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
$CaCO_3(s;\ calcite)$	−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

TERMOKEMIJA

…..obravnava energijske spremembe pri kemijskih reakcijah:

- $C + O_2 \rightarrow CO_2 + 395.01\ kJ/mol$ eksotermna reakcija
- $H_2O \rightarrow H_2 + 1/2\ O_2 - 287.01\ kJ/mol$ endotermna reakcija
- Q_V , Q_P..... reakcijski toploti pri konstantnem volumnu oz. tlaku
- $Q_V = \Delta E$ sprememba notranje energije
- $Q_P = \Delta H$ sprememba entalpije
- Če sistem energijo odda (eksotermna reakcija)

  sta ΔE in $\Delta H < 0$

- Če sistem energijo sprejme (endotermna reakcija)

  sta ΔE in $\Delta H > 0$

TERMOKEMIJSKI IZRAČUNI

Pri izračunu entalpij kemijskih reakcij, moramo upoštevati naslednje:

ker je entalpija odvisna od T in P, podajamo entalpije reakt. in prod.po dogovoru pri standardnih pogojih:

25 °C =298 K in **ΔH_r^0 = standardna reakcijska entalpija**

100,0 kPa=1 bar

- **Pretvornik: 1cal/mol= 4,18J/mol**
- **Informacijo o reakcijah lahko izrazimo na dva načina:**
  1. **s termokemijsko enačbo**
  2. **z energijskim (entalpijskim) diagramom**

HESSOV ZAKON

- Energija, ki se pri neki kemijski reakciji sprosti ali porabi je odvisna le od začetnega in končnega stanja
- Standardna reakcijska entalpija ΔH_r^0 je enaka vsoti standardnih reakcijskih entalpij vmesnih stopenj, na katere lahko formalno razdelimo dano reakcijo
- Pravila:

  a) Če reakcijo obrnemo, se spremeni predznak ΔH_r

  b) Če reakcijo pomnožimo z nekim faktorjem, moramo pomnožiti tudi ΔH_r

Termokemijska enačba

Če reakcijo obrnemo, se spremeni predznak ΔHr :

$$H_2O(g) \xrightarrow{+241.8\ kJ} H_2(g) + \tfrac{1}{2}\ O_2(g) \qquad \Delta H = +241.8\ kJ$$

Change is endothermic; ΔH is positive

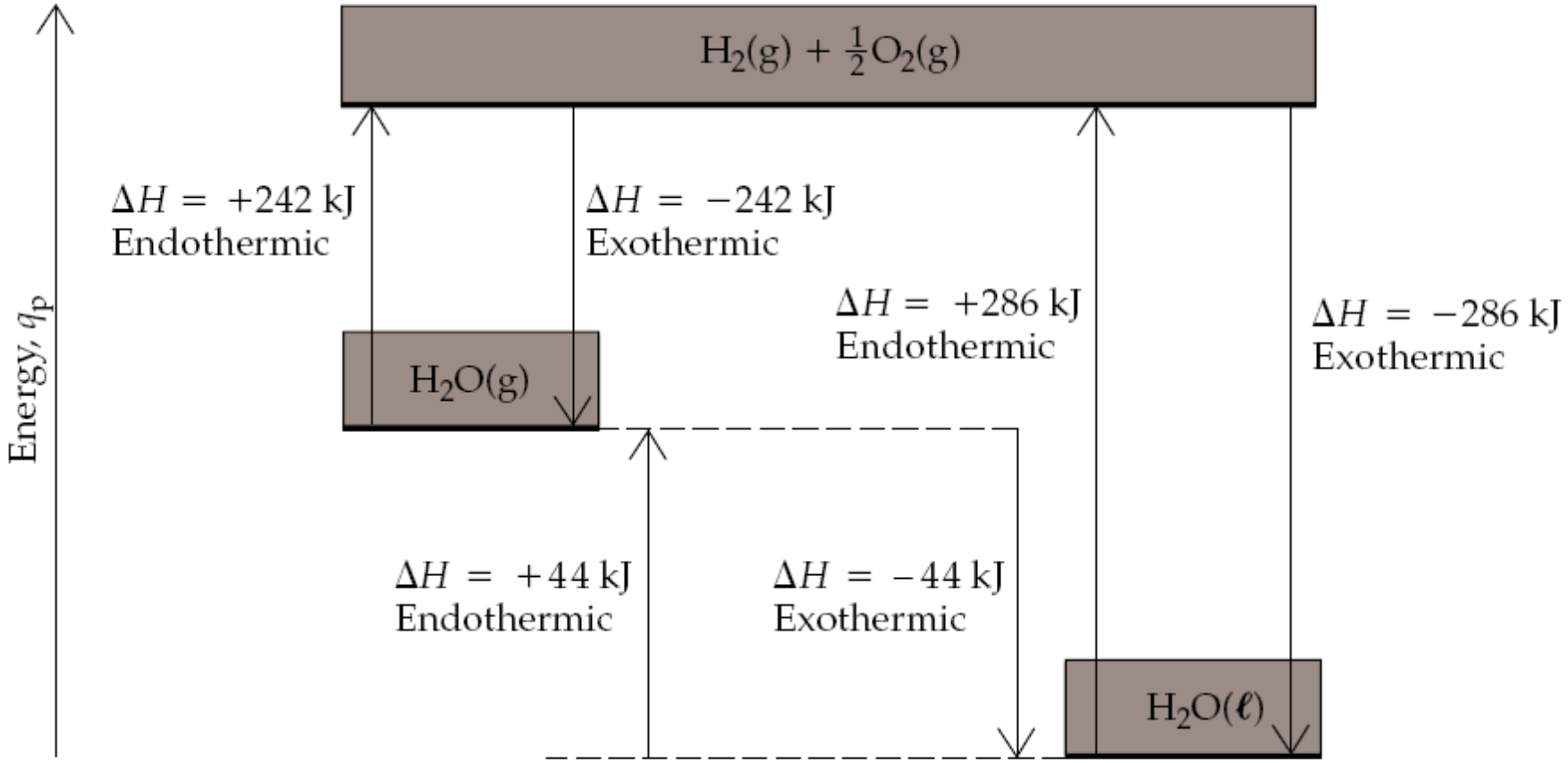
Decomposition of 1 mol of water vapor requires 241.8 kJ of energy to be transferred in from the surroundings

$$H_2(g) + \tfrac{1}{2}\ O_2(g) \xrightarrow{-241.8\ kJ} H_2O(g) \qquad \Delta H = -241.8\ kJ$$

