Dodatne vsebine Splošna kemija
Samostojno delo

4.del

P4 in S4: Termokemija

Entalpija-termokemijski izračuni,
Energija ionske vezi,
Entropija

EXAMPLE 3.11 Using a Born–Haber cycle to determine a lattice enthalpy

Calculate the lattice enthalpy of KCl(s) using a Born–Haber cycle and the information in the margin.

Answer The required cycle is shown in Fig. 3.48. The sum of the enthalpy changes around the cycle is zero, so

$$\Delta H_L^{\ominus}/(\text{kJ mol}^{-1}) = 438 + 425 + 89 + 244/2 - 355 = 719$$

Note that the calculation becomes more obvious by drawing an energy level diagram showing the signs of the various steps of the cycle; all lattice enthalpies are positive. Also as only one Cl atom from $Cl_2(g)$ is required to produce KCl, half the dissociation energy of Cl_2, $\frac{1}{2} \times 244$ kJ mol^{-1}, is used in the calculation.

	$\Delta H^{\ominus}$/(kJ mol^{-1})
Sublimation of K(s)	+89
Ionization of K(g)	+425
Dissociation of Cl_2(g)	+244
Electron gain by Cl(g)	−355
Formation of KCl(s)	−438

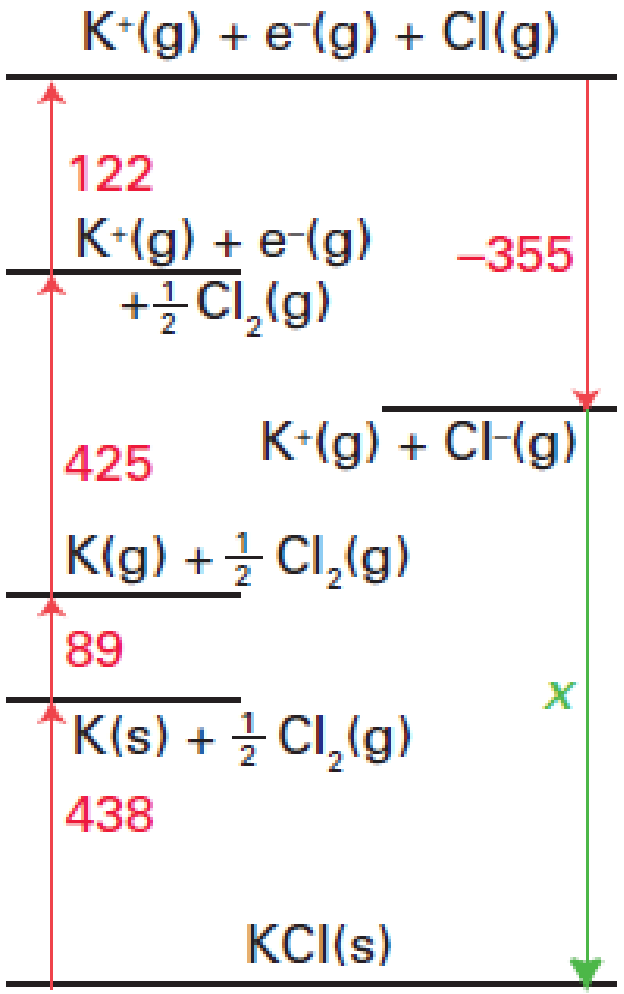

Fig. 3.48 The Born–Haber cycle for KCl. The lattice enthalpy is equal to $-x$. All numerical values are in kilojoules per mole.

Izračunaj mrežno entalpijo za $MgBr_2$:

	$\Delta H^{\ominus}$ / (kJ mol^{-1})
Sublimation of Mg(s)	+148
Ionization of Mg(g) to Mg^{2+}(g)	+2187
Vaporization of Br_2(l)	+31
Dissociation of Br_2(g)	+193
Electron gain by Br(g)	−331
Formation of $MgBr_2$(s)	−524

Table 3.7 Lattice enthalpies of some simple inorganic solids

Compound	Structure type	$\Delta H_L^{\ominus}$ / (kJ mol^{-1})	Compound type	Structure	$\Delta H_L^{\ominus}$ / (kJ mol^{-1})
LiF	Rock salt	1030	$SrCl_2$	Fluorite	2125
LiI	Rock salt	757	LiH	Rock salt	858
NaF	Rock salt	923	NaH	Rock salt	782
NaCl	Rock salt	786	KH	Rock salt	699
NaBr	Rock salt	747	RbH	Rock salt	674
NaI	Rock salt	704	CsH	Rock salt	648
KCl	Rock salt	719	BeO	Wurtzite	4293
KI	Rock salt	659	MgO	Rock salt	3795
CsF	Rock salt	744	CaO	Rock salt	3414
CsCl	Caesium chloride	657	SrO	Rock salt	3217
CsBr	Caesium chloride	632	BaO	Rocksalt	3029
CsI	Caesium chloride	600	Li_2O	Antifluorite	2799
MgF_2	Rutile	2922	TiO_2	Rutile	12150
CaF_2	Fluorite	2597	CeO_2	Fluorite	9627

2.Izračun mrežnih entalpij

- Ko poznamo mrežno entalpijo lahko sklepamo na naravo **kemijske vezi** v trdni snovi.
- Če je ***vrednost***, ki jo izračunamo po **predpostavki**, da je **mreža zgrajena iz ionov**, med katerimi so elektrostatske sile, v sladu z **izmerjeno**, potem je primeren za razlago **pretežno ionski model.**
- Odstopanja predstavljajo neko stopnjo kovalentne vezi.
- **Ocena, izračun: a) Born–Mayer enačba**
- **Pomembno:** Born–Mayer enačba se uporablja za oceno mrežne entalpije za ionsko mrežo. Madelung-ova konstanta **A** izraža vpliv geometrije mreže na jakost neto Columb-ovih interakcij.

Izračunane in eksperimentalno določene mrežne entalpije se dobro ujemajo za halogenide alkalijskih kovin, za halogenide npr. srebra pa ne. Ta razlika je posledica kovalentnega značaja vezi. Čisti ionski model v tem primeru odpove.

Table 3.9 Comparison of experimental and theoretical lattice enthalpies for rock-salt structures

	$\Delta H_L^{calc} / (\text{kJ mol}^{-1})$	$\Delta H_L^{exp} / (\text{kJ mol}^{-1})$	$(\Delta H_L^{exp} - \Delta H_L^{calc}) / (\text{kJ mol}^{-1})$
LiF	1029	1030	1
LiCl	834	853	19
LiBr	788	807	19
LiI	730	757	27
AgF	920	953	33
AgCl	832	903	71
AgBr	815	895	80
AgI	777	882	105

a) Born–Mayer enačba

Za izračun ΔH_L , mreže, ki naj bi bila ionska moramo upoštevati:

- **Privlačne in odbojne sile med ioni**, ko pride do prekrivanja elektronskih gostot ionov
- Za izračun uporabimo **Born–Mayer enačbo** za mrežno entalpijo pri $T = 0$:

$$\Delta H_L^{\ominus} = \frac{N_A |z_A z_B| e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{d^*}{d}\right)A$$

$d = r_+ + r_-$ is the distance between centres of neighbouring cations and anions,

3.1). In this expression N_A is Avogadro's constant, z_A and z_B the charge numbers of the cation and anion, e the fundamental charge, ε_0 the vacuum permittivity, and d^* a constant (typically 34.5 pm) used to represent the repulsion between ions at short range. The quantity A is called the **Madelung constant**, and depends on the structure (specifically, on the relative distribution of ions, Table 3.8). The Born–Mayer equation in fact gives the lattice energy as distinct from the lattice enthalpy, but the two are identical at $T = 0$ and the difference may be disregarded in practice at normal temperatures.

A-Madelungova konstanta, odvisna od strukture in razporeditve ionov..

$$\Delta H_L^{\ominus} = \frac{N_A |z_A z_B| e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{d^*}{d}\right)A$$

Table 3.8 Madelung constants

Structural type	*A*
Caesium chloride	1.763
Fluorite	2.519
Rock salt	1.748
Rutile	2.408
Sphalerite	1.638
Wurtzite	1.641

Z uporabo Born-Mayer-jeve enačbe ocenite vrednost mrežne entalpije za NaCl!

