Reaktions-Enthalpie

$$dU = \delta Q + \delta W = \delta Q - p \cdot dV = \left(\frac{\partial U}{\partial T}\right)_{V,\xi} dT + \left(\frac{\partial U}{\partial V}\right)_{T,\xi} dV + \left(\frac{\partial U}{\partial \xi}\right)_{T,V} d\xi$$

$$dH = dU + p\,dV + V\,dp = \delta Q + V\,dp$$

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

$dT = 0$, $dV = 0$: isotherm + isochor:

$$\boxed{\delta Q = \left(\frac{\partial U}{\partial \xi}\right)_{T,V} d\xi}$$

$dT = 0$, $dp = 0$: isotherm + isobar:

$$\boxed{\delta Q = \left(\frac{\partial H}{\partial \xi}\right)_{p,T} d\xi}$$

Definition:

$$\boxed{\frac{\partial U}{\partial \xi} \overset{!}{=} \Delta_r U} \qquad \boxed{\frac{\partial H}{\partial \xi} \overset{!}{=} \Delta_r H}$$

$\xi = \frac{n_i}{\nu_i}$ Reaktionslaufzahl $\qquad d\xi = \frac{dn_i}{\nu_i}$

$$U_{anfang} = n_1^a \cdot U_1 + n_2^a \cdot U_2 + \ldots$$

$$U_{ende} = n_1^e \cdot U_1 + n_2^e \cdot U_2 + \ldots$$

$$dU = U_1\,dn_1 + U_2\,dn_2 + \ldots$$

$$= U_1 \nu_1 \cdot d\xi + U_2 \nu_2\,d\xi + \ldots$$

$$= \sum_i \nu_i U_i\,d\xi$$

$$\left(\frac{\partial U}{\partial \xi}\right)_{V,T} = \Delta_r U = \sum_{i=1}^{k} \nu_i \cdot U_i$$

$$\left(\frac{\partial H}{\partial \xi}\right)_{p,T} = \Delta_r H = \sum_{i=1}^{k} \nu_i H_i$$

Heßscher Satz

$\Delta_r H$ ist ebenfalls Zustandsfktn !

<u>Germain Henri Hess (1802 - 1850)</u>

Die Enthalpie H einer Reaktion ist gleich der Summe der Reaktionen, in die die betreffende Reaktion formal zerlegt werden kann.

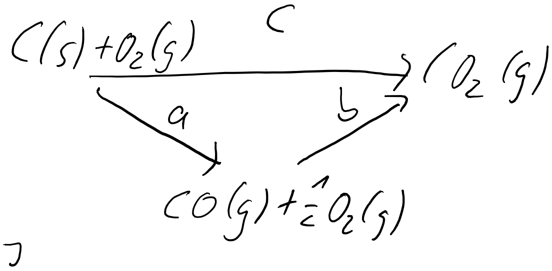
<u>Bsp</u>

a) $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g) \quad \Delta_r H = ?$

b) $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g) \quad \Delta_r H = -283 \frac{kJ}{mol}$

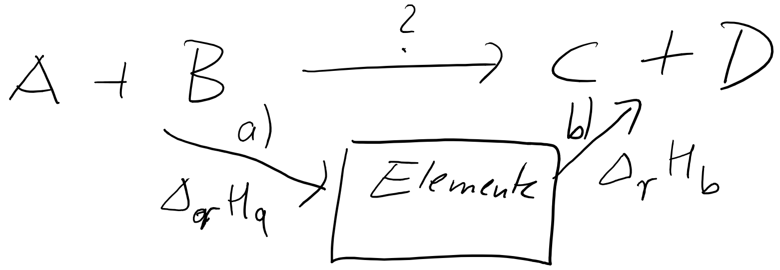
c) $C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta_r H = -393{,}7 \frac{kJ}{mol}$

a) + b) = c)

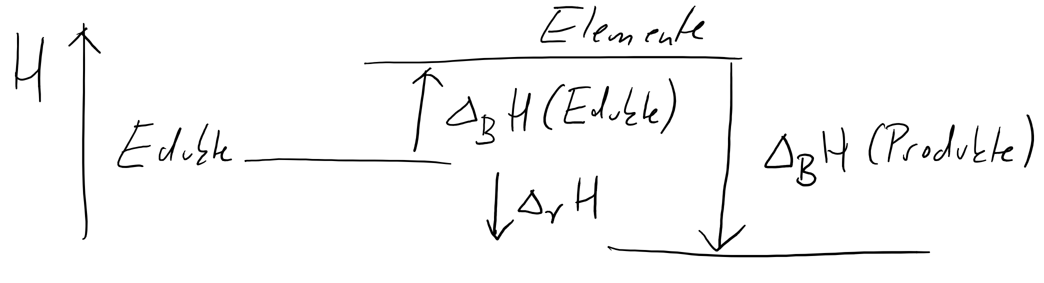


$$\Delta_r H_a + \Delta_r H_b = \Delta_r H_c$$

$$\Delta H_a = -110.6 \frac{kJ}{mol}$$



$$\Delta_r H = \Delta_B H(\text{Produkten}) - \Delta_B(\text{Edukten}) = \sum_i \nu_i \Delta_B H_i$$



<u>Bsp</u>: $2\, HN_3(l) + 2\, NO(g) \longrightarrow H_2O_2(l) + 4\, N_2(g)$

Edukte: $2\,HN_3(l) \longrightarrow 3\,N_2\,(g) + H_2\,(g)$

+264   0   0 $\Delta_B H \left[\frac{kJ}{mol}\right]$

$2\,NO\,(g) \longrightarrow N_2\,(g) + O_2\,(g)$

+90.25   0   0 $\Delta_B H \left[\frac{kJ}{mol}\right]$

Produkte: $H_2\,(g) + O_2\,(g) \longrightarrow H_2O_2\,(l)$

0   0   −187.8 $\Delta_B H \left[\frac{kJ}{mol}\right]$

$$\Delta_T H = -2 \cdot \Delta_B H(HN_3) - 2\,\Delta_B H(NO) + \Delta_B H(H_2O_2)$$

$$= -896{,}3\ \frac{kJ}{mol}$$

Bindungsenergien

Bindungs-E (H – O) in H_2O

$$H_2O(g) \longrightarrow H_2(g) + \frac{1}{2} O_2(g)$$

$-241 \frac{kJ}{mol}$ 0 0 $\Delta_B H$

$$\Delta_r H = 241{,}8 \frac{kJ}{mol}$$

$$H_2(g) \longrightarrow 2H(g)$$

0 $+218 \frac{kJ}{mol}$ $\Delta_B H$

$$\frac{1}{2} O_2(g) \longrightarrow O(g)$$

$+249.2 \frac{kJ}{mol}$ $\Delta_B H$

$$H_2O(g) \longrightarrow 2H(g) + O(g) \quad \Delta_r H = 927 \frac{kJ}{mol}$$

1 mol 3 mol

mittlere Bindungsenthalpie H–O $\frac{927}{2} \frac{kJ}{mol} = 463.5 \frac{kJ}{mol}$

$$\Delta U = \Delta H - \Delta(p \cdot V) = \Delta H - \Delta n \cdot R \cdot T$$

$$927 \frac{kJ}{mol} - 2 \cdot 8.314 \frac{J}{mol\,K} \cdot 298 K$$

$\Delta U = 922 \frac{kJ}{mol}$ pro Bindung: $461 \frac{kJ}{mol}$

Beispiele:

H – H	$432 \frac{kJ}{mol}$
C – C	346 "
C = C	602

C ≡ C	835
C – O	358
C = O	799
C – $\overline{F}$	485
Si – Si	222