Change is exothermic; ΔH is negative

Formation of 1 mol of water vapor transfers 241.8 kJ of energy to the surroundings

Entalpijski diagram:



- ***Spremembe entalpij pri kemijskih reakcijah*** podajamo običajno pri standardnih pogojih – **standardne reakcijske entalpije, ΔH_r^0.**
- V primeru, da gre za reakcijo nastanka spojine iz elementov, je seveda

$$\Delta H_t^0 = \Delta H_r^0$$

- **$\Delta H_r^0 = \sum \Delta H_t^0$ (produkti) - $\sum \Delta H_t^0$ (reaktanti)**
- S pomočjo standardnih tvorbenih entalpij **ΔH_t^0** (tabelirane vrednosti) lahko izračunamo standardne reakcijske entalpije po formuli:

- **Primer:** Entalpije ΔH_t^0, so podane v kJ/mol:
- **C_2H_5OH (l) + 3 O_2 (g) = 2 CO_2 (g) + 3 H_2O (g)**

  -277,6 0 -393,1 -241,8 tabele!

ΔH_r^0 = 2 mol . (-393,1 kJ mol-1) + 3 mol . (-241,8 kJ mol-1) – 1 mol . (-277,6 kJ mol -1) = = -1234 kJ

Primer 1:

Izračunaj *spremembo standardne entalpije* spodnje reakcije,če poznaš naslednje reakcije:

$C(s) + 1/2\ O_2(g) = CO(g)$ $\quad \Delta H_1 = ?$

$CO(g) + 1/2\ O_2(g) = CO_2(g)$ $\quad \Delta H_2 = -283{,}0$ kJ/mol

$C(s) + O_2(g) = CO_2(g)$ $\quad \Delta H_3 = -393{,}5$ kJ/mol

---

- postopni sežig v dveh stopnjah
- takojšnji sežig
- $\Delta H_3 = \Delta H_1 + \Delta H_2$
- $\Delta H_1 = \Delta H_3 - \Delta H_2$ možnost, da spremembe izračunamo tudi za reakcije, ki jih ne moremo izvesti
- $\Delta H_1 = -393{,}5$ kJ/mol – (-283,0 kJ/mol) = -110,5 kJ/mol

Entalpijski diagram:

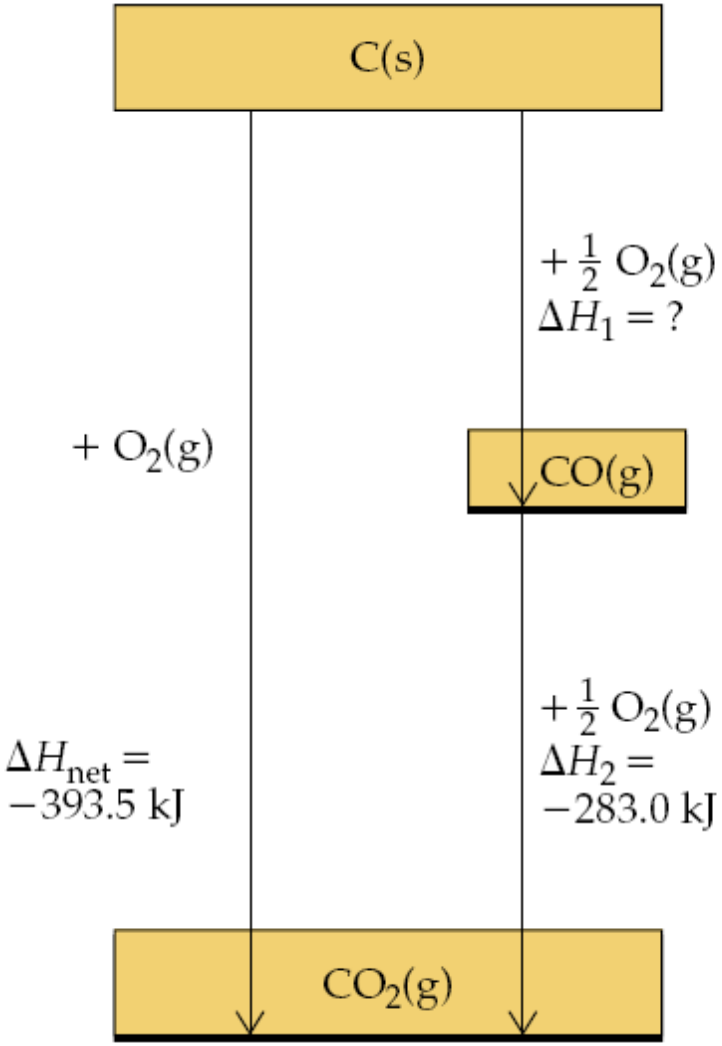


Figure 6.15 One mole of carbon dioxide can be formed from carbon and oxygen in a direct reaction ($\Delta H_{net} = -393.5$ kJ) or in two steps. Hess's law states that the sum of the enthalpy changes for the two steps must equal that for the direct reaction. That is, $\Delta H_1 + \Delta H_2 = \Delta H_{net}$. Knowing any two of these values, therefore, allows us to calculate the third.

Primer 2:

- Podatki:

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$$

$$\Delta H_1^o = -1300\ kJ$$

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

$$\Delta H_2^o = -394\ kJ$$

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

$$\Delta H_3^o = -286\ kJ$$

- Izračunaj ΔH_r^o za reakcijo:

$$2C(s) + H_2(g) \rightarrow C_2H_2(g)$$

- (R: 226 kJ)

EXAMPLE 6.6 *Using Hess's Law*

Suppose we want to know the enthalpy change for the formation of methane, CH_4, from solid carbon (as graphite) and hydrogen gas.

$$C(s) + 2\ H_2(g) \longrightarrow CH_4(g) \qquad \Delta H = ?$$

The enthalpy change for the direct combination of the elements would be extremely difficult to measure in the laboratory. We can measure ΔH, however, when the elements and methane burn in oxygen (Section 6.9).

	Reaction	ΔH (kJ)
(1)	$C(s) + O_2(g) \longrightarrow CO_2(g)$	−393.5
(2)	$H_2(g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O(\ell)$	−285.8
(3)	$CH_4(g) + 2\ O_2(g) \longrightarrow CO_2(g) + 2\ H_2O(\ell)$	−890.3

Solution The three reactions (1, 2, and 3), as they are now written, cannot be added together to obtain the equation for the formation of CH_4 from its elements. CH_4 should be a product, but it is a reactant in equation (3). The solution to this is to reverse equation (3). At the same time, the sign of ΔH for the reaction is reversed. If a reaction is exothermic in one direction (the combustion of methane evolves energy), its reverse must be endothermic.