■ **A brief illustration.** To estimate the lattice enthalpy of sodium chloride, we use $z(Na^+) = +1$, $z(Cl^-) = -1$, from Table 3.8, $A = 1.748$, and from Table 1.4 $d = r_{Na^+} + r_{Cl^-} = 283$ pm; hence (using fundamental constants from inside the back cover):

$$\Delta H_L^{\ominus} = \frac{N_A |z_A z_B| e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{d^*}{d}\right)A$$

Table 1.4 Ionic radii, r/pm*

Li^+	Be^{2+}	B^{3+}			N^{3-}	O^{2-}	F^-
59(4)	27(4)	11(4)			146	135(2)	128(2)
76(6)						138(4)	131(4)
						140(6)	133(6)
						142(8)	
Na^+	Mg^{2+}	Al^{3+}			P^{3-}	S^{2-}	Cl^-
99(4)	49(4)	39(4)			212	184(6)	181(6)
102(6)	72(6)	53(6)					
132(8)	103(8)						
K^+	Ca^{2+}	Ga^{3+}			As^{3-}	Se^{2-}	Br^-
138(6)	100(6)	62(6)			222	198(6)	196(6)
151(8)	112(8)						
159(10)	123(10)						
160(12)	134(12)						
Rb^+	Sr^{2+}	In^{3+}	Sn^{2+}	Sn^{4+}		Te^{2-}	I^-
148(6)	118(6)	80(6)	83(6)	69(6)		221(6)	220(6)
160(8)	125(8)	92(8)	93(8)				
173(12)	144(12)						
Cs^+	Ba^{2+}	Tl^{3+}					
167(6)	135(6)	89(6)					
174(8)	142(8)	Tl^+					
188(12)	175(12)	150(6)					

■ **A brief illustration.** To estimate the lattice enthalpy of sodium chloride, we use $z(Na^+) = +1$, $z(Cl^-) = -1$, from Table 3.8, $A = 1.748$, and from Table 1.4 $d = r_{Na^+} + r_{Cl^-} = 283$ pm; hence (using fundamental constants from inside the back cover):

$$\Delta H_L^{\ominus} = \frac{(6.022\times10^{23}\ \text{mol}^{-1})\times|(+1)\times(-1)|\times(1.602\times10^{-19}\ \text{C})^2}{4\pi\times(8.854\times10^{-12}\ \text{J}^{-1}\,\text{C}^2\ \text{m}^{-1})\times(2.82\times10^{-10}\ \text{m})}\times\left(1-\frac{34.5\ \text{pm}}{283\ \text{pm}}\right)\times1.748$$
$$= 7.56\times10^5\ \text{J mol}^{-1}$$

or 756 kJ mol^{-1}. This value compares reasonably well with the experimental value from the Born–Haber cycle, 788 kJ mol^{-1}. ■

- **Born Mayer enačba** nam torej omogoča izračun mrežnih entalpij; njen pomemben člen je:

$$\Delta H_L^{\circ} \propto \frac{|z_A z_B|}{d}$$

- Prikazuje odvisnost od naboja in radijev ionov v ionski mreži
- Torej **velik d** pomeni majhno mrežno energijo oz. **velik naboj** pomeni tudi veliko mrežno energijo.
- Glej spodnjo tabelo!

Table 3.7 Lattice enthalpies of some simple inorganic solids

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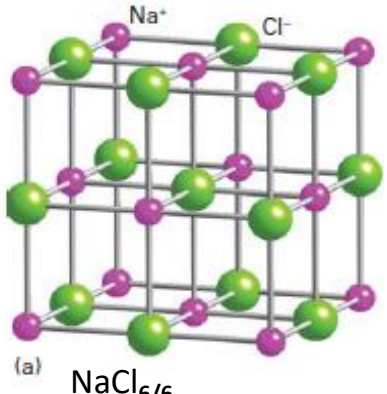
MgF_2	Rutile	2922	TiO_2	Rutile	12150
CaF_2	Fluorite	2597	CeO_2	Fluorite	9627

- Pri alkalijskih halidih padajo mrežne entalpije od LiF do LiI. In od LiF do CsF, z naraščanjem ionskih radijev.
- Prav tako lahko opazimo, da je ΔH_L za MgO skoraj 4x večji od ΔH_L za NaCl zaradi povečanega naboja. Vrednost d je enaka, prav tako konstanta A.

$(|z_A z_B| = 4)$ $(|z_A z_B| = 1)$

Madelungova konstanta **A** v splošnem narašča s KŠ.
Ta odvisnost kaže na to, da je velik vpliv najbližjih sosedov in teh je več če je višje KŠ.



$NaCl_{6/6}$

Table 3.8 Madelung constants

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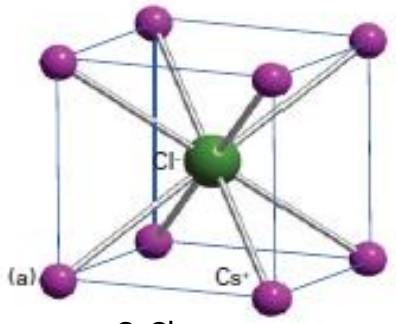
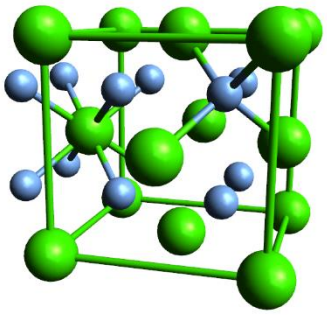
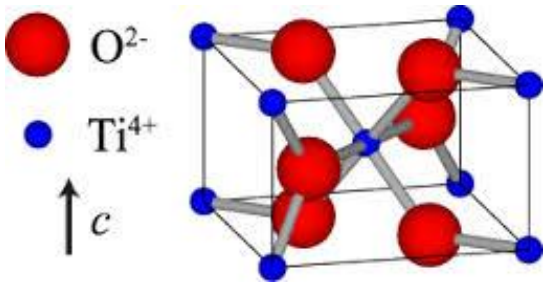


CsCl


CaF_2-fluorite

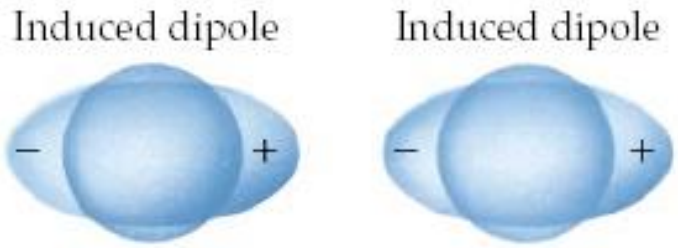


TiO_2-rutil

b) Ostali prispevki k mrežnim entalpijam

Predstavljajo jih **neelektrostatski prispevki** k mrežni entalpiji, ki vključujejo **van der Waalsove interakcije**, predvsem **disperzijske sile. („Londonove interakcije)“**

Le te so posledica nastanka trenutnih dipolov:



Molska potencialna energija V teh interakcij se spreminja kot:

C...konstanta, odvisna od snovi

$$V = -\frac{N_A C}{d^6}$$

- če je polarizabilnost nizka je prispevek teh interakcij le okoli 1%
- Vendar pa za zelo polarizabilne ione (npr. I^-) velja, da bolj doprinesejo k skupni mrežni energiji
- Tako za LiF ali CsBr lahko ocenimo, da je ta prispevek 16 kJ/mol oz. 50 kJ/mol.

Kapustinskii enačba

$$\Delta H_L^{\ominus} = \frac{N_{ion}\left|z_A z_B\right|}{d}\left(1 - \frac{d^*}{d}\right)\kappa$$

Se uporablja za oceno mrežnih entalpij ionskih snovi in za oceno ***termokemijskih radijev*** ionov v mreži.
Kapustinskii je namreč ugotovil, da če Madelungovo konstanto za določeno število struktur delimo z številom ionov na formulsko enoto - N_{ion}, dobimo enako vrednost za vse strukture.
Ugotovil je tudi, da tako dobljena vrednost s KŠ narašča. Ker tudi ionski radiji s KŠ naraščajo, je predpostavil, da **obstaja hipotetična struktura NaCl ,** ki je energetsko ekvivalentna pravi strukturi katerekoli ionske snovi. Tako lahko izračunamo mrežno entalpijo z uporabo Madelungove konstante za NaCl in ionskimi radiji za (6,6) koordinacijo (enačba).

$$\kappa = 1.21 \times 10^5 \text{ kJ pm mol}^{-1}.$$

- Ta enačba nam torej omogoča, da lahko napovemo radije nesferičnih molekularnih ionov (tabela spodaj), dokler so mrežne entalpije primerljive z eksperimentalnimi, dobljenimi iz Born-Haber cikla- **Termokemijski radiji.**

- Z njimi lahko ocenimo ΔH_L in ΔH_{tvorb} za za vrsto spojin, ne da bi poznali njihovo strukturo, s predpostavko, da gre za ionske vezi.

$$KNO_3 \rightarrow K^+ + NO_3^-$$

■ **A brief illustration.** To estimate the lattice enthalpy of potassium nitrate, KNO_3 we need the number of ions per formula unit ($N_{ion} = 2$), their charge numbers, $z(K^+) = +1, z(NO_3^-) = -1$, and the sum of their thermochemical radii, 138 pm + 189 pm = 327 pm. Then, with $d^* = 34.5$ pm,

$$\Delta H_L^{\ominus} = \frac{2|(+1)(-1)|}{327\ \text{pm}} \times \left(1 - \frac{34.5\ \text{pm}}{327\ \text{pm}}\right) \times (1.21 \times 10^5\ \text{kJ pm mol}^{-1})$$
$$= 622\ \text{kJ mol}^{-1}$$

■

d*=konstanta 34,5 pm

$$\kappa = 1.21 \times 10^5\ \text{kJ pm mol}^{-1}.$$

Tabela termokemijskih radijev ionov r (pm)

