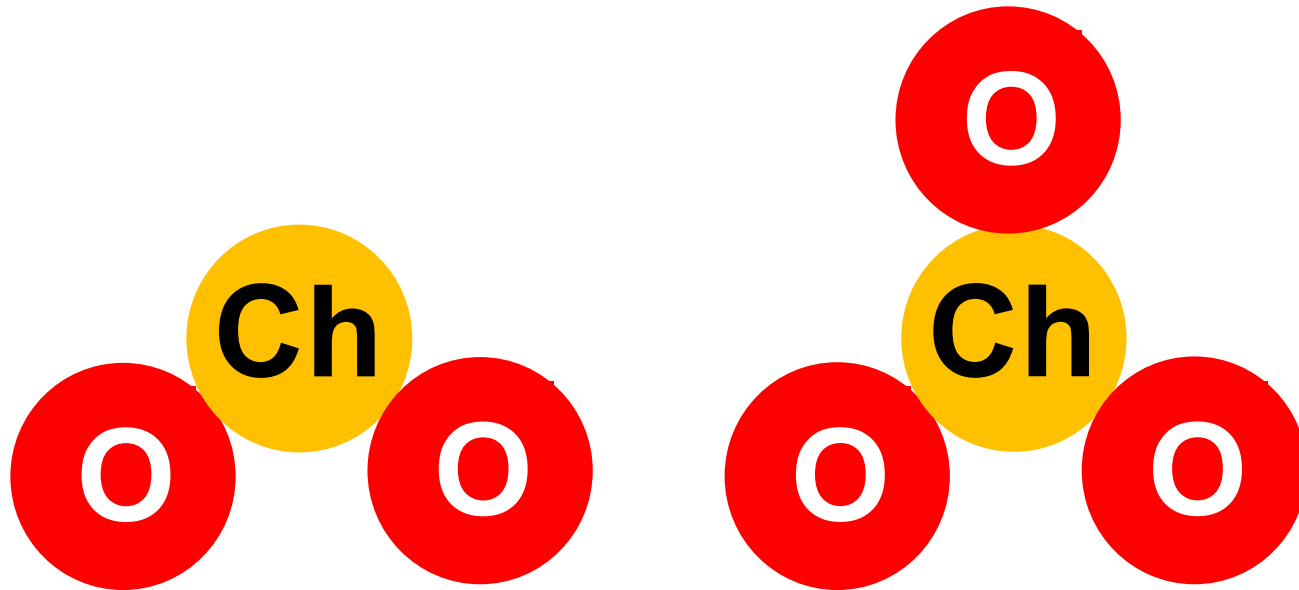


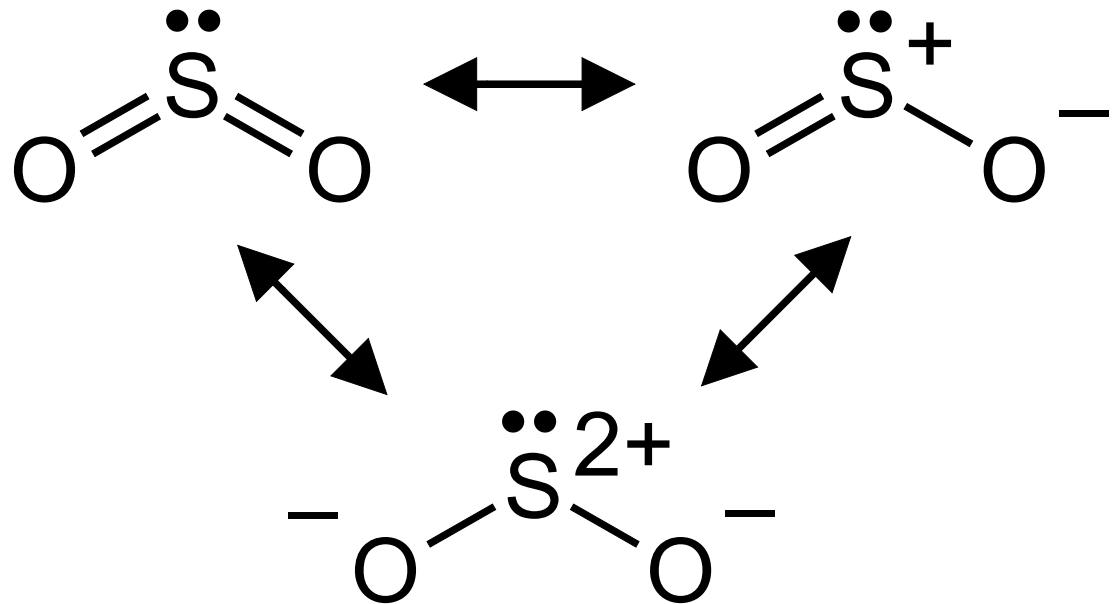
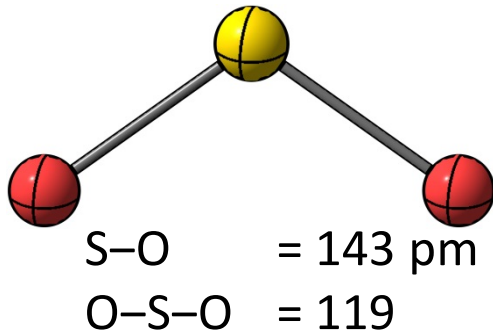
Chalkogen Oxide



hgruetzmacher@ethz.ch

SO₂ (Gas bei Raumtemp., 1 atm.)