(3)′ $\quad CO_2(g) + 2\ H_2O(\ell) \longrightarrow CH_4(g) + 2\ O_2(g)$

$$\Delta H = -\Delta H_3 = +890.3\ \text{kJ}$$

Next, we see that two moles of $H_2O(\ell)$ is required as a product, whereas equation (2) is written for only one mole of water. We therefore multiply the stoichiometric coefficients in (2) by 2 and multiply the value of ΔH by 2.

2 × (2) $\quad 2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(\ell)$

$$2\ \Delta H_2 = 2(-285.8\ \text{kJ}) = -571.6\ \text{kJ}$$

With these modifications, we can add the three equations to give the equation for the formation of methane from its elements.

	Reaction	**ΔH (kJ)**
(1)	$C(s) + O_2(g) \longrightarrow CO_2(g)$	−393.5 kJ
2 × (2)	$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(\ell)$	−571.6 kJ
(3)′	$CO_2(g) + 2\ H_2O(\ell) \longrightarrow CH_4(g) + 2\ O_2(g)$	+890.3 kJ
Net	$C(s) + 2\ H_2(g) \longrightarrow CH_4(g)$	−74.8 kJ

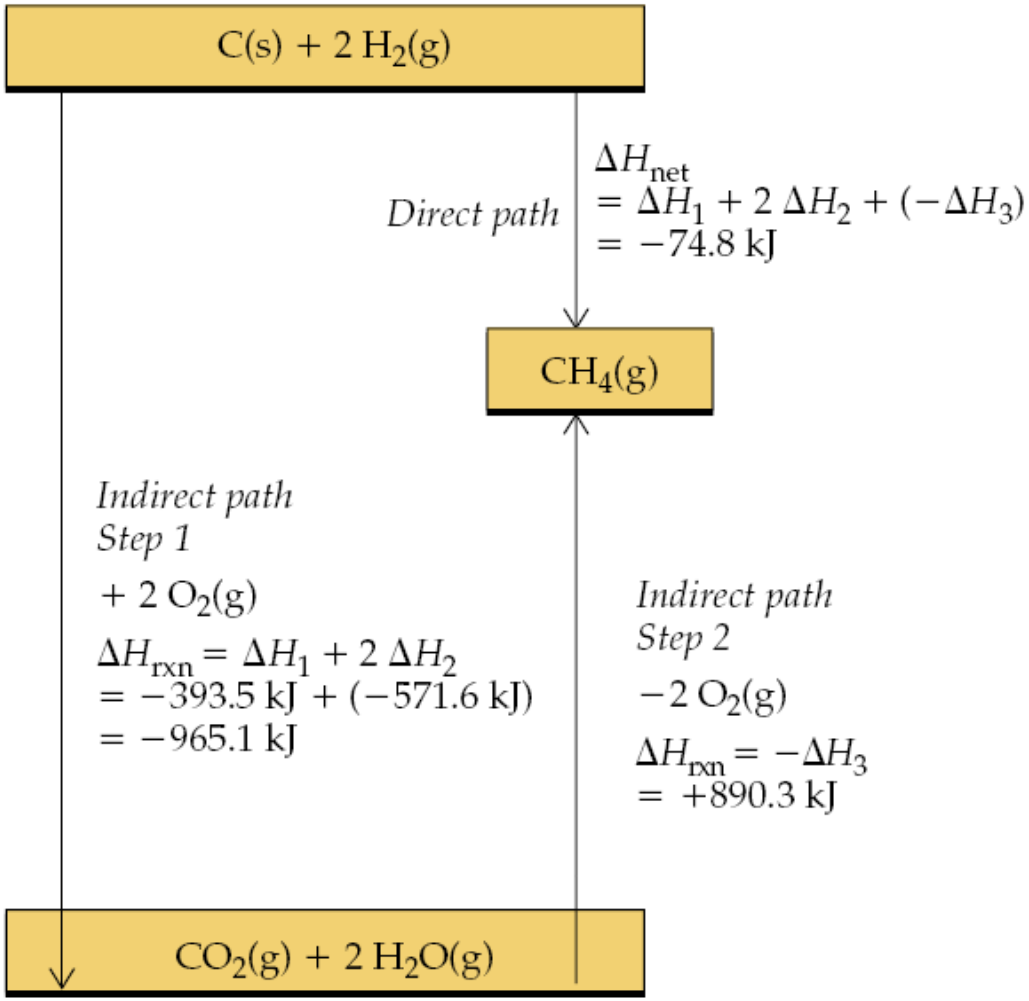


Figure 6.16 Methane may be formed directly from the elements. Alternatively, the carbon may be burned to $CO_2(g)$ and the hydrogen burned to water. Then CO_2 and H_2O are combined to form CH_4 (and the O_2 used in the combustion is returned). Hess's law states that the enthalpy change for the direct reaction (ΔH_{net}) is the sum of the enthalpy changes along the alternative path ($\Delta H_{net} = \Delta H_1 + 2\Delta H_2 + (-\Delta H_3)$). See Example 6.6 for a more complete designation of the ΔH values.

Entalpije prehodov

- oz. procesa, pri katerem pride do spremembe agregatnega stanja
- *Uparitev vode pri normalnem tlaku* ΔH_{izp}
- $H_2O(l) \Rightarrow H_2O(g)$ $\Delta \mathbf{H_{izp}}(373\ K) = 40{,}7\ kJ\ mol^{-1}$
- *Taljenje ledu* ΔH_{tal}
- $H_2O(s) \Rightarrow H_2O(l)$ $\Delta \mathbf{H_{tal}}\ (273\ K) = 6{,}01\ kJ\ mol^{-1}$
- *Sežigna entalpija* $\Delta H_{sež}$ *je sprememba entalpije na enoto množine snovi pri gorenju.*
- $CH_4 + 2O_2 \Rightarrow 2CO_2 + 2H_2O$ $\Delta \mathbf{H_{sež}} = -890{,}4\ kJ/mol$
- Ker se pri sežiganju energija sprošča je po definiciji predznak negativen!!

- *Tvorbena entalpija spojine ΔH_{tvor} je enaka spremembi entalpije pri reakciji nastanka spojine iz elementov*

- $C(s) + 2H_2(g) \Rightarrow CH_4(g)$ $\Delta H_{tvor} =$ -74,8 kJ/mol
- $6C(s) + 3H_2(g) \Rightarrow C_6H_6(\ell)$ $\Delta H_{tvor} =$ 49,0 kJ/mol
- po dogovoru so entalpije elementov v najstabilnejši fazi enake nič.
- Standardna tvorbena entalpija je lahko pozitivna ali negativna Med reakcijo se energija porablja ali pa sprošča.
- Reakcijske entalpije lahko izračunamo iz podatkov za sežigne in tvorbene entalpije. Ocenimo lahko spremembo entalpije pri katerikoli reakciji , tudi za reakcije , ki jih nismo eksperimentalno izvedli.