Main-group elements nesferični molekularni ioni

BeF_2^{2-}	BF_4^-	CO_3^{2-}	NO_3^-	OH^-	
245	228	185	189	140	
		CN^-	NO_3^-	O_2^{2-}	
		182	155	180	
			PO_4^{3-}	SO_4^{2-}	ClO_4^-
			238	230	236
			AsO_4^{3-}	SeO_4^{2-}	
			248	243	
			SbO_4^{3-}	TeO_4^{2-}	IO_4^-
			260	254	249
					IO_3^-
					182

Complex ions *d-Metal oxoanions*

$[TiCl_6]^{2-}$	$[IrCl_6]^{2-}$	$[SiF_6]^{2-}$	$[GeCl_6]^{2-}$	CrO_4^{2-}	MnO_4^-
248	254	194	243	230	240
$[TiBr_6]^{2-}$	$[PtCl_6]^{2-}$	$[GeF_6]^{2-}$	$[SnCl_6]^{2-}$	MoO_4^{2-}	
261	259	201	247	254	
$[ZrCl_6]^{2-}$			$[PbCl_6]^{2-}$		
247			248		

Complex ions				*d-Metal oxoanions*	
$[TiCl_6]^{2-}$	$[IrCl_6]^{2-}$	$[SiF_6]^{2-}$	$[GeCl_6]^{2-}$	CrO_4^{2-}	MnO_4^-
248	254	194	243	230	240
$[TiBr_6]^{2-}$	$[PtCl_6]^{2-}$	$[GeF_6]^{2-}$	$[SnCl_6]^{2-}$	MoO_4^{2-}	
261	259	201	247	254	
$[ZrCl_6]^{2-}$			$[PbCl_6]^{2-}$		
247			248		

Source: A.F. Kaputinskii, *Q. Rev. Chem. Soc.*, 1956, ***10***, 283.

Posledice mrežnih entalpij ΔH_L (i, ii, iii)

Born-Mayer enačba kaže, da za določen tip mreže (z konstanto A) tudi ΔH_L narašča z naraščajočim nabojem:

$$\xi = \frac{\left| z_A z_B \right|}{d}$$

Energije ki se spreminjajo kot elektrostatski parametr, ξ, so za večino anorganskih ionskih spojin značilne in kažejo na to, da je ionski model sprejemljiv.

i) Termična stabilnost ionskih spojin

ΔH_L lahko uporabimo tudi za razlago kemijskih lastnosti **ionskih trdnih snovi ,** prav tako njihovega **termičnega razpada.**

T, pri kateri pride do termičnega razpada. npr. karbonatov:

$$MCO_3(s) \rightarrow MO\ (s) + CO_2(g)$$

$MgCO_3$ razpade npr. pri segrevanju do npr. 300 ^oC.

$CaCO_3$ moram segrevati do 800 ^oC, da spojina rapade.

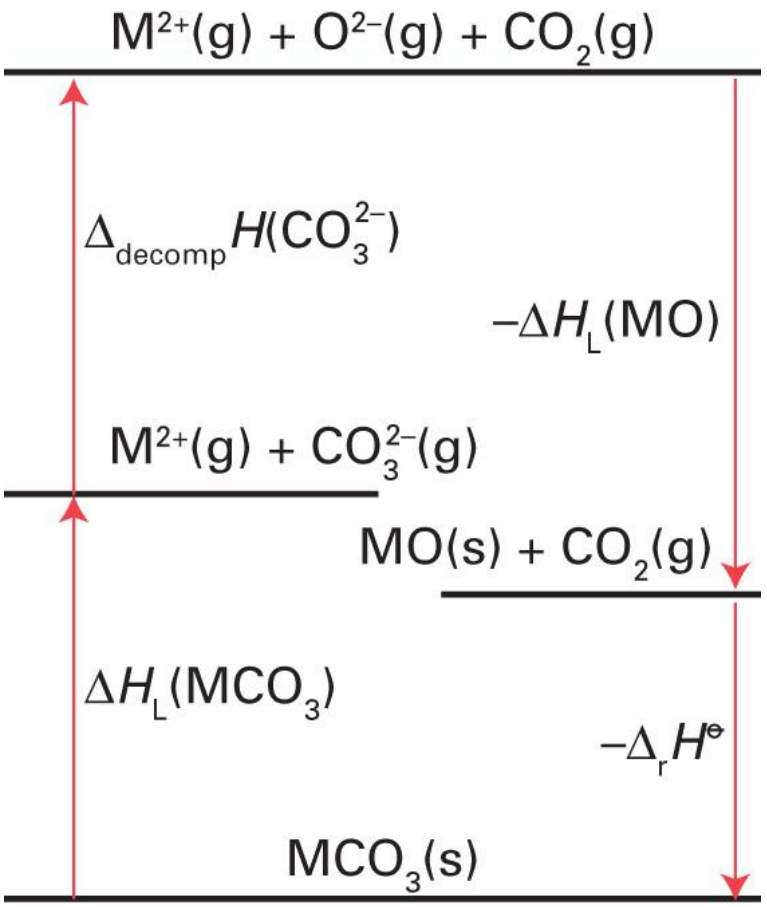
V splošnem lahko vidimo, da T razpada termično nestabilnih spojin (kot so karbonati) naraščajo z radijem kationa. V splošnem veliki kationi stabilizirajo velike anione (in obratno).

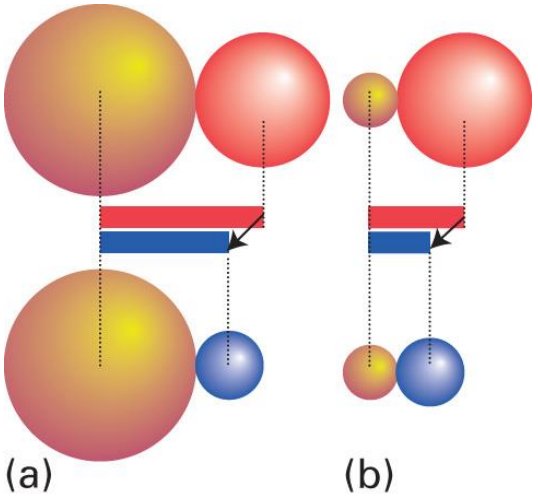
Table 3.11 Decomposition data for carbonates*

	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
$\Delta G^{\ominus} / (\text{kJ mol}^{-1})$	+48.3	+130.4	+183.8	+218.1
$\Delta H^{\ominus} / (\text{kJ mol}^{-1})$	+100.6	+178.3	+234.6	+269.3
$\Delta S^{\ominus} / (\text{kJ mol}^{-1})$	+175.0	+160.6	+171.0	+172.1
$\theta_{\text{decomp}} / °C$	300	840	1100	1300

*Data are for the reaction $MCO_3(s) \rightarrow MO(s) + CO_2(g)$ at 298 K. θ is the temperature required to reach $p(CO_2) = 1$ bar and has been estimated from the thermodynamic data at 298 K.

Entalpijske spremembe pri razpadu MCO_3





Standardna entalpija razkroja MCO_3 je

$$\Delta H^{\ominus} \approx \Delta_{\text{decomp}} H^{\ominus} + \Delta H_{\text{L}}{}^{\ominus}(\text{MCO}_3, \text{s}) - \Delta H_{\text{L}}{}^{\ominus}(\text{MO}, \text{s})$$

Change in Lattice Parameter for Cation of Different Sizes

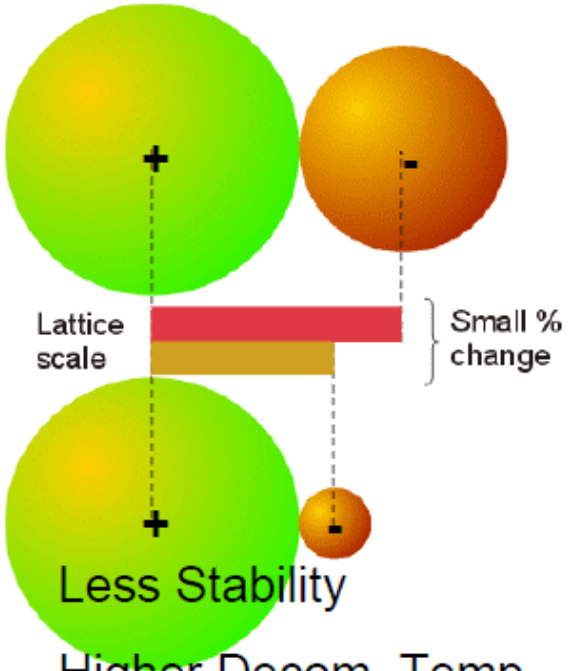
$MCO_3 \longrightarrow MO + CO_2$

M: Group 2 metals

$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$

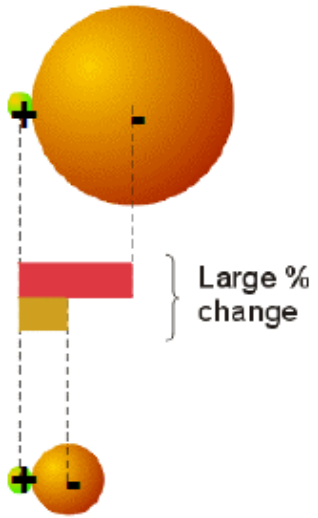
ΔS_{rxn} similar for Mg, Ca, Sr, Ba

Smaller r^+ ⇨ larger ΔH_L



Less Stability

Higher Decom. Temp.