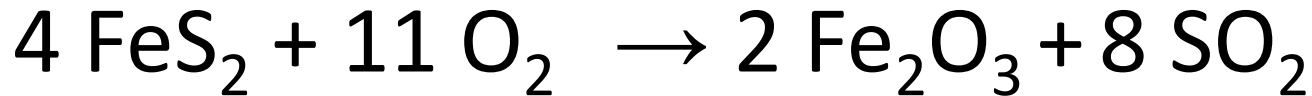
Schmp.: 197.5 K (−75.7 °C); Sdp.: 263 K (−10 °C)



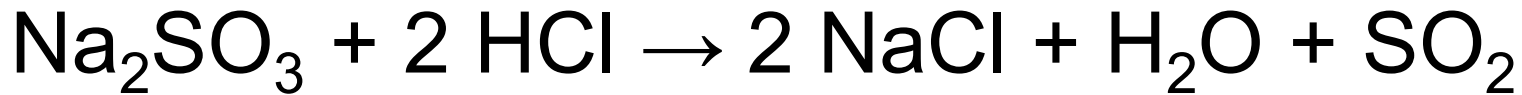
ausgewählte mesomere Grenzstrukturen
mit Formalladungen

Herstellung:

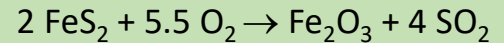
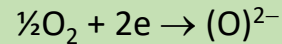
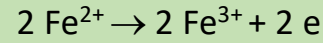
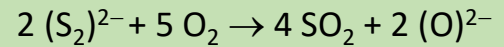
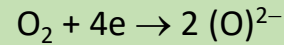
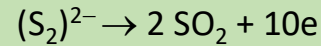
- Verbrennung von Schwefel oder H_2S
- Rösten von Sulfiderzen, z.B.:



- Ansäuren von Sulfiten:



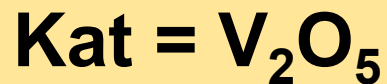
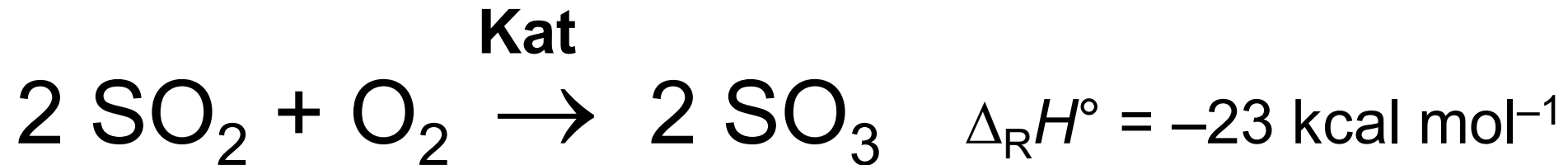
- Reduktion von Sulfaten ($T > 1620 \text{ K}$):



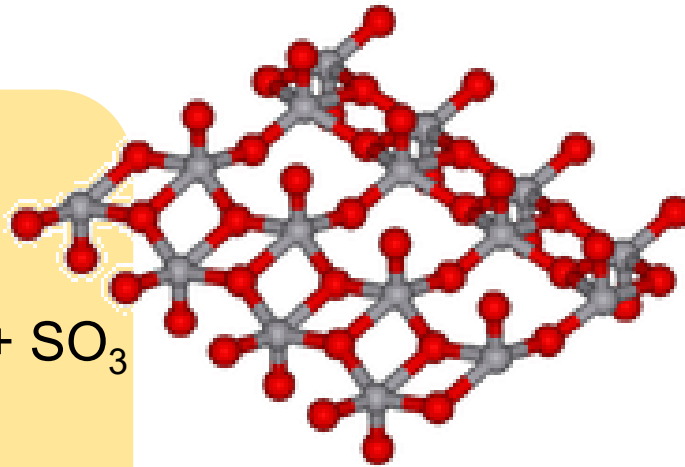
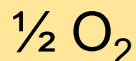
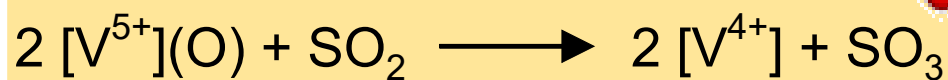


Schmelztp.: 290 K (17 °C); Siedep.: 318 K (45 °C)

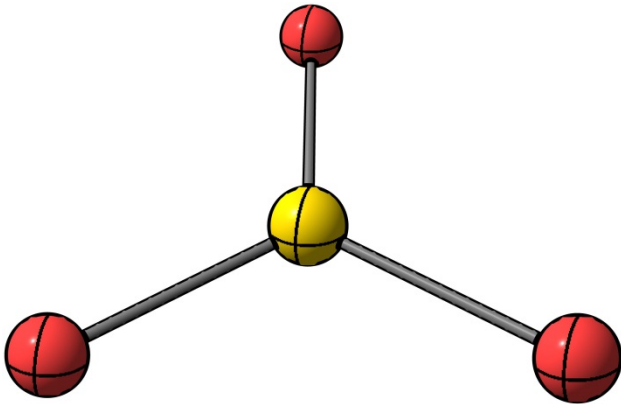
Synthese nach dem **Kontaktverfahren**:



