Lecture General Chemistry
WS 2023/24

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- Website (Slides, Excercises):
- http://www.chemie.uni-siegen.de/pc/lehre/genchem/

Login Data for slides:

User: Ludwig

Passwort: Boltzmann

Sign conventions for q and w.
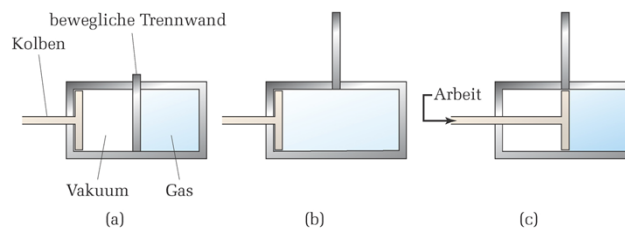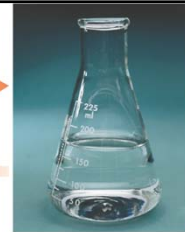