More Stability

Lower Decom. Temp.

Large Cation
Stabilize
Large Anion

Small Cation
Stabilize
Small Anion

- Vpliv stabilizacije velikega kationa(M^{2+}) na *nestabilni anion* *(CO_3^{2-})* lahko razložimo z mrežnimi entalpijami.
- $T_{dec.}$ razpada trdnih anorganskih spojin lahko razložimo z Gibbs-ovo prosto energijo razpada spojine na določene produkte.
- Standardna $\Delta G^{\ominus}$ za razpad trdne snovi:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

- Če drugi člen prevlada nad prvim , potem je negativna. (spontan razpad)

- To je takrat ko temperatura preseže: $T = \frac{\Delta H^{\ominus}}{\Delta S^{\ominus}}$

- Standardna entalpija razkroja MCO_3 je:

* $\Delta H^{\ominus} \approx \Delta_{\text{decomp}} H^{\ominus} + \Delta H_{\text{L}}^{\ominus}(\text{MCO}_3, \text{s}) - \Delta H_{\text{L}}^{\ominus}(\text{MO}, \text{s})$

- Osredotočimo se na spremembo entalpije reakcije saj je reakcijska entropija odvisna le od nastanka plinastega CO_2.
- Entalpija razkroja $\Delta_{\text{decomp}} H^{\ominus}$ pa je povezana z reakcijo razkroja CO_3^{2-}:

$$CO_3^{2-}(g) \rightarrow O^{2-}(g) + CO_2(g)$$

- in je endotermna ter velika, zato je reakcijska ent. ΔH^0 pozitivna.*
- Vendar je manj pozitivna, če je entalpija oksida znatno večja od entalpije karbonata, saj je potem drugi del enačbe negativen.

Katera spojina je glede na termični razkroj stabilnejša? $MgCO_3$ ali $CaCO_3$? Razložite!

ii) Stabilnost oksidacijskih stanj

- Bistvo:

Relativna obstojnost-stabilnost različnih oksidacijskih stanj v trdnih snoveh se pogosto lahko napove iz premisleka o mrežnih entalpijah.

- Visoka oksidacijska stanja kovinskih ionov stabilizirajo majhne anione.

- <u>Primer:</u>

a. F ima večjo sposobnost, v primerjavi z ostalimi halogeni, da stabilizira **velike katione kovin.** Zato so edini poznani halogenidi Ag^{2+}, Co^{3+}, Mn^{4+} fluoridi *

$$MX(s) + \frac{1}{2}X_2(g) \rightarrow MX_2(s)$$

b. Tudi O^{2-} stabilizira visoka oksid. stanja kovin, saj ima velik naboj in je je majhen.

iii) Topnost nekaterih ionskih spojin v vodi

NaCl se npr. dobro raztaplja v vodi, kar pa ne moremo trditi za vse ionsko zgrajene snovi.
Raztapljanje (topnost) pomeni prekinitev vezi v mreži, zato jo lahko razložimo z ***mrežno*** in ***hidratacijsko entalpijo.***

Topilna entalpija

- Do raztapljanja lahko pride le v primeru, ko so vezi med gradniki v topljencu in vezi med gradniki v topilu približno enako močne.
- Množino toplote, ki se sprošča oz. porablja pri raztapljanju 1 mola topljenca imenujemo ***topilna entalpija.***
- Lahko jo ocenimo iz primerjav **mrežne** in **solvatacijske energije**.

$$\Delta H_{topilna} = \Delta H_{mrežna} + \Delta H_{solvatacije(hidratacije)}$$

Primer:

Za prekinitev vezi v molu LiCl potrebujemo 837 kJ:

$LiCl(s) \rightarrow Li^+(g) + Cl^-(g)$ $\quad \Delta H_{mrežna}$ (LiCl) = 837 kJ/mol

Pri hidrataciji 1 mola litijevih in 1 mola natrijevih ionov:

$Li^+(g) + Cl^-(g) \rightarrow Li^+(aq) + Cl^-(aq)$ $\quad \Delta H_{solvatacije}$= -886kJ

$\Delta H_{topilna} = \Delta H_{mrežna}$ (LiCl) + $\Delta H_{solvatacije}$ = 837kJ/mol + (-886kJ/mol) = - 49kJ

Izmerjena vrednost je -37 kJ/mol.

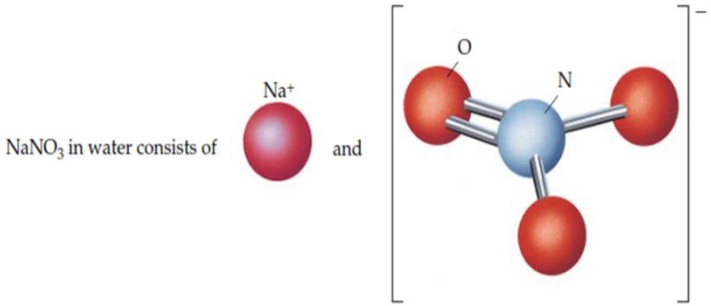
Lahko uporabimo ***splošna pravila*** o topnosti ionskih snovi v vodi:

- *Spojine z zelo različnimi radiji K in A so v splošnem dobro topne v vodi*
- *Spojine s podobnimi radiji K in A so najmanj topne v vodi*

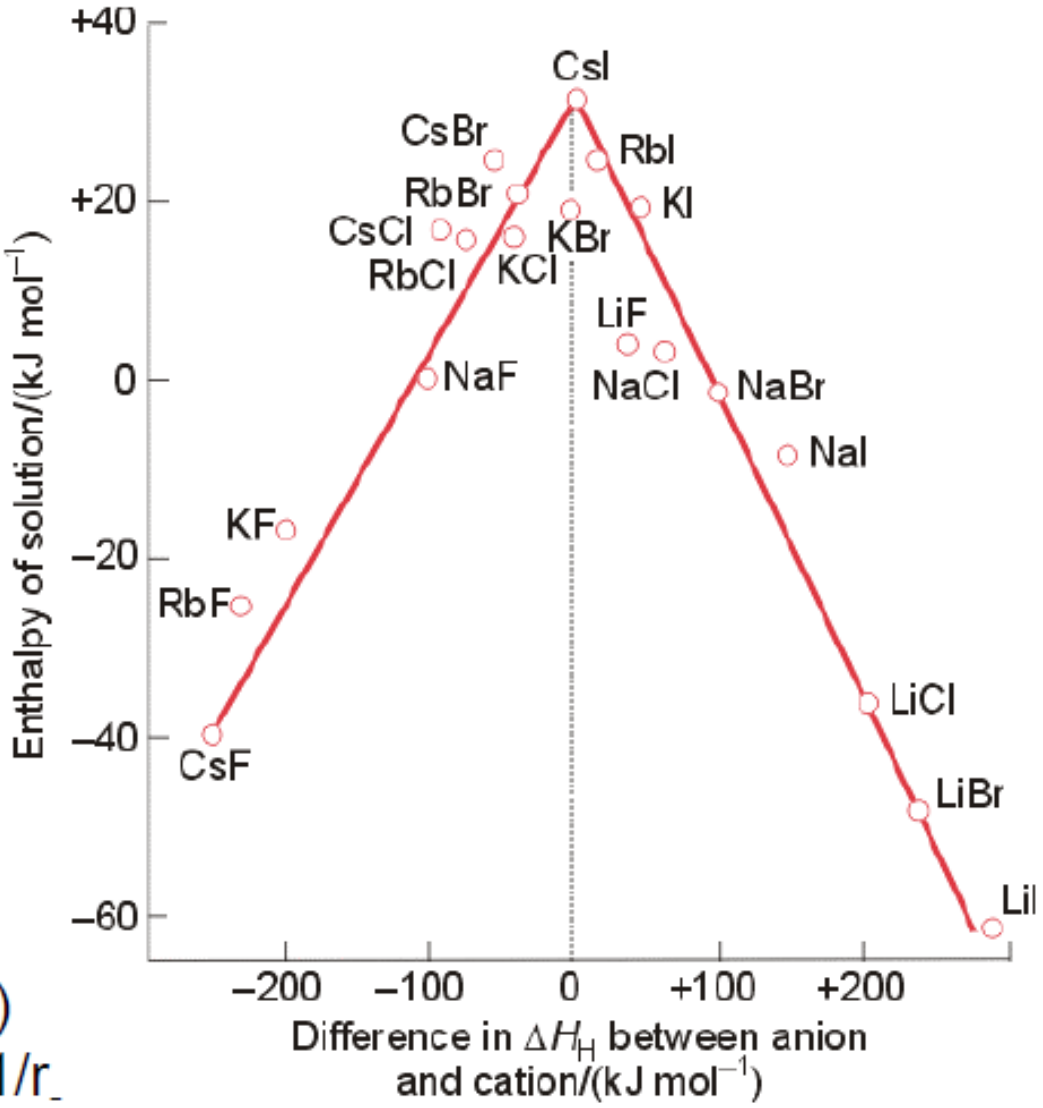
Tabele *(spodaj)* nam prikazujejo topnosti nekaterih ionskih snovi v vodi.