Redox & Oxotranfer

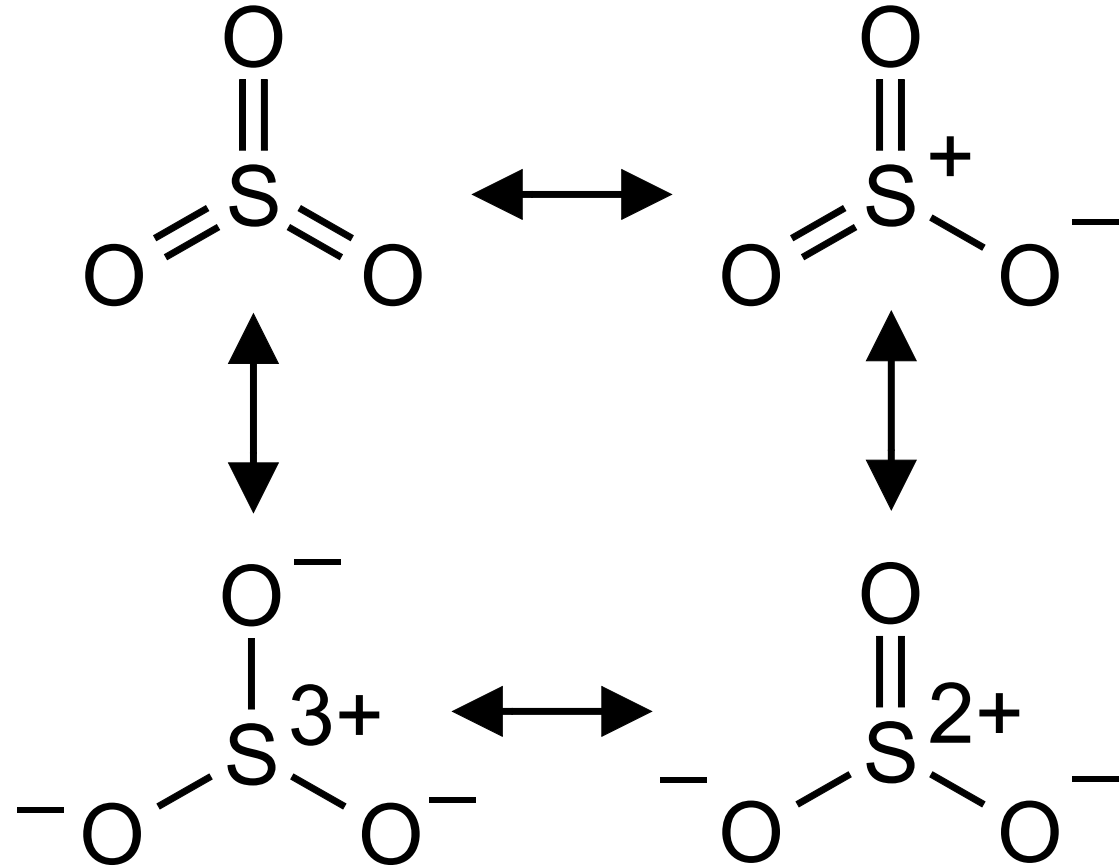


Struktur in der Gasphase ($> 45\text{ }^{\circ}\text{C}$)



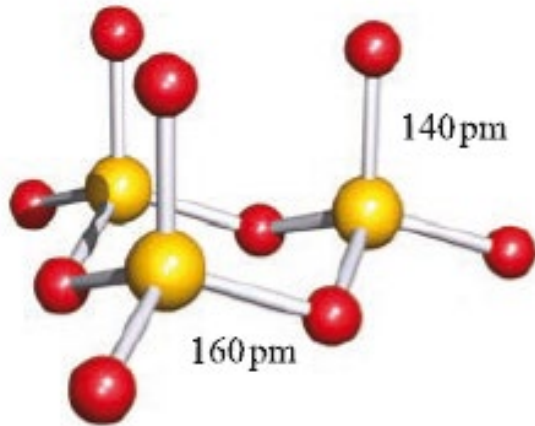
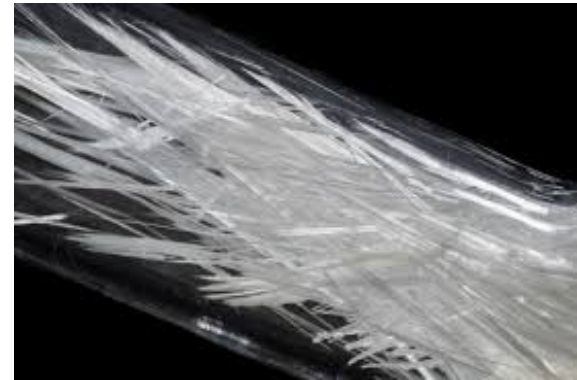
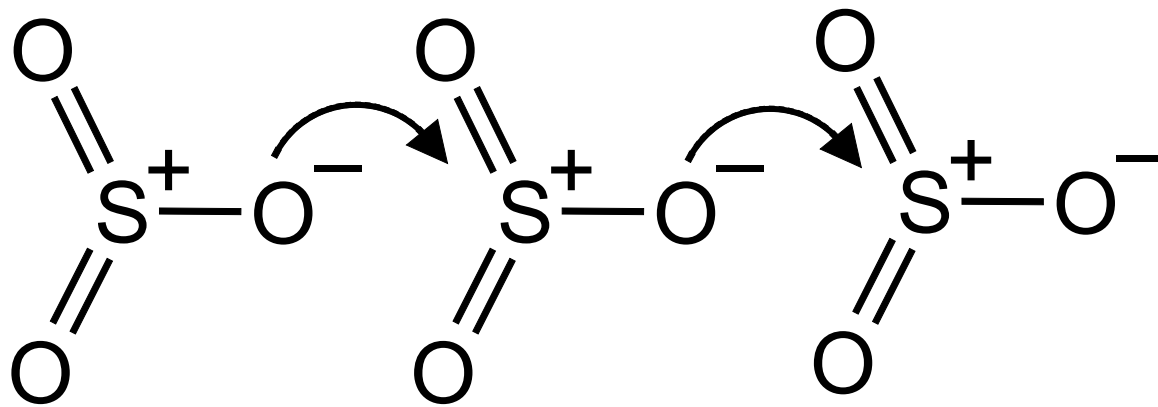
S-O = 142 pm

