19.05.17

5.6 Beschreibung des Reaktionsfortgang

$\nu_A A + \nu_B B \longrightarrow \nu_C C + \nu_D D$

ν_i: stöchiometr. Koeff. Prod. pos
Ed. neg

z.B. $3H_2 + N_2 \longrightarrow 2NH_3$

ν -3 -1 +2

Reaktionsfortgang? $d\xi = \frac{dn_i}{\nu_i}$

↑

Reaktionslaufzahl

z.B. $3H_2 + N_2 \longrightarrow 2NH_3$

$d\xi = \frac{-3\,mol}{-3} = \frac{-1\,mol}{-1} = \frac{+2\,mol}{+2} = 1\,mol$

$dn_i = n_i - n_i^{\circ} = \nu_i\, d\xi$

$H = f(p, T, \xi)$

$\hookrightarrow dH = \left(\frac{\partial H}{\partial p}\right)_{T,\xi} dp + \left(\frac{\partial H}{\partial T}\right)_{p,\xi} dT + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} d\xi$

Komb. 1. HS: $dH = dq + Vdp$

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Komb. 1. HS: $dH = dq + V dp$

$p,T = \text{const} \longrightarrow dq = \left(\frac{\partial H}{\partial \xi}\right)_{p,T} d\xi$

$$\left(\frac{dq}{d\xi}\right)_{p,T} = \left(\frac{\partial H}{\partial \xi}\right)_{p,T} = \boxed{\Delta_R H = \sum_i \nu_i \tilde{H}_i}$$

$\frac{\partial}{\partial \xi} \longrightarrow$ Operator

5.7. Temperaturabhängigkeit der Rktsenth.

Wärme kap. $\tilde{C}_p = \left(\frac{\partial \tilde{H}}{\partial T}\right)_p$

mehrere Komponente $\left(\frac{\partial \Delta_R H}{\partial T}\right)_p = \Delta_R C_p = \sum \nu_i \tilde{C}_{p,i}$

Druckabh. gering $\boxed{\frac{d\,\Delta_R H}{dT} = \Delta_R C_p} \boxed{\frac{d\Delta_R U}{dT}} = \Delta_R C_V$

Kirchhoffscher Satz

falls $\hat{C}_p$ temp.abh., dann

$\tilde{C}_p(T) = a + bT + cT^{-2}$ (a,b,c tabelliert)

Integration zw. T_1 u. T_2

$$\Delta_R H(T_2) = \Delta_R H(T_1) + \int_{T_1}^{T_2} \hat{C}_p(T)\, dT$$

z.B. Verdampfung von Wasser

$$H_2O\ (l) \longrightarrow H_2O\ (g) \qquad \Delta_r H = 40{,}7 \frac{kJ}{mol}$$

$$\frac{d\Delta_r H}{dT} = \Delta C_p = \tilde{C}_p\ (g) - \tilde{C}_p\ (l)$$

0° – 100°C :

$$\left.\begin{array}{l} \tilde{C}_p\ (g) \approx 8 \frac{cal}{mol\,K} \\ \tilde{C}_p\ (l) \approx 18 \frac{cal}{mol\,K} \end{array}\right\} \Delta C_p \approx -10 \frac{cal}{mol\,K}$$

$$\hookrightarrow \frac{d\Delta_r H}{dT} \approx -10 \frac{cal}{mol\,K} \approx -42 \frac{J}{mol\,K}$$

$\boxed{6.}$ Adiab. Zustandsgleichung u. Effekt

6.1 ~~Vorbeme~~ Vorbem.

isotherm. rev. Exp. eines id Gas

1 HS. $\quad dU = C_v\, dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{=0} dV = dq + dw$

$\hookrightarrow dT = 0$

$\longrightarrow dU = 0$

$$\boxed{dq = -dw}$$

> isoth. rev. Exp. eines realen Gases

$$\left(\frac{\partial U}{\partial V}\right)_T > 0 \quad \text{(WW. kräfte!)}$$

$$\hookrightarrow \boxed{dq = -dw + \left(\frac{\partial U}{\partial V}\right)_T dV}$$

↑ zusätzliche Wärmezufuhr

6.2 Adiabat. Exp. u. Kompr.

__adiab.:__ kein Wärmeaustausch mit Umgebung

$$dq = 0 \longrightarrow \boxed{dU = dw}$$

__id. Gas:__ $dU = C_V\, dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{=0} dV = C_V\, dT$

$$\Delta U = \int_{T_1}^{T_2} C_V\, dT = C_V \Delta T = W$$

__Bsp:__ Exp.

$$W = -p_{außen} \Delta V = C_V \Delta T$$

$$\hookrightarrow \boxed{\Delta T = \frac{-p_{außen} \Delta V}{C_V}}$$

Realisierung?

1). Isolierung des Systems → kein Wärmeaustausch
(Dewar)

2). Prozess ist sehr schnell → " "
(Luftpumpe)

Adiab. Exp. id Gases (rev.)

$$\underbrace{dU = dw = -p\,dV \qquad dU = C_V\,dT}$$

$$C_V\,dT = -p\,dV$$

id Gasgesetz: $C_V\,dT = -\frac{RnT}{V}\,dV$

$$\cancel{n}\tilde{C}_V\,dT = -R\cancel{n}T\,\frac{dV}{V}$$

$R = \tilde{C}_p - \tilde{C}_V \qquad \tilde{C}_V\,dT = -\left(\tilde{C}_p - \tilde{C}_V\right)T\,\frac{dV}{V}$

$$\frac{dT}{T} = -\left(\underbrace{\frac{\tilde{C}_p}{\tilde{C}_V}}_{\gamma} - 1\right)\frac{dV}{V}$$

$$\frac{dT}{T} = -(\gamma - 1)\int_{V_1}^{V_2}\frac{dV}{V}$$

Poissonsche Gl.

$$\boxed{T \cdot V^{\gamma-1} = const}$$

$$\ln\frac{T_2}{T_1} = \ln\frac{V_1}{V_2}^{(\gamma-1)} \rightarrow \boxed{\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}}$$

Bsp.: 1 atm id Gas (3

$1/10$ seines Anfangsvol. kompr. $T = ?$

$$T_1 = 300\,K \qquad \gamma = \frac{\tilde{C}_p}{\tilde{C}_V} = \frac{5/2}{3/2} = \frac{5}{3} = 1{,}6667$$

$$T_2 = T_1 \cdot 10^{0{,}6667} \qquad \underline{\approx 90\,K}$$