Primer $NaNO_3$ vsebuje tako alkalijski Na^+ kot nitratni ion. Če pogledamo v tabelo* lahko vidimo, da prisotnost obeh ionov pomeni, da bo sol topna v vodi.
In ker so ionske snovi, ki se raztapljajo v vodi tudi elektroliti, $NaNO_3$ sestavljajo izolirani hidratizirani ioni:

$NaNO_3$ v vodi:
Je elektrolit



Odvisnost med topilno entalpijo spojine in razliko med hidratacijskimi entalpijami!

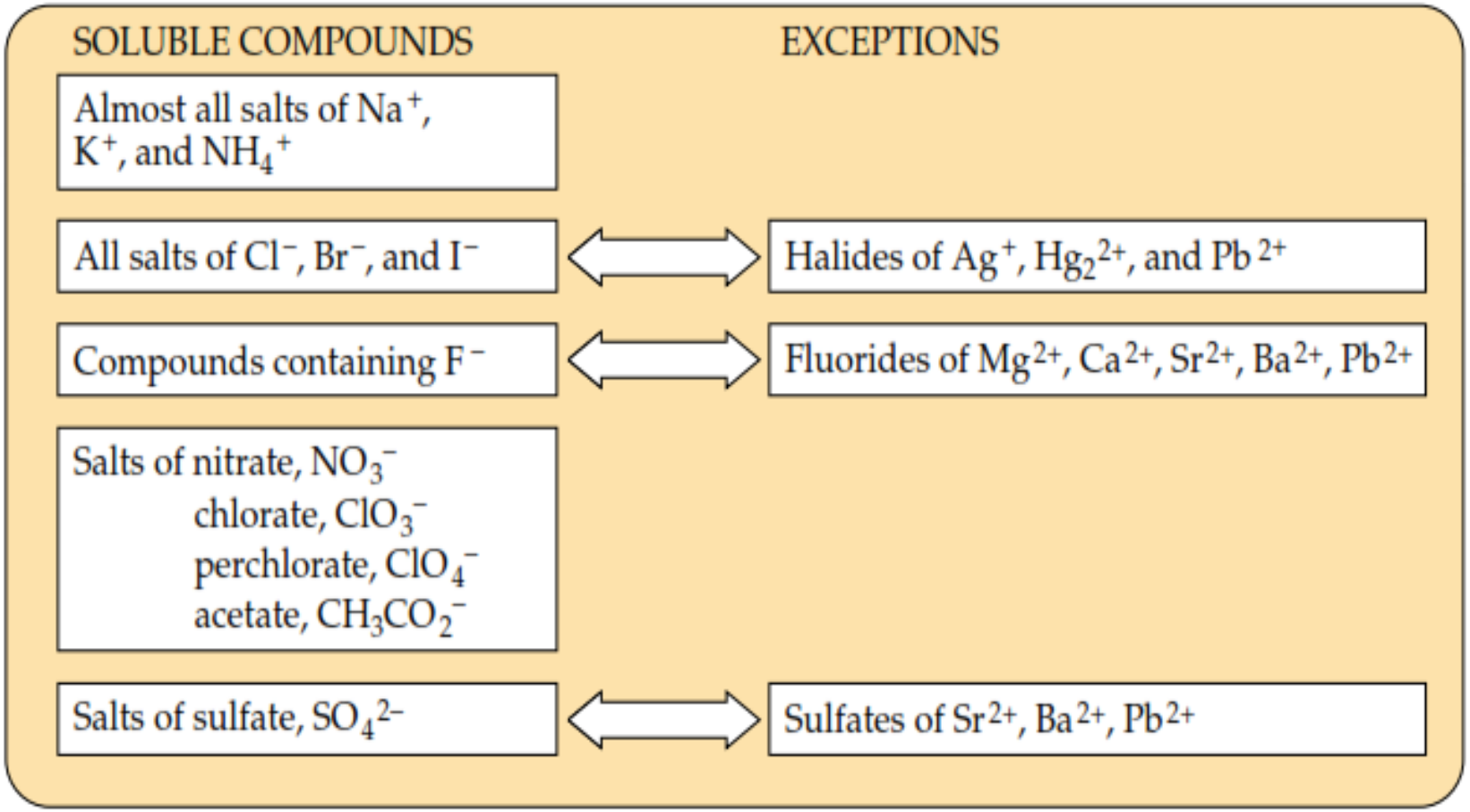


ΔH_L Proportional to $1/(r_+ + r_-)$

ΔH_{hyd} Proportional to $1/r_+ + 1/r_-$

2.19 a) Katera sol je bolj topna $MgSO_4$ ali $SrSO_4$?

2.19 b) Katera sol je bolj topna NaF ali $NaBF_4$?


SOLUBLE COMPOUNDS
EXCEPTIONS
Almost all salts of Na^+, K^+, and NH_4^+
All salts of Cl^-, Br^-, and I^-
Halides of Ag^+, Hg_2^{2+}, and Pb^{2+}
Compounds containing F^-
Fluorides of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}
Salts of nitrate, NO_3^-
chlorate, ClO_3^-
perchlorate, ClO_4^-
acetate, $CH_3CO_2^-$
Salts of sulfate, SO_4^{2-}
Sulfates of Sr^{2+}, Ba^{2+}, Pb^{2+}

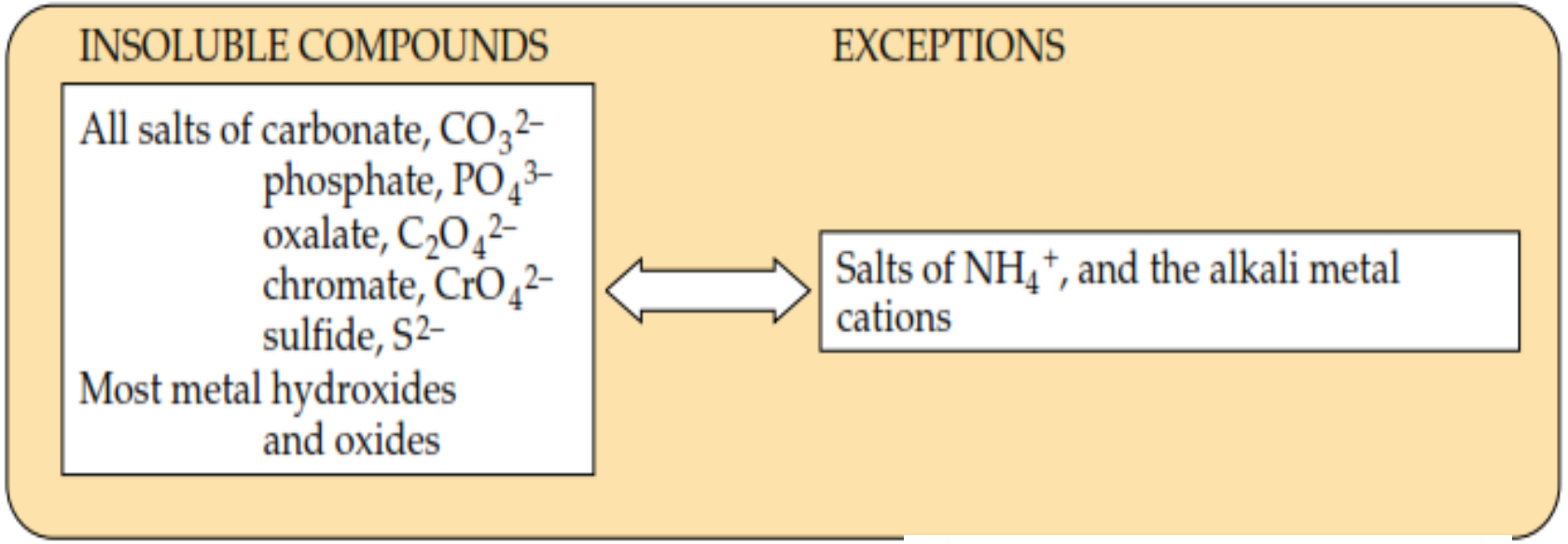


Figure 4.7 Guidelines to predict the solubility of ionic compounds. If a compound contains *one of the ions* in the column on the left in the top chart, the compound is predicted to be at least moderately soluble in water. There are a few exceptions, and those are noted at the right. Poorly soluble ionic compounds are usually formed by the anions listed at the bottom of the chart, with the exceptions of compounds with NH_4^+ and the alkali metal cations.

Vprašanja

- Katera izmed spojin je najbolj topna v vodi? Zakaj-razloži! NaCl, KBr, RbBr ali NaF?

Izračuni za entropijo

For the decomposition of iron(III) oxide to its elements,

$$2\ Fe_2O_3(s) \longrightarrow 4\ Fe(s) + 3\ O_2(g)$$

we would also predict an increase in entropy, because 3 mol of gaseous oxygen is present in the products, whereas the reactant is a solid. Because gases usually have much higher entropies than solids or liquids, gaseous substances are most important in determining entropy changes. Indeed, $\Delta S^\circ = +551.7\ J/K$ in this case.