O-S-O = 120°



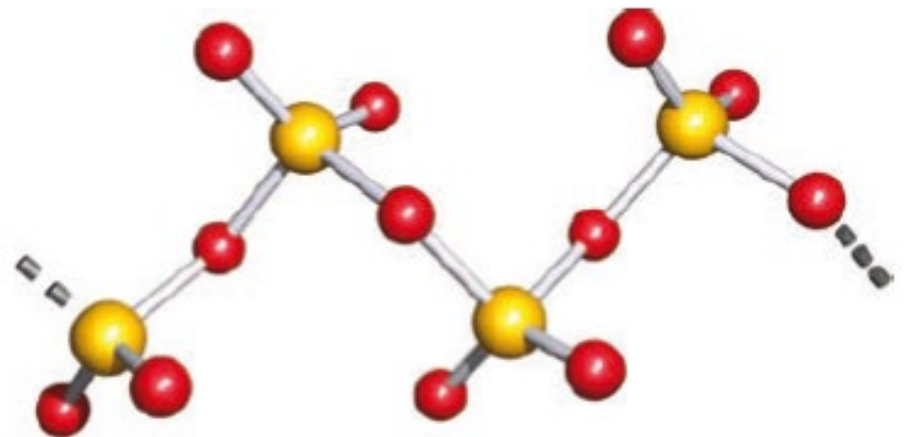
ausgewählte mesomere Grenzstrukturen
mit Formalladungen

SO_3 polymerisiert leicht zu Ringen
oder faserartigen Polymeren



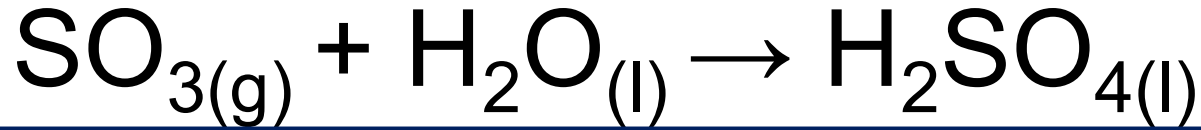
$\gamma\text{-SO}_3$ (Trimer)

tiefe Temperaturen



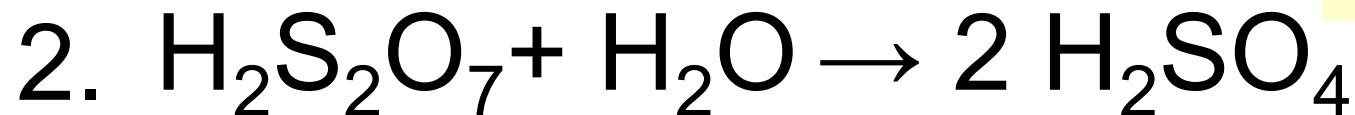
$\alpha, \beta\text{-SO}_3$ (polymere Ketten)

Solvolyse von SO_3

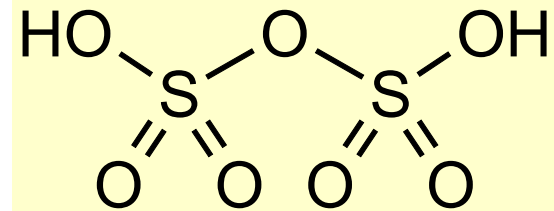


Starke Säure,
vollständige Dissoziation
 HSO_4^- : $pK_s = 1.9$

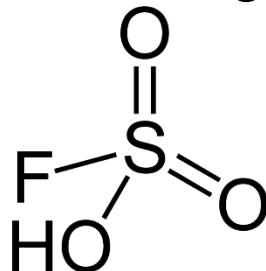
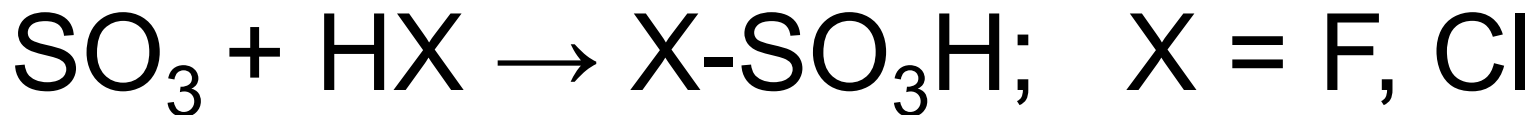
Zweistufiges Verfahren da Reaktion von SO_3 mit H_2O langsam:



Pyroschwefelsäure



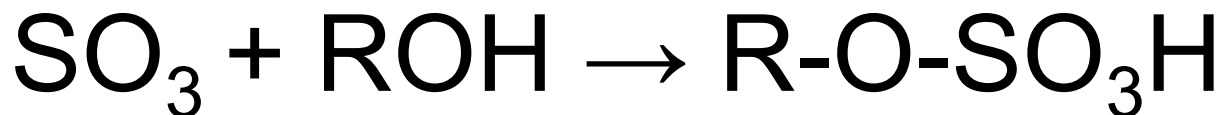
Fluor und Chlorsulfonsäure



Fluorsulfonsäure: eine der stärksten kommerziell erhältlichen Säuren.
Hammett-Funktion, $H_0 = -15$ (vgl. H_2SO_4 : $H_0 = -12$).

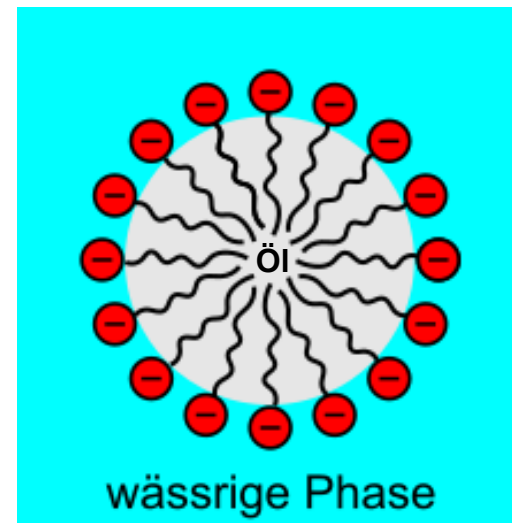
Ein 1 : 9 Gemisch aus HSO_3F / SbF_5 ist «Magische Säure», $H_0 \approx -27$.

