Elementarladung; $e N_L = F$: Faraday-Konstante

elektr. Arbeit $dW_e = -zF \, d\xi \, E$
$[J = CV]$ $[\frac{C}{mol}][mol][V]$ E: GG-Zellsp. (EMK)

Zelle reversibel ; $p, T = const$

$dW_e = dG$ (vgl 9,2)

$dG = -zFE \, d\xi$

$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \boxed{-zFE = \Delta_R G}$

freiwilliger Prozess? $\Delta_R G < 0 \longrightarrow E > 0$
GG $\Delta_R G = 0 \longrightarrow E = 0$