An example in which a decrease in entropy would be predicted is

$$2\ CO(g) + O_2(g) \longrightarrow 2\ CO_2(g)$$

Here there are 3 mol of gaseous substances (2 of CO and 1 of O_2) at the beginning of the reaction but only 2 mol of gaseous substances at the end. Two moles of gas (of whatever kind) contain less entropy than 3 mol of gas, and so ΔS is negative. The actual value is $\Delta S^\circ = -173.0\ J/K$.

Another example of decreased entropy is the process

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

Here the reactant ions are free to move about among water molecules in aqueous solution, but those same ions are held in a crystal lattice in the solid, a situation with much greater constraint. As a result, $\Delta S^\circ = -33.1\ J/K$.

Entropija okolice je v splošnem definirana kot :

$\Delta S_{(okolica)} = - \Delta H^o_r / T$

pri exo reakciji, kjer E prehaja v okolico, se entropija poveča!

Standardno reakcijsko entropijo **pa obravnavamo kot entropijo sistema in je za reakcijo rjavenja železa:**

$$4Fe(s) + 3O_2(g) \Rightarrow 2Fe_2O_3\,(s) \quad \Delta H_r = -1648 kJ/mol$$

$$\Delta S^0_{(sistema)} = \Delta S^0_{(reakc.)} = \Sigma S^0_{(prod.)} - \Sigma S^0_{(reakt.)}$$

Tabele!

Entropija se zmanjšuje, zakaj je reakcija spontana?

$\Delta S^{o}_{m\ (sistema)} = 2\times\Delta S_{Fe2O3} - (4\times \Delta S^{o}_{Fe} + 3\times\Delta S^{o}_{O2}) =$

$\Delta S^{0}_{\ (sistema)} = 2x87,4JK^{-1}mol^{-1} – (4x27,78\ JK^{-1}mol^{-1} + 3x\ 205\ JK^{-1}mol^{-1}) = -549,4\ JK^{-1}mol^{-1} = -549J/Kmol$

$$4Fe(s) + 3O_2(g) \Rightarrow 2Fe_2O_3\ (s)$$

Entropija se zmanjša: plin (kisik) iz prostora se lokalizira v spojini (oksid železa), vendar pa je reakcija eksotermna!!

Čeprav se S zmanjšuje je reakcija spontana.

Upoštevati moramo še spremembo entropije okolice, ki jo dobimo iz energije ΔH^o_r , ki je v okolico prešla pri eksotermnem procesu:

$$\Delta S_{(okolica)} = - \Delta H^o_r / T$$

$$= -(- 1648kJ/mol/298,15K)=5527J/Kmol$$

Povečanje entropije je posledica energije, ki se pri reakciji sprosti v okolico.

$$\Delta S_{(celotna)} = \Delta S_{(okolica)} + \Delta S_{(sistema)}=$$

$$5527J/Kmol -549,4\ JK^{-1}mol^{-1} = 4978\ J/Kmol$$

PRIMER 20.1 **Izračunajte entropijske spremembe kemijske reakcije!**

Dušikov dioksid nastane kot produkt med dušikovim monoksidom in kisikom pri 25 °C. Definirajte standardno entropijsko spremembo ΔS^0 za omenjeno reakcijo, ΔS^0_r (= $\Delta S^0_{sist.}$).

Tabele: slide 84!

EXAMPLE 20.1 *Calculating an Entropy Change for a Chemical Reaction*

Nitrogen dioxide is formed from nitrogen monoxide and oxygen in a product-favored reaction at 25 °C (page 414). Determine the standard entropy change, ΔS°, for the reaction, ΔS°_{rxn} $(= \Delta S^\circ_{system})$.

Solution As in any problem involving a chemical reaction, first write the balanced equation.

$$2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)$$

Next, subtract the entropies of the reactants from the entropies of the products (Appendix K), paying careful attention to scale each entropy by the number of moles of reactant or product involved.

$$\begin{aligned}\Delta S^\circ_{rxn} &= (2\ \text{mol}\ NO_2)(240.1\ \text{J/K}\cdot\text{mol}) \\ &\quad - [(2\ \text{mol}\ NO)(210.8\ \text{J/K}\cdot\text{mol}) + (1\ \text{mol}\ O_2)(205.1\ \text{J/K}\cdot\text{mol})] \\ &= -146.5\ \text{J/K}\end{aligned}$$

or -73.25 J/K for the formation of 1 mol of NO_2.

Notice that the sign of the entropy change is negative. This is largely due to the fact that the chemical reaction began with 3 mol of gaseous reactants and ended with 2 mol of gaseous product.

$$\Delta G^{o}_{r} = \Delta H^{o}_{r} - T\Delta S^{o}$$

PRIMER 20.4 **V katero smer se pomakne reakcija, v smer reaktantov ali v smer produktov?**

Klasificiraj naslednje reakcije, ki so zbrane v spodnji preglednici.

REAKCIJA	$\Delta H^{0}_{r.}$ (298 K) [kJ]	$\Delta S^{0}_{sist.}$ (298 K) [J/K]
a.) $CH_4\,(g)+O_2\,(g) \longrightarrow 2H_2O\,(l)+CO_2\,(g)$	-890,3	-243,0
b.) $2Fe_2O_3\,(s)+3C \longrightarrow 4Fe\,(s)+3CO_2\,(g)$	+467,9	+560,3
c.) $C(grafit)+O_2\,(g) \longrightarrow CO_2\,(g)$	-393,5	+2,9
d.) $N_2\,(g)+3Cl_2\,(g) \longrightarrow 2NCl_3\,(g)$	-460	-275

20.4. **(a)** Both ΔH° and ΔS° are negative, so the outcome depends on T.

(b) Both ΔH° and ΔS° are positive, so the outcome depends on T.

(c) Reaction is exothermic (ΔH° is negative), and ΔS° is positive. The reaction is product-favored.

(d) Both ΔH° and ΔS° are negative, so the outcome depends on T.

$$\Delta G^o_r = \Delta H^o_r - T\Delta S^o$$

PRIMER 20.2 Izračunajte ΔG^0_r iz ΔH^0_r in ΔS^0_r!

Izračunaj spremembo strandardne proste energije pri reakciji nastanka metana pri 298 K.

$$C + 2H_2\,(g) \longrightarrow CH_4\,(g)$$

Solution The following values for ΔH_f° and S° are provided in Appendix K.

	C(graphite)	$H_2(g)$	$CH_4(g)$
ΔH_f° (kJ/mol)	0	0	−74.8
S° (J/K · mol)	5.7	130.7	186.3

From these values, we can find both ΔH° and ΔS° for the reaction.

$$\begin{aligned}\Delta H^\circ_{rxn} &= \Delta H^\circ_f\,[CH_4(g)] - \{\Delta H^\circ_f\,[C(\text{graphite})] + 2\,\Delta H^\circ_f\,[H_2(g)]\}\\ &= -74.8\text{ kJ} - (0 + 0)\\ &= -74.8\text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ_{rxn} &= S^\circ\,[CH_4(g)] - \{S^\circ\,[C(\text{graphite})] + 2\,S^\circ\,[H_2(g)]\}\\ &= 186.3\text{ J/K}\cdot\text{mol} - [1\text{ mol}(5.7\text{ J/K}\cdot\text{mol}) + 2\text{ mol}\,(130.7\text{ J/K}\cdot\text{mol})]\\ &= -80.8\text{ J/K}\end{aligned}$$

Both the enthalpy change and the entropy change for this reaction are negative. In Table 20.2 this is a case when the reaction is predicted to be product-favored at ''low temperature.'' These values alone do not tell us if the temperature is low enough, however. By combining them in the Gibbs equation, and calculating ΔG°_{rxn} for a temperature of 25 °C, we can predict with certainty the outcome of the reaction.

$$\begin{aligned}\Delta G^\circ_{rxn} &= \Delta H^\circ_{rxn} - T\,\Delta S^\circ_{rxn}\\ &= -74.8\text{ kJ} - (298\text{ K})\,(-80.8\text{ J/K})\,(1\text{ kJ}/1000\text{ J})\\ &= -74.8\text{ kJ} - (-24.1\text{ kJ})\\ &= -50.7\text{ kJ}\end{aligned}$$

ΔG°_{rxn} is negative at 298 K, so the reaction is predicted to be product-favored.

In this case the product $T\,\Delta S^\circ$ is negative and smaller than ΔH°_{rxn} because the entropy change is relatively small. Chemists call this an ''enthalpy-controlled reaction'' because the exothermic nature of the reaction overcomes the decline in entropy of the system.

PRIMER 20.4 Izračunajte K_p iz $\Delta G^0_{r.}$!

Sprememba standardne proste energije za reakcijo, $\Delta G^0_{r.}$,

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

je -32.9 kJ. Izračunajte konstanto ravnotežja za to reakcijo pri 25 °C.