Schwefelsäureester

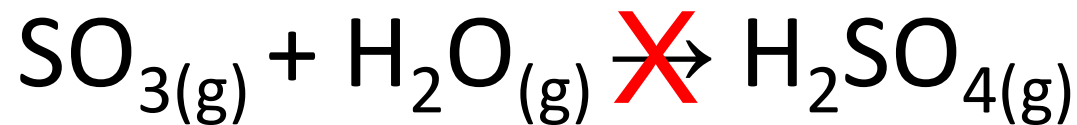
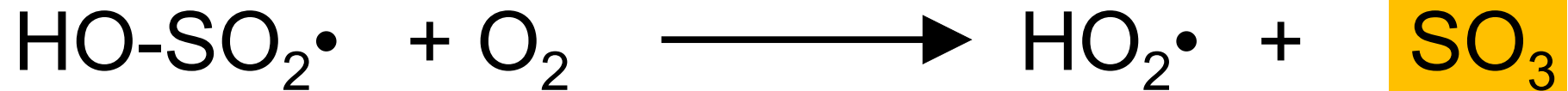
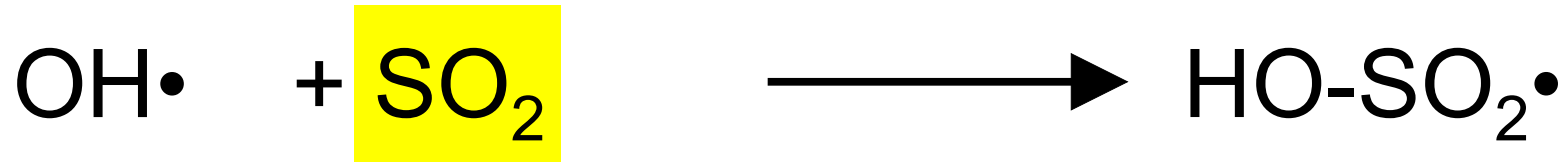
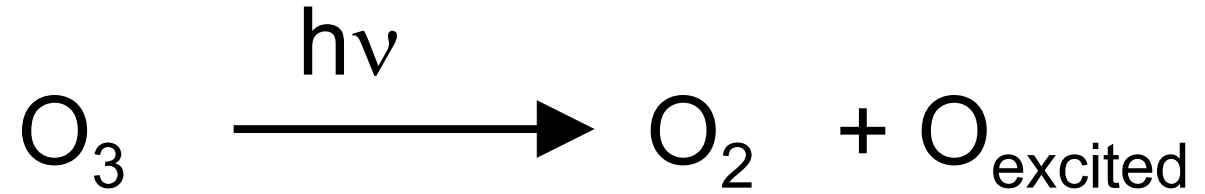


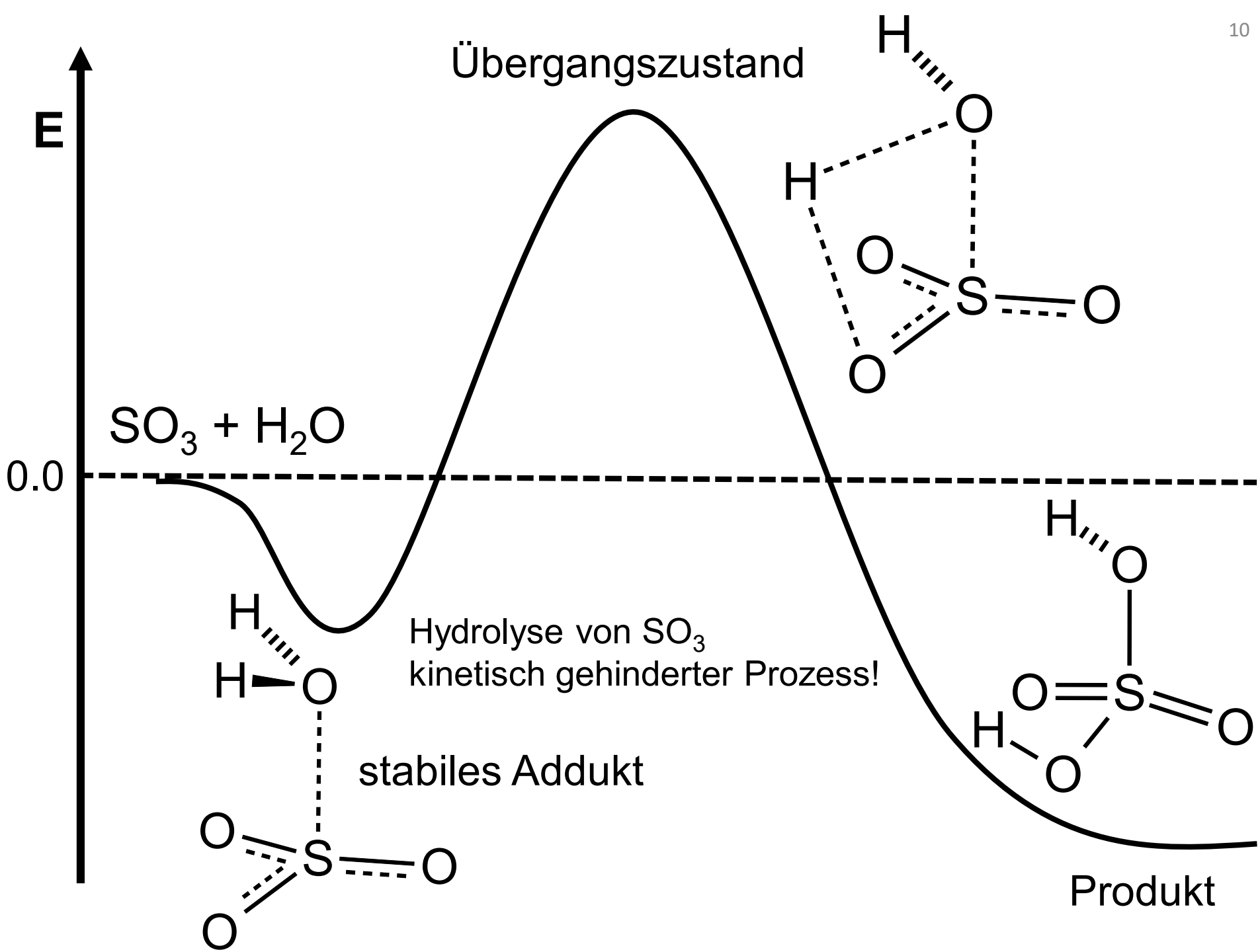
Natriumsalze mit $\text{R} =$ langkettiges Alkyl (z.B. dodekyl = Tenside (Shampoos, SDS oder SLS))