- (97) Izračunaj standardno entalpijo reakcije:

  Al_2O_3 (s) + 3 H_2 (g) = 3 H_2O (l) + 2 Al (s)!

R: 817,6 kJ

- (101) Za reakcijo:

  CO (g) + H_2O (g) = CO_2 (g) + H_2 (g)

  je standardna entalpija reakcije - 40,9 kJ. Izračunaj standardno tvorbeno entalpijo CO (g)!

R: -110 kJ

- (103) Koliko toplote (v kJ) se sprosti, če popolnoma zgori 10 g metanola CH_3OH?

  $2\ CH_3OH\ (l) + 3O_2\ (g) = 2\ CO_2\ (g) + 4\ H_2O\ (g)$

- R: 199kJ

- (107) Iz standardnih entalpij za reakciji:

  $Cu\ (s) + Cl_2\ (g) = CuCl_2(s) \qquad \Delta Hr^0 = -206kJ$

  $2\ Cu\ (s) + Cl_2\ (g) = 2\ CuCl\ (s) \qquad \Delta Hr^0 = -136\ kJ$

  izračunaj standardno entalpijo reakcije:

  $CuCl_2\ (s) + Cu\ (s) = 2\ CuCl\ (s)$

- R: 70kJ

EXERCISE 6.10 *Using Hess's Law*

What is the enthalpy change for forming ethane, C_2H_6 from C(s) and $H_2(g)$?

$$2\ C(s) + 3\ H_2(g) \longrightarrow C_2H_6(g) \qquad \Delta H = ?$$

Use information from Example 6.6 together with the experimentally determined ΔH value for the combustion of ethane.

$$C_2H_6(g) + \tfrac{7}{2}\ O_2(g) \longrightarrow 2\ CO_2(g) + 3\ H_2O(\ell) \qquad \Delta H = -1559.7\ \text{kJ}$$ ■

EXERCISE 6.11 *Using Hess's Law*

Lead has been known and used for centuries. To obtain the metal, lead(II) sulfide (PbS; in the form of a common mineral called galena) is first roasted in air to form lead(II) oxide (PbO).

$$PbS(s) + \tfrac{3}{2}\ O_2(g) \longrightarrow PbO(s) + SO_2(g) \qquad \Delta H = -413.7\ \text{kJ}$$

and then lead(II) oxide is reduced with carbon to the metal.

$$PbO(s) + C(s) \longrightarrow Pb(s) + CO(g) \qquad \Delta H = +106.8\ \text{kJ}$$

What is the enthalpy change for the following reaction?

$$PbS(s) + C(s) + \tfrac{3}{2}\ O_2(g) \longrightarrow Pb(s) + CO(g) + SO_2(g)$$

Is the reaction exothermic or endothermic? How much energy, in kilojoules, is required (or evolved) when 454 g (1.00 pound) of PbS is converted to lead? ■

	Reaction	ΔH (kJ)
(1)	$C(s) + O_2(g) \longrightarrow CO_2(g)$	-393.5
(2)	$H_2(g) + \frac{1}{2}\, O_2(g) \longrightarrow H_2O(\ell)$	-285.8
(3)	$CH_4(g) + 2\, O_2(g) \longrightarrow CO_2(g) + 2\, H_2O(\ell)$	-890.3

6.10.

$$2\, CO_2(g) + 3\, H_2O(\ell) \longrightarrow C_2H_6(g) + \tfrac{7}{2}\, O_2(g) \qquad \Delta H = +1559.7 \text{ kJ}$$

$$2\, C(s) + 2\, O_2(g) \longrightarrow 2\, CO_2(g) \qquad \Delta H = 2(-393.5 \text{ kJ})$$

$$3\, H_2(g) + \tfrac{3}{2}\, O_2(g) \longrightarrow 3\, H_2O(\ell) \qquad \Delta H = 3(-285.8 \text{ kJ})$$

$$2\, C(s) + 3\, H_2(g) \longrightarrow C_2H_6(g) \qquad \Delta H = -84.7 \text{ kJ}$$

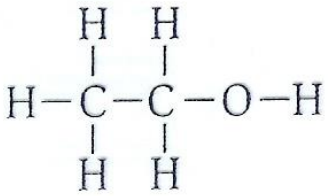
6.11.

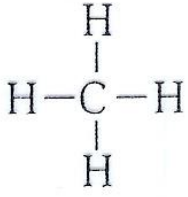
$$\Delta H_{\text{overall}} = -413.7 \text{ kJ} + 106.8 \text{ kJ} = -306.9 \text{ kJ}$$

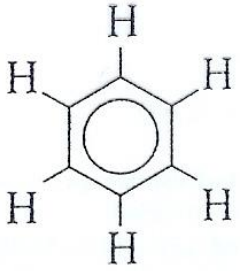
$$(454 \text{ g}) \left(\frac{1 \text{ mol PbS}}{239.3 \text{ g}} \right) (-306.9 \text{ kJ}) = 582 \text{ kJ}$$

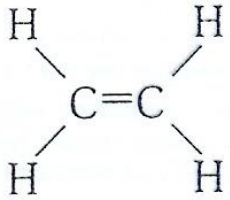
POVPREČNA ENTALPIJA (ENERGIJA) VEZI

Energija, potrebna za prekinitev vezi, ni odvisna le od vrste atomov, ki to vez tvorita, ampak tudi od okolja teh atomov. Npr.: v etanolu vse vezi C–H niso enako močne, ker nanje vpliva tudi bližina kisikovega atoma.









Podobno vezi C–H v metanu CH_4 niso čisto enake tistim v benzenu C_6H_6 ali v etenu C_2H_4. Na srečo te razlike niso velike, zato uporabljamo povprečne vezne energije.

Spremembo entalpije, povezano s prekinitvijo **posamezne** vezi, imenujemo **entalpija disociacije vezi** (izražena na mol vezi). Za katero prekinitev vezi gre, najbolje izrazimo z enačbo, kot je prikazano naslednji strani za postopno disociacijo metana.