EXAMPLE 20.4 *Calculating K_p from ΔG°_{rxn}*

The standard free energy change for the reaction, ΔG°_{rxn},

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

is -32.9 kJ. Calculate the equilibrium constant for this reaction at 25 °C.

Solution In this case, we need only substitute the appropriate values into Equation 20.4, taking care that the units of ΔG°_{rxn} are the same as those of RT.

$$\begin{aligned}
\Delta G^\circ_{rxn} &= -RT \ln K_p \\
(-32.9\text{ kJ})(1000\text{ J/kJ}) &= -(8.3145\text{ J/K}\cdot\text{mol})(298\text{ K}) \ln K_p \\
\ln K_p &= 13.3 \\
K_p &= e^{13.3} \\
&= 6 \times 10^5
\end{aligned}$$

The equilibrium constant has a very large value, which means the equilibrium position lies very far to the product side at 25 °C. (To find K_p using a calculator, enter 13.3 and then strike the key labeled "e^x" or "inv(erse) ln x." See Appendix A for more information.)

PRIMER 20.5 Izračunajte ΔG^0_r iz K_p!

Izračunajte ΔG^0_r za reakcijo razpada amonijevega klorida pri 25 °C, če je $K_p = 1{,}1 \times 10^{-16}$.

$$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$$

EXAMPLE 20.5 *Calculating ΔG°_{rxn} from K_p*

Calculate ΔG°_{rxn} for the decomposition of ammonium chloride at 25 °C from $K_p = 1.1 \times 10^{-16}$.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

Solution Here we substitute the value of K_p into Equation 20.4 at a temperature of 25 °C (=298 K).

$$\begin{aligned}\Delta G^\circ_{rxn} &= -RT \ln K_p = -(8.3145\ \text{J/K} \cdot \text{mol})(298\ \text{K}) \ln (1.1 \times 10^{-16}) \\ &= 9.1 \times 10^4\ \text{J} \\ &= 91\ \text{kJ}\end{aligned}$$

PRIMER 20.6 Uporaba ΔH^0_f, S^0, ΔG^0_f in izračun K!

Potek kemijskih reakcij: Ena od pomembnih spoznanj je tvorba produkta v plinastem stanju, ki lahko „pobegne“, kadar gre za reakcijo odprtega tipa. Poglejmo primer take reakcije iz kvantitativnega, termodinamskega stališča.

$$MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$$

1. Ali reakcija poteče pri sobni temperaturi, npr. 25°C?
2. Ali je reakcija eksotermna ali endotermna?
3. Kakšna je vrednost K_p pri 25 °C?
4. Pri kateri temperaturi je K_p=1? **$\Delta G^o = - RT \ln K$**
5. Ali pri povišani temperaturi dobimo več ali manj produkta?

Podatki: $\Delta H^0_f(MgO)$= -601,7 kJ/mol; $\Delta H^0_f(CO_2)$= -393,5 kJ/mol; $\Delta H^0_f(MgCO_3)$=-1095,8 kJ/mol; $\Delta S^0(MgO)$= 26,9 J/molK; $\Delta S^0(CO_2)$= 213,7 J/molK; $\Delta S^0(MgCO_3)$= 65,7 J/molK; R=8,3245 J/molK

Solution To answer the first two questions we need to know ΔG°_{rxn} and its sign, as well as ΔH°_{rxn}. Using data from Appendix K, we have

$$\begin{aligned}\Delta H^\circ_{rxn} &= \Delta H^\circ_f[MgO(s)] + \Delta H^\circ_f[CO_2(g)] - \Delta H^\circ_f[MgCO_3(s)] \\ &= 1\text{ mol }(-601.7\text{ kJ/mol}) + 1\text{ mol }(-393.5\text{ kJ/mol}) \\ &\quad - 1\text{ mol }(-1095.8\text{ kJ/mol}) \\ &= +100.6\text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ_{rxn} &= S^\circ[MgO(s)] + S^\circ[CO_2(g)] - S^\circ[MgCO_3(s)] \\ &= 1\text{ mol }(26.9\text{ J/K}\cdot\text{mol}) + 1\text{ mol }(213.7\text{ J/K}\cdot\text{mol}) - 1\text{ mol }(65.7\text{ J/K}\cdot\text{mol}) \\ &= +174.9\text{ J/K}\end{aligned}$$

With the enthalpy and entropy changes for reaction known, we can combine them to calculate the free energy change for the reaction.

$$\begin{aligned}\Delta G^\circ_{rxn} &= \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn} = 100.6\text{ kJ} - (298\text{ K})(174.9\text{ J/K})(1\text{ kJ}/1000\text{ J}) \\ &= 48.5\text{ kJ}\end{aligned}$$

The decomposition of magnesium carbonate to give carbon dioxide is reactant-favored at 298 K. What little reaction that does occur at 298 K is entropy-driven because the entropy change is positive. The enthalpy change is positive and too large to be offset by the increase in entropy to make the reaction product-favored at this temperature.

Having found ΔG°_{rxn}, K_p can now be calculated at 298 K from

$$\Delta G^\circ_{rxn} = -RT \ln K_p \qquad \Delta G^o = - RT \ln K$$

or

$$\ln K_p = -\frac{\Delta G^\circ_{rxn}}{RT} = -\frac{48{,}500\ \text{J}}{(8.3145\ \text{J/K} \cdot \text{mol})(298\ \text{K})} = -19.6$$

$$K_p = e^{-19.6} = 3 \times 10^{-9}$$

This means that $K_p = P_{CO_2} = 3 \times 10^{-9}$, or that the partial pressure of CO_2 is 3×10^{-9} atm at equilibrium at 25 °C. The partial pressure is extremely small because ΔG°_{rxn} has such a large, positive value.

At what temperature does $K_p = 1$? From the preceding analysis you know that ΔS°_{rxn} drives the reaction. This means that, at a sufficiently high temperature, the negative value of $-T\Delta S^\circ$ could become large enough to outweigh the inhibiting effect of a positive ΔH°_{rxn}, and ΔG°_{rxn} would become negative. A balance between ΔH° and $-T\Delta S^\circ$ is reached when $\Delta G^\circ = 0$, that is, when $K = 1$. The breakeven temperature is

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{100.6\ \text{kJ}}{0.1749\ \text{kJ/K}} = 575.2\ \text{K (or } 302.0\ ^\circ\text{C)}$$

At approximately 300 °C the equilibrium constant is 1; that is, $P_{CO_2} = 1$ atm. At still higher temperatures, the $-T\Delta S^\circ$ term increasingly dominates the ΔH° term, and the yield increases because K increases. This means the answer to question 5 is "more product-favored," and this is true for any reaction with $\Delta S^\circ_{rxn} > 0$.

Tabele

Selected Thermodynamic Values*

Species	ΔH_f°(298.15K) kJ/mol	S°(298.15K) J/K · mol	ΔG_f°(298.15K) kJ/mol
Aluminum			
$Al(s)$	0	28.3	0
$AlCl_3(s)$	−704.2	110.67	−628.8
$Al_2O_3(s)$	−1675.7	50.92	−1582.3
Barium			
$BaCl_2(s)$	−858.6	123.68	−810.4
$BaO(s)$	−553.5	70.42	−525.1
$BaSO_4(s)$	−1473.2	132.2	−1362.2
Beryllium			
$Be(s)$	0	9.5	0
$Be(OH)_2$	−902.5	51.9	−815.0
Bromine			
$Br(g)$	111.884	175.022	82.396
$Br_2(\ell)$	0	152.2	0
$Br_2(g)$	30.907	245.463	3.110
$BrF_3(g)$	−255.60	292.53	−229.43
$HBr(g)$	−36.40	198.695	−53.45
Calcium			
$Ca(s)$	0	41.42	0
$Ca(g)$	178.2	158.884	144.3
$Ca^{2+}(g)$	1925.90	—	—
$CaC_2(s)$	−59.8	69.96	−64.9
$CaCO_3(s;\ \text{calcite})$	−1206.92	92.9	−1128.79
$CaCl_2(s)$	−795.8	104.6	−748.1
$CaF_2(s)$	−1219.6	68.87	−1167.3
$CaH_2(s)$	−186.2	42	−147.2

Selected Thermodynamic Values* (*Continued*)

Species	ΔH_f°(298.15K) kJ/mol	S°(298.15K) J/K · mol	ΔG_f°(298.15K) kJ/mol
CaS(s)	−482.4	56.5	−477.4
$Ca(OH)_2$(s)	−986.09	83.39	−898.49
$Ca(OH)_2$(aq)	−1002.82	−74.5	−868.07
$CaSO_4$(s)	−1434.11	106.7	−1321.79
Carbon			
C(s, graphite)	0	5.740	0
C(s, diamond)	1.895	2.377	2.900
C(g)	716.682	158.096	671.257
$CCl_4(\ell)$	−135.44	216.40	−65.21
CCl_4(g)	−102.9	309.85	−60.59
$CHCl_3$(liq)	−134.47	201.7	−73.66
$CHCl_3$(g)	−103.14	295.71	−70.34
CH_4(g, methane)	−74.81	186.264	−50.72
C_2H_2(g, acetylene)	226.73	200.94	209.20
C_2H_4(g, ethylene)	52.26	219.56	68.15
C_2H_6(g, ethane)	−84.68	229.60	−32.82
C_3H_8(g, propane)	−103.8	269.9	−23.49
$C_6H_6(\ell$, benzene)	49.03	172.8	124.5
$CH_3OH(\ell$, methanol)	−238.66	126.8	−166.27
CH_3OH(g, methanol)	−200.66	239.81	−161.96
$C_2H_5OH(\ell$, ethanol)	−277.69	160.7	−174.78
C_2H_5OH(g, ethanol)	−235.10	282.70	−168.49
CO(g)	−110.525	197.674	−137.168
CO_2(g)	−393.509	213.74	−394.359