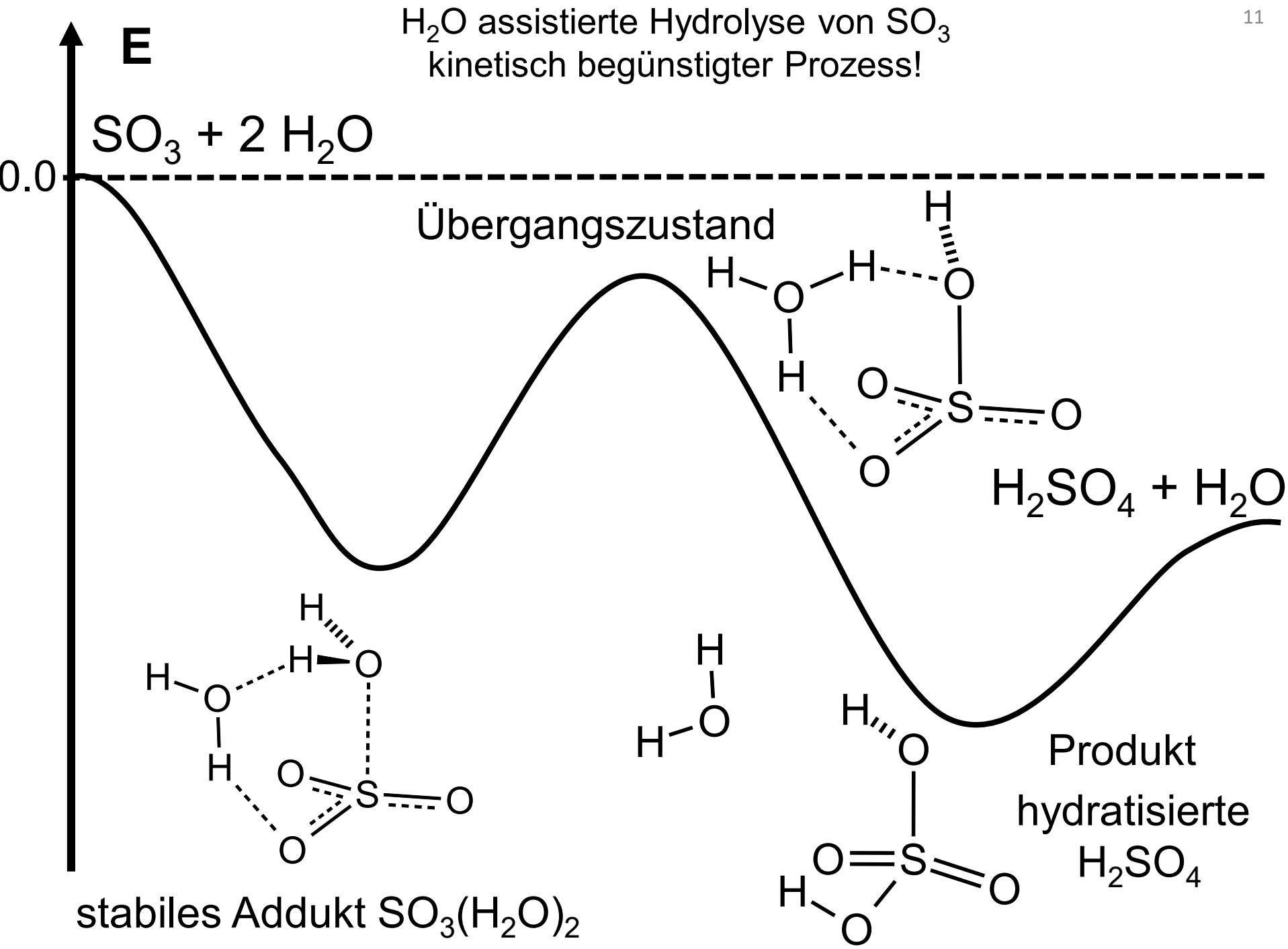
SDS = sodium dodecyl sulfate; SLS = sodium lauryl sulfate