Reakcija	Entalpija disociacije vezi/kJ mol^{-1}
$CH_4(g) \rightarrow CH_3(g) + H(g)$	+435
$CH_3(g) \rightarrow CH_2(g) + H(g)$	+444
$CH_2(g) \rightarrow CH(g) + H(g)$	+440
$CH(g) \rightarrow C(g) + H(g)$	+343

Spremembo entalpije za popolno disociacijo metana na atome v plinastem stanju ob prekinitvi vseh C—H vezi dobimo s seštetjem vseh štirih enačb:

$$CH_4(g) \rightarrow C(g) + 4H(g);\ \Delta H^{\ominus} = +1662\ kJ\ mol^{-1}$$

Povprečna entalpija vezi C—H v metanu je srednja vrednost štirih disociacijskih entalpij in jo označimo $\bar{E}$ (C—H). Izračunamo jo tako:

$$\bar{E}\ (C—H) = (1662/4)\ kJ\ mol^{-1} = 415\ kJ\ mol^{-1}$$

Entalpij vezi ne moremo vedno izračunati na opisani način, ker ne poznamo vedno disociacijskih entalpij. Takrat uporabimo drugačno metodo.

Tabela 9.4 Srednje vezne entalpije/kJ mol^{-1}

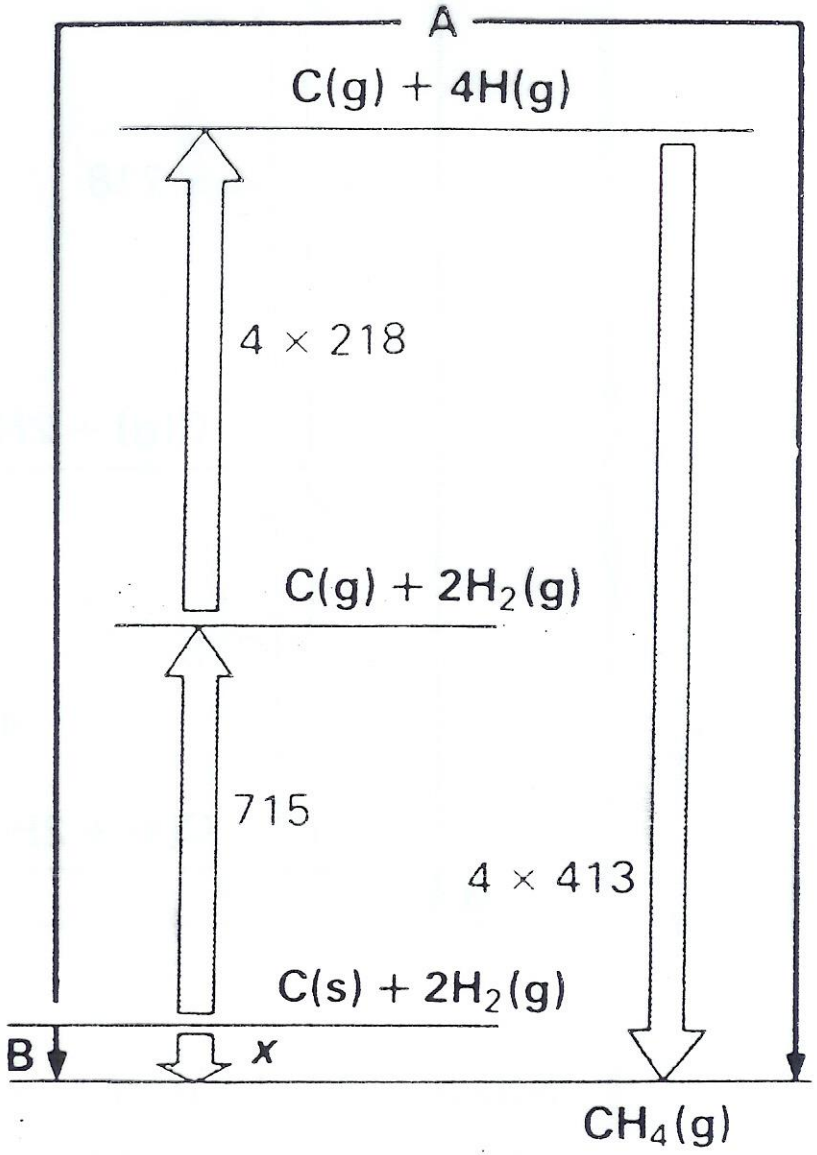
H–H	436*	F–F	158*	H–O	463
C–C	348	Cl–Cl	242*	C–O	360
C=C	612	Br–Br	193*	C=O	743
Si–Si	176	I–I	151*	C–N	305
N–N	163	H–F	562*	C=N	613
N=N	409	H–Cl	431*	C≡N	890
N≡N	944*	H–Br	366*	C–F	484
O–O	146	H–I	299*	C–Cl	338
O=O	496*	H–C	415	C–Br	276
S–S	264	H–N	388	C–I	238

Oceni standardno tvorbeno entalpijo metana na podlagi srednjih veznih entalpij.

METODA Enačba za reakcijo nastanka metana je:

$$C(s) + 2H_2(g) \rightarrow CH_4(g)$$

Da lahko ocenimo standardno tvorbeno entalpijo metana, moramo najprej atomizirati ogljik ($\Delta H_a^{\ominus} = +715$ kJ mol^{-1}). Enako velja za $2H_2$ ($\Delta H_a^{\ominus} = +218$ kJ mol^{-1}). Nato nastanejo štiri C–H vezi (srednje vezne entalpije v tabeli 9.4). Celoten proces je predstavljen kot cikel na sliki 9.14.


A
C(g) + 4H(g)
4 × 218
C(g) + 2H2(g)
715
4 × 413
C(s) + 2H2(g)
B
x
CH4(g)

Disociacijska entalpija in sublimacijska entalpija

- **Standardna disociacijska entalpija** *dvoatomskih molekul* je enaka entalp. spremembi pri razpadu *1 mola molekul* na atome, pri čemer so vse snovi v standardnih stanjih*
- $Cl_2(g) \Rightarrow 2\,Cl(g) \quad \Delta H_{dis} = 242$ kJ/mol
- **Standardna atomizacijska entalpija** *elementa* je enaka entalpijski spremembi pri razpadu na atome, preračunani na *1mol atomov*. * :
- $1/2Cl_2(g) \Rightarrow Cl(g) \quad \Delta H_{atom} = 121$ kJ/mol
- Za trdne elemente, ki izparevajo v obliki atomov, je standardna atomizacijska entalpija enaka **standardni sublimacijski entalpiji:**
- $Na(s) \Rightarrow Na(g) \quad \Delta H_{subl} = 108$ kJ/mol .