Cesium			
$Cs(s)$	0	85.23	0
$Cs^+(g)$	457.964	—	—
$CsCl(s)$	−443.04	101.17	−414.53
Chlorine			
$Cl(g)$	121.679	165.198	105.680
$Cl^-(g)$	−233.13	—	—
$Cl_2(g)$	0	223.066	0
$HCl(g)$	−92.307	186.908	−95.299
$HCl(aq)$	−167.159	56.5	−131.228
Chromium			
$Cr(s)$	0	23.77	0
$Cr_2O_3(s)$	−1139.7	81.2	−1058.1
$CrCl_3(s)$	−556.5	123.0	−486.1
Copper			
$Cu(s)$	0	33.150	0
$CuO(s)$	−157.3	42.63	−129.7
$CuCl_2(s)$	−220.1	108.07	−175.7
Fluorine			
$F_2(g)$	0	202.78	0
$F(g)$	78.99	158.754	61.91
$F^-(g)$	−255.39	—	—
$F^-(aq)$	−332.63	−13.8	−278.79
$HF(g)$	−271.1	173.779	−273.2
$HF(aq)$	−332.63	−13.8	−278.79

Species	ΔH_f°(298.15K) kJ/mol	S°(298.15K) J/K · mol	ΔG_f°(298.15K) kJ/mol
Hydrogen			
$H_2(g)$	0	130.684	0
$H(g)$	217.965	114.713	203.247
$H^+(g)$	1536.202	—	—
$H_2O(\ell)$	−285.830	69.91	−237.129
$H_2O(g)$	−241.818	188.825	−228.572
$H_2O_2(\ell)$	−187.78	109.6	−120.35
Iodine			
$I_2(s)$	0	116.135	0
$I_2(g)$	62.438	260.69	19.327
$I(g)$	106.838	180.791	70.250
$I^-(g)$	−197.	—	—
$ICl(g)$	17.78	247.551	−5.46
Iron			
$Fe(s)$	0	27.78	0
$FeO(s)$	−272	—	—
Fe_2O_3(s, hematite)	−824.2	87.40	−742.2
Fe_3O_4(s, magnetite)	−1118.4	146.4	−1015.4
$FeCl_2(s)$	−341.79	117.95	−302.30
$FeCl_3(s)$	−399.49	142.3	−344.00
FeS_2(s, pyrite)	−178.2	52.93	−166.9
$Fe(CO)_5(\ell)$	−774.0	338.1	−705.3
Lead			
$Pb(s)$	0	64.81	0
$PbCl_2(s)$	−359.41	136.0	−314.10
PbO(s, yellow)	−217.32	68.70	−187.89
$PbS(s)$	−100.4	91.2	−98.7

Lithium			
$Li(s)$	0	29.12	0
$Li^+(g)$	685.783	—	—
$LiOH(s)$	−484.93	42.80	−438.95
$LiOH(aq)$	−508.48	2.80	−450.58
$LiCl(s)$	−408.701	59.33	−384.37
Magnesium			
$Mg(s)$	0	32.68	0
$MgCl_2(s)$	−641.32	89.62	−591.79
$MgCO_3(s)$	−1095.8	65.7	−1012.1
$MgO(s)$	−601.70	26.94	−569.43
$Mg(OH)_2(s)$	−924.54	63.18	−833.51
$MgS(s)$	−346.0	50.33	−341.8
Mercury			
$Hg(\ell)$	0	76.02	0
$HgCl_2(s)$	−224.3	146.0	−178.6
$HgO(s, red)$	−90.83	70.29	−58.539
$HgS(s, red)$	−58.2	82.4	−50.6
Nickel			
$Ni(s)$	0	29.87	0
$NiO(s)$	−239.7	37.99	−211.7
$NiCl_2(s)$	−305.332	97.65	−259.032
Nitrogen			
$N_2(g)$	0	191.61	0
$N(g)$	472.704	153.298	455.563

Selected Thermodynamic Values* (*Continued*)

Species	ΔH_f°(298.15K) kJ/mol	S°(298.15K) J/K · mol	ΔG_f°(298.15K) kJ/mol
$NH_3(g)$	−46.11	192.45	−16.45
$N_2H_4(\ell)$	50.63	121.21	149.34
$NH_4Cl(s)$	−314.43	94.6	−202.87
$NH_4Cl(aq)$	−299.66	169.9	−210.52
$NH_4NO_3(s)$	−365.56	151.08	−183.87
$NH_4NO_3(aq)$	−339.87	259.8	−190.56
$NO(g)$	90.25	210.76	86.55
$NO_2(g)$	33.18	240.06	51.31
$N_2O(g)$	82.05	219.85	104.20
$N_2O_4(g)$	9.16	304.29	97.89
$NOCl(g)$	51.71	261.69	66.08
$HNO_3(\ell)$	−174.10	155.60	−80.71
$HNO_3(g)$	−135.06	266.38	−74.72
$HNO_3(aq)$	−207.36	146.4	−111.25
Oxygen			
$O_2(g)$	0	205.138	0
$O(g)$	249.170	161.055	231.731
$O_3(g)$	142.7	238.93	163.2
Phosphorus			
P_4(s, white)	0	164.36	0
P_4(s, red)	−70.4	91.2	−48.4
$P(g)$	314.64	163.193	278.25
$PH_3(g)$	5.4	310.23	13.4
$PCl_3(g)$	−287.0	311.78	−267.8
$P_4O_{10}(s)$	−2984.0	228.86	−2697.7
$H_3PO_4(s)$	−1279.0	110.5	−1119.1

Potassium			
$K(s)$	0	64.18	0
$KCl(s)$	−436.747	82.59	−409.14
$KClO_3(s)$	−397.73	143.1	−296.25
$KI(s)$	−327.90	106.32	−324.892
$KOH(s)$	−424.764	78.9	−379.08
$KOH(aq)$	−482.37	91.6	−440.50
Silicon			
$Si(s)$	0	18.83	0
$SiBr_4(\ell)$	−457.3	277.8	−443.9
$SiC(s)$	−65.3	16.61	−62.8
$SiCl_4(g)$	−657.01	330.73	−616.98
$SiH_4(g)$	34.3	204.62	56.9
$SiF_4(g)$	−1614.94	282.49	−1572.65
SiO_2(s, quartz)	−910.94	41.84	−856.64
Silver			
$Ag(s)$	0	42.55	0
$Ag_2O(s)$	−31.05	121.3	−11.20
$AgCl(s)$	−127.068	96.2	−109.789
$AgNO_3(s)$	−124.39	140.92	−33.41
Sodium			
$Na(s)$	0	51.21	0
$Na(g)$	107.32	153.712	76.761
$Na^+(g)$	609.358	—	—
$NaBr(s)$	−361.062	86.82	−348.983

Species	ΔH_f°(298.15K) kJ/mol	S°(298.15K) J/K · mol	ΔG_f°(298.15K) kJ/mol
NaCl(s)			
NaCl(g)	−176.65	229.81	−196.66
NaCl(aq)	−407.27	115.5	−393.133
NaOH(s)	−425.609	64.455	−379.494
NaOH(aq)	−470.114	48.1	−419.150
Na_2CO_3(s)	−1130.68	134.98	−1044.44
Sulfur			
S(s, rhombic)	0	31.80	0
S(g)	278.805	167.821	238.250
S_2Cl_2(g)	−18.4	331.5	−31.8
SF_6(g)	−1209	291.82	−1105.3
H_2S(g)	−20.63	205.79	−33.56
SO_2(g)	−296.830	248.22	−300.194
SO_3(g)	−395.72	256.76	−371.06
$SOCl_2$(g)	−212.5	309.77	−198.3
$H_2SO_4(\ell)$	−813.989	156.904	−690.003
H_2SO_4(aq)	−909.27	20.1	−744.53
Tin			
Sn(s, white)	0	51.55	0
Sn(s, gray)	−2.09	44.14	0.13
$SnCl_4(\ell)$	−511.3	258.6	−440.1
$SnCl_4$(g)	−471.5	365.8	−432.2
SnO_2(s)	−580.7	52.3	−519.6
Titanium			
Ti(s)	0	30.63	0
$TiCl_4(\ell)$	−804.2	252.34	−737.2
$TiCl_4$(g)	−763.2	354.9	−726.7
TiO_2	−939.7	49.92	−884.5
Zinc			
Zn(s)	0	41.63	0
$ZnCl_2$(s)	−415.05	111.46	−369.398