Saurer Regen: Eine komplexe Reaktion



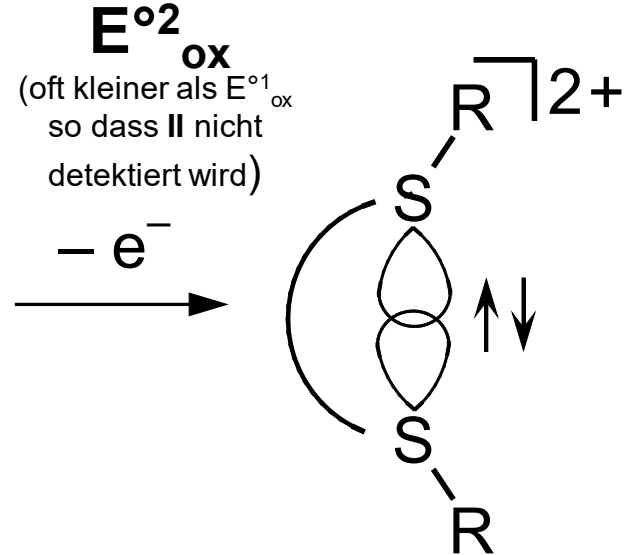
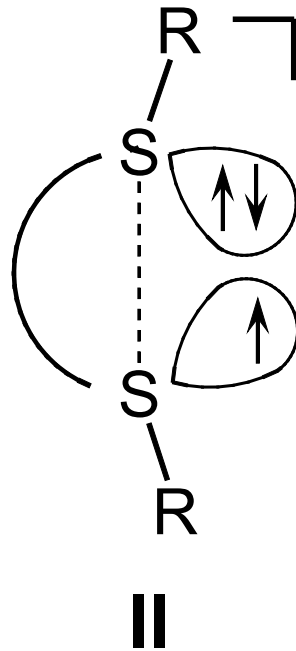
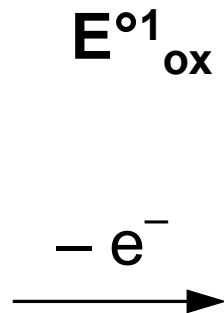
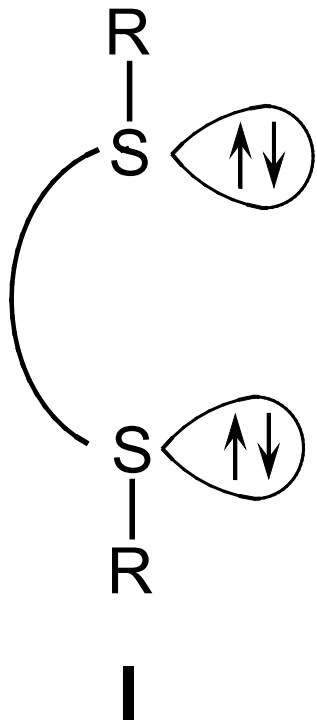
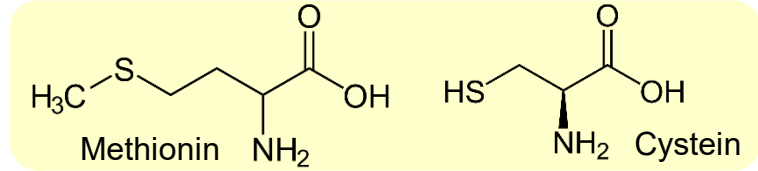




Oxidationen organischer Schwefelverbindungen (Cystein/ Methionin haltige Proteine)

Mehrelektronenprozesse verlaufen immer stufenweise!

Die Oxidation von schwefelreichen Proteinen (biologische Redox-Prozesse):



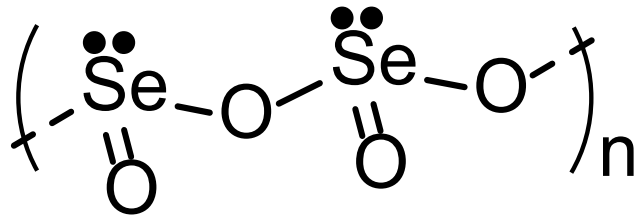
Zwei proximale
Thioetherfunktionen,
2Z-4e-Wechselwirkung
(B.O. = 0).

1. Einelektronenoxidation
Radikalkation
(Zwischenprodukt) mit
S \cdot :S-2Z-3e-Bindung
(B.O. = 0.5).

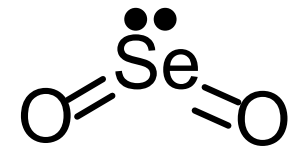
2. Einelektronenoxidation
Dikation mit
S $^+$ -S $^+$ -2Z-2e-Bindung
(B.O. = 1).

Selen und Tellurdioxide

SeO₂

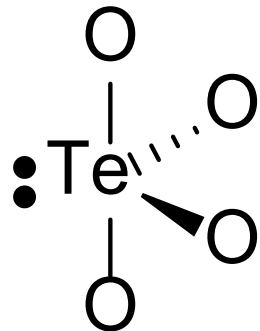


298 K (25 °C)

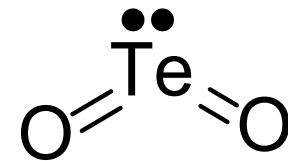
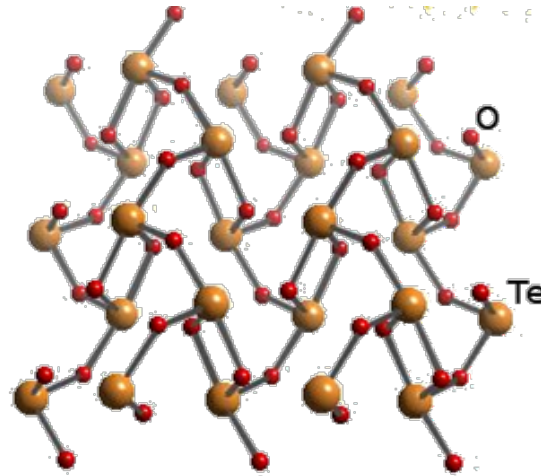