Mrežna entalpija

.....je standardna entalpija razpada kristalne mreže na ione:

$$\mathbf{NaCl(s) \rightarrow Na^{+}(g) + Cl^{-}(g)} \qquad \mathbf{\Delta H_m = 787\ kJ/mol}$$

.... je merilo za energijo ionske kristalne mreže

V primeru, da je MX=NaCl, je ΔH_m = 787 kJ/mol. Vse mrežne entalpije so endotermne. Njihova vrednost izračunana za primer ionskega kristala, je odvisna od treh faktorjev:

- Naboj iona (čim večji je, večja je ΔHm)
- Radij iona (čim manjši je večja je ΔHm)
- Ureditev ionov v kristalu

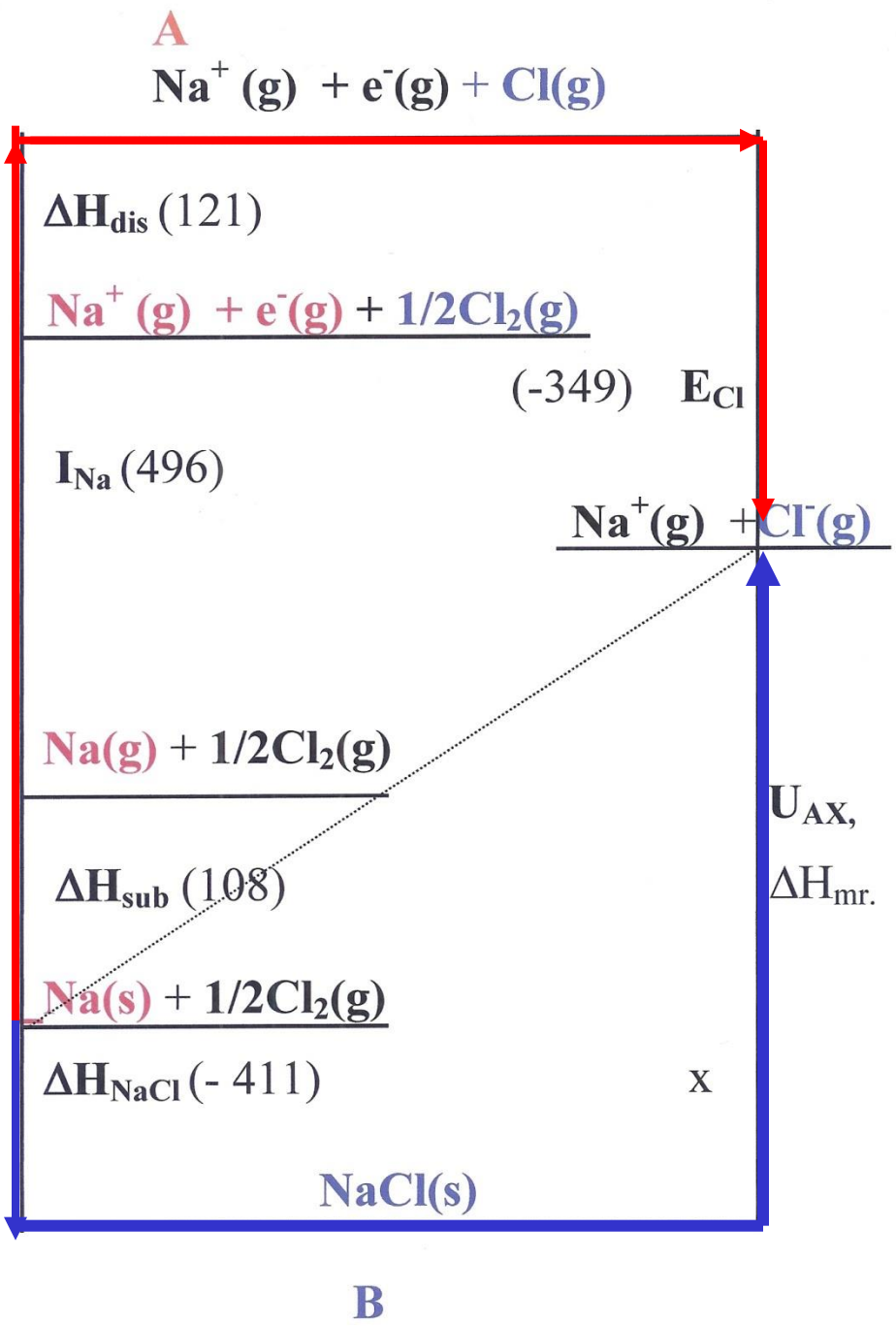
TABLE 8.6 Lattice Energies of Some Ionic Compounds*

Compound	$\Delta H_{lattice}$ (kJ/mol)
LiF	−1037
LiCl	−852
LiBr	−815
LiI	−761
NaF	−926
NaCl	−786
NaBr	−752
NaI	−702
KF	−821
KCl	−717
KBr	−689
KI	−649
RbCl	−695

*D. Cubicciotti, *Journal of Chemical Physics*, Vol. 31, p. 1646, 1959.

Born-Haber cikel

Mrežno energijo lahko izračunamo posredno iz drugih podatkov s pomočjo Born-Haber-jevega cikla. Reakcijo razcepa mreže smiselno razdelimo na več stopenj in sestavimo cikel. Pri tem tvori mrežna energija člen v tem ciklu.


A
Na+ (g) + e-(g) + Cl(g)
ΔHdis (121)
Na+ (g) + e-(g) + 1/2Cl2(g)
(-349) ECl
INa (496)
Na+(g) + Cl-(g)
Na(g) + 1/2Cl2(g)
UAX,
ΔHsub (108)
ΔHmr.
Na(s) + 1/2Cl2(g)
ΔHNaCl (- 411)
x
NaCl(s)
B

- **Primer izračuna za NaCl:**

- $\Delta H_{Na(subl)}$=108 kJ/mol — $Na(s) \rightarrow Na(g)$ — Atomizacija kov. Na
- $I_{Na} = \Delta H_{na(ion)}$ = 496 kJ/mol — $Na(g) \rightarrow Na^+(g) + e^-$ — Ionizacija atomov plin. Na
- $\Delta H_{dis(Cl)}$ =121 kJ/mol — $1/2\ Cl_2 \rightarrow Cl\ (g)$ — Atomizacija plinastega Cl
- $E_{Cl} = \Delta H_{af(Cl)}$ = - 349 kJ/mol — $Cl\ (g) + e^- \rightarrow Cl^-(g)$ — Atom Cl sprejme e Na
- $\Delta H_{NaCl(tvor)}$= - 411 kJ/mol — $Na\ (s) + 1/2\ Cl_2(g) \rightarrow NaCl(s)$

- $U_{AX} + \Delta H_{AX(tvor)} = \Delta H_{A(subl)} + I_A + \Delta H_{X\ (dis)} + E_X$
- U_{AX} - 411 = 108 +496 +121 -349

U_{AX}= 787 kJ/mol

Empirični izraz za mrežno energijo v Born-Haber ciklu:

$\Delta H_{A(subl)} + I_A + \Delta H_{X(dis)} - E_X = U_{AX} + \Delta H_{AX(tvor)}$

ΔH_{AX} = tvorbena entalpija nastanka spojine

ΔH_X = disociacija aniona (Cl)

ΔH_A = sublimacija kationa (Na)

I_A = ionizacijska energija (Na)

E_X = elektroafiniteta (Cl)

- Izračunane in eksp. 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.

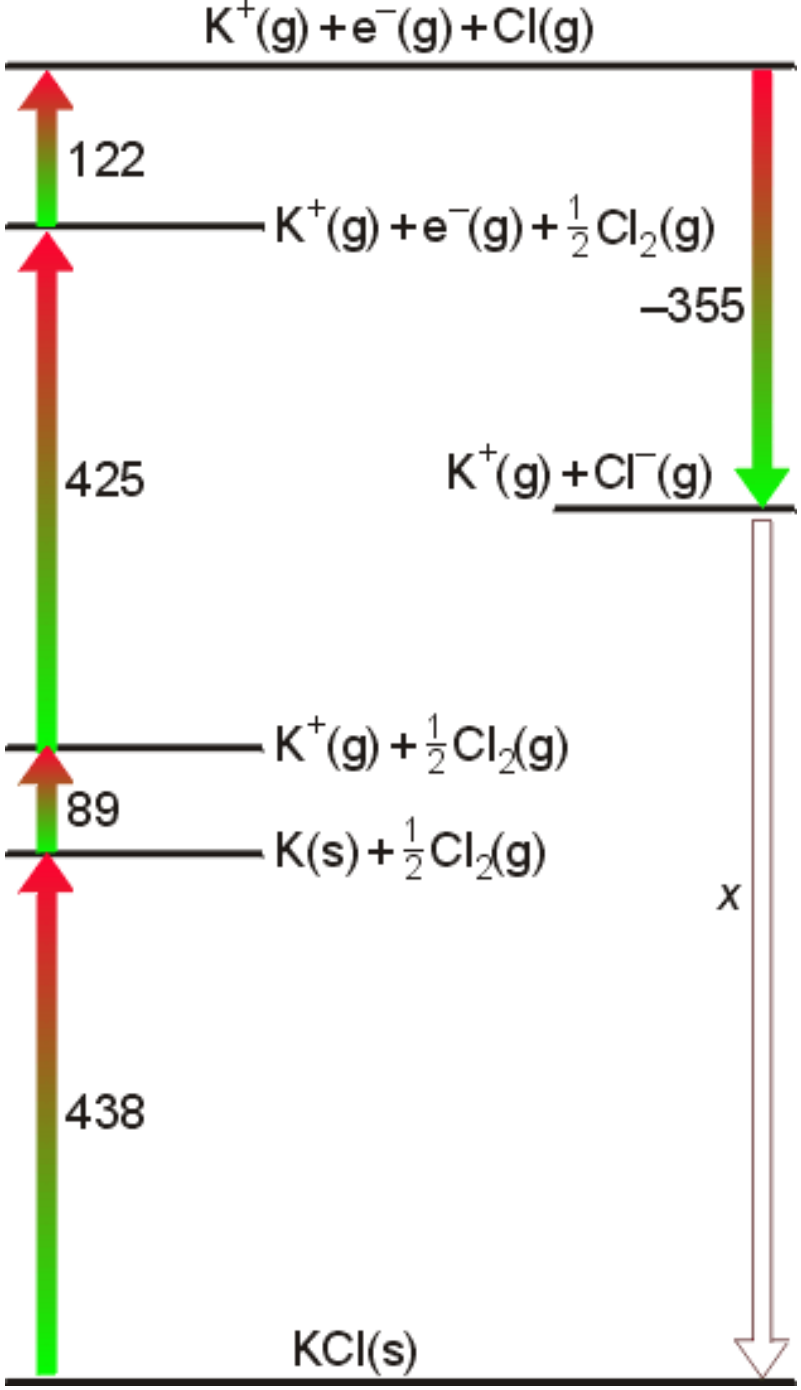
Ionski radiji	(Å)	Mrežne entalpije	ΔHm (kJ/mol)
Na^+	0,95	NaCl	787
K^+	1,33	NaF	927
F^-	1,36	KCl	719
Cl^-	1,81	$MgBr_2$	2421