>588 K (315 °C)

TeO₂



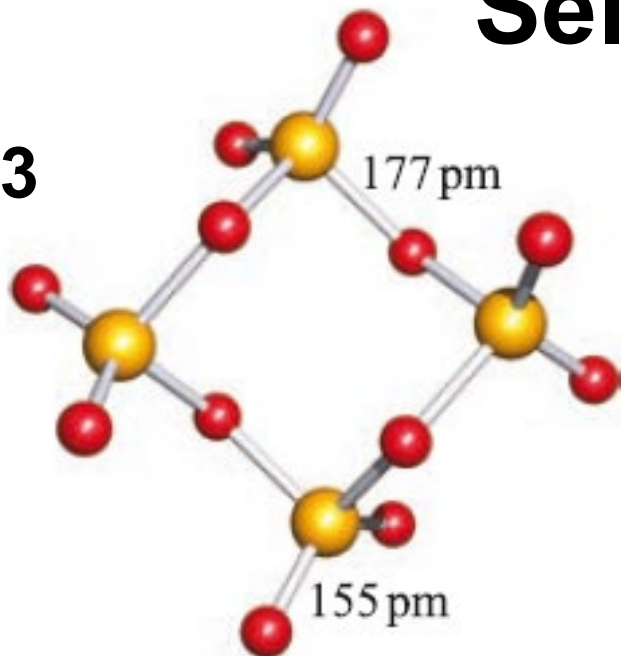
Schmp.: 1006 K (733 °C)



>1500K (1227 °C)

Selen und Tellurtrioxide

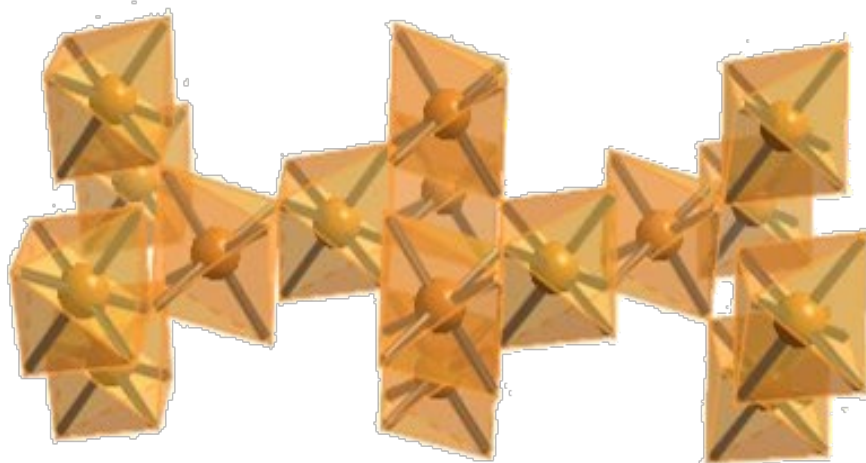
SeO₃



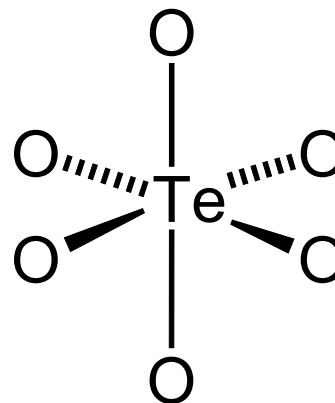
instabil >165 °C



TeO₃



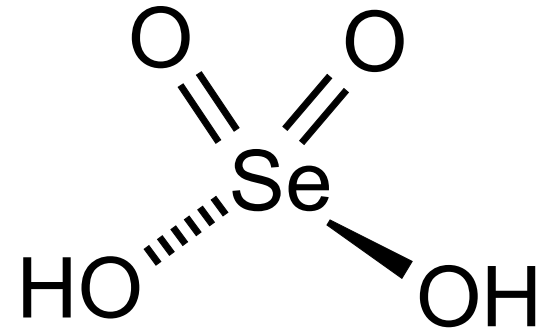
instabil >397 °C



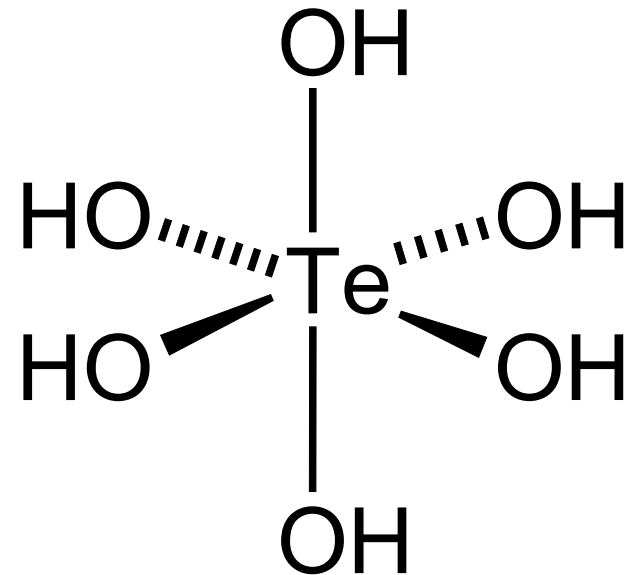
Zunehmender Atomradius

Zunehmend polarere Ch-O
Bindungen (erhöhter
ionischer Charakter)

Höhere Koordinationszahlen



Starke Säure,
vollständige Dissoziation
 HSeO_4^- : $\text{p}K_s = 1.74$



$\text{p}K_s^1 = 7.70$; $\text{p}K_s^2 = 10.95$