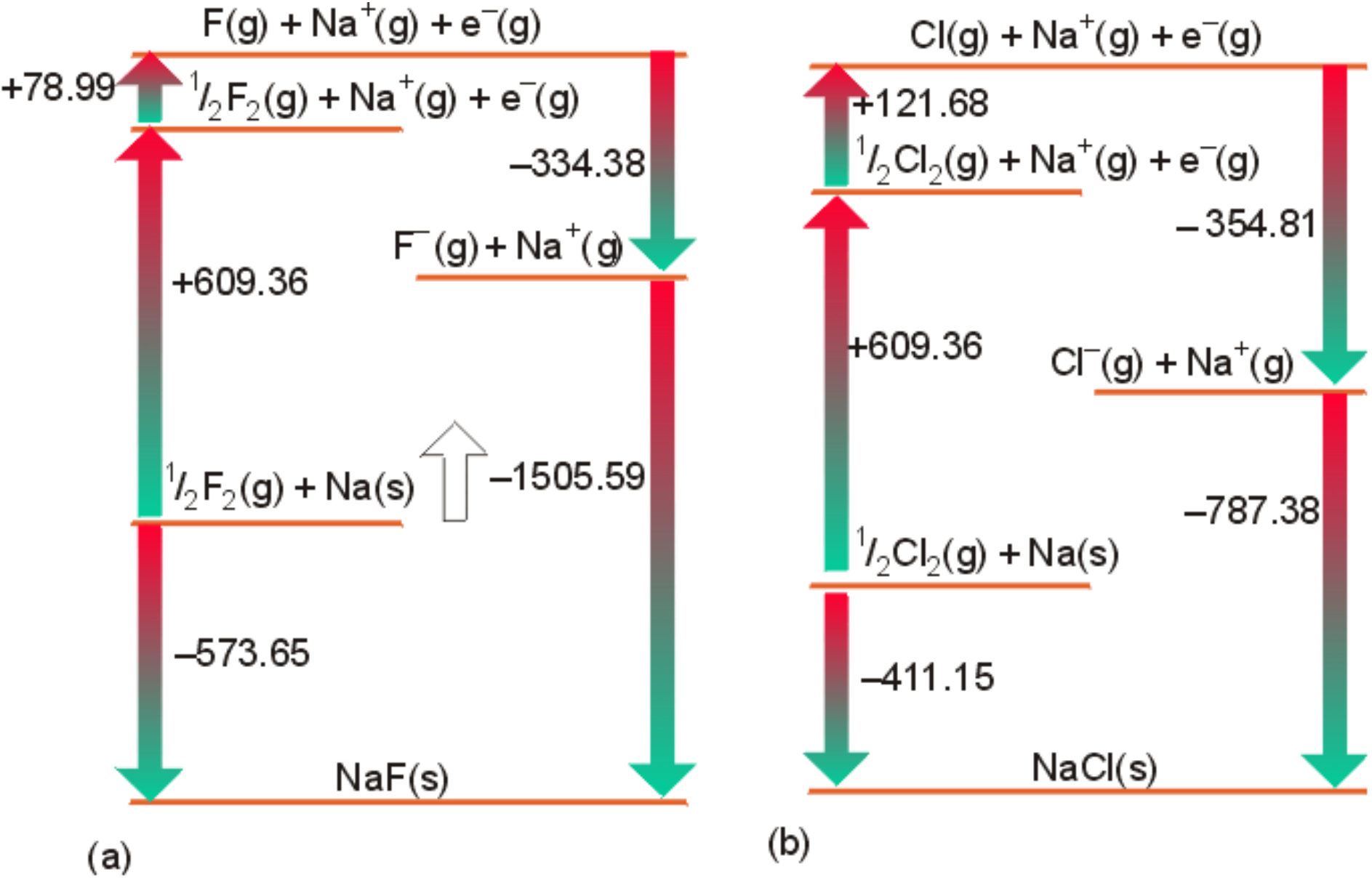
Table 3.7 Lattice enthalpies of some simple inorganic solids

Compound	Structure type	$\Delta H_L^{exp} / (kJ\ mol^{-1})$	Compound type	Structure	$\Delta H_L^{exp} / (kJ\ mol^{-1})$
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

KCl

Izračunaj mrežno entalpijo za KCl(s) z uporabo Born-Haber cikla in podatkov:


$K^+(g) + e^-(g) + Cl(g)$
122
$K^+(g) + e^-(g) + \frac{1}{2}Cl_2(g)$
–355
425
$K^+(g) + Cl^-(g)$
$K^+(g) + \frac{1}{2}Cl_2(g)$
89
$K(s) + \frac{1}{2}Cl_2(g)$
x
438
KCl(s)


F(g) + Na+(g) + e−(g)
+78.99
½F2(g) + Na+(g) + e−(g)
–334.38
F−(g) + Na+(g)
+609.36
½F2(g) + Na(s)
–1505.59
–573.65
NaF(s)
(a)
Cl(g) + Na+(g) + e−(g)
+121.68
½Cl2(g) + Na+(g) + e−(g)
–354.81
+609.36
Cl−(g) + Na+(g)
–787.38
½Cl2(g) + Na(s)
–411.15
NaCl(s)
(b)

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.***

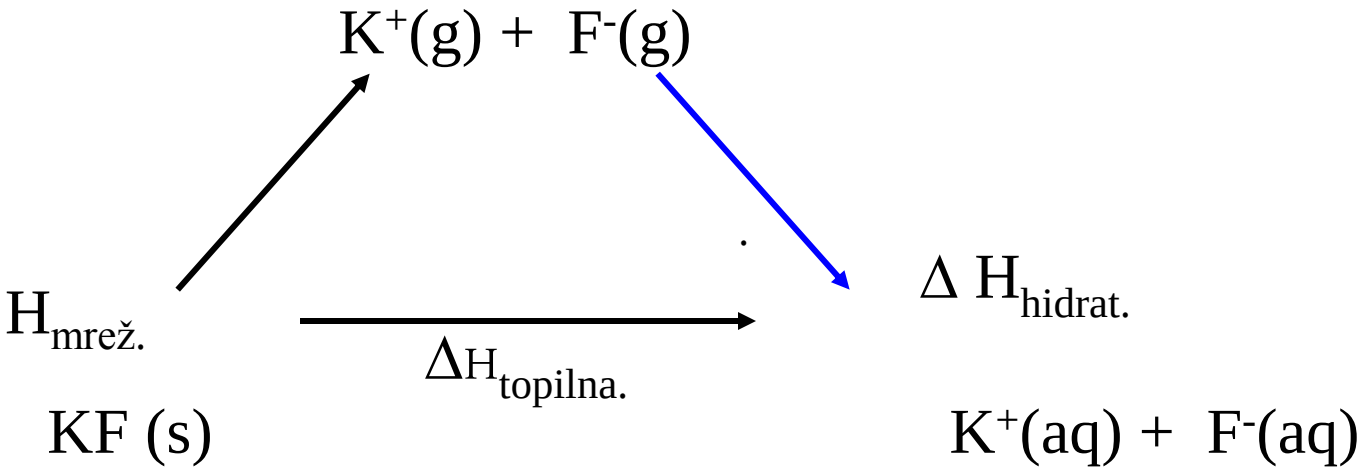
- Lahko jo ocenimo iz primerjav **mrežne** in **solvatacijska energije**.

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

Primer:

- **Za prekinitev vezi v molu LiCl potrebujemo 837 kJ:**
- **$LiCl(s) \rightarrow Li^+(g) + Cl^-(g)$ $U_{mrežna}$ (LiCl) = 837 kJ/mol**
- **Pri hidrataciji 1 mola litijevih in 1 mola natrijevih ionov:**
- **$Li^+(g) + Cl^-(g) \rightarrow Li^+(aq) + Cl^-(aq)$ $\Delta H_{solvatacije}$= -886kJ**
- **$\Delta H_{topilna} = U_{mrežna}$ (LiCl) + $\Delta H_{solvatacije}$ = 837kJ/mol + (-**
- **886kJ/mol) = - 49kJ/mol, izmerjena vrednost je -37 kJ/mol.**

S pomočjo Hessovega zakona lahko proces raztapljanja **ionskih snovi** zapišemo (npr. KF):



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

$\Delta H\ H_{topilna} = 821$ kJ/mol + (-819 kJ/mol)=+2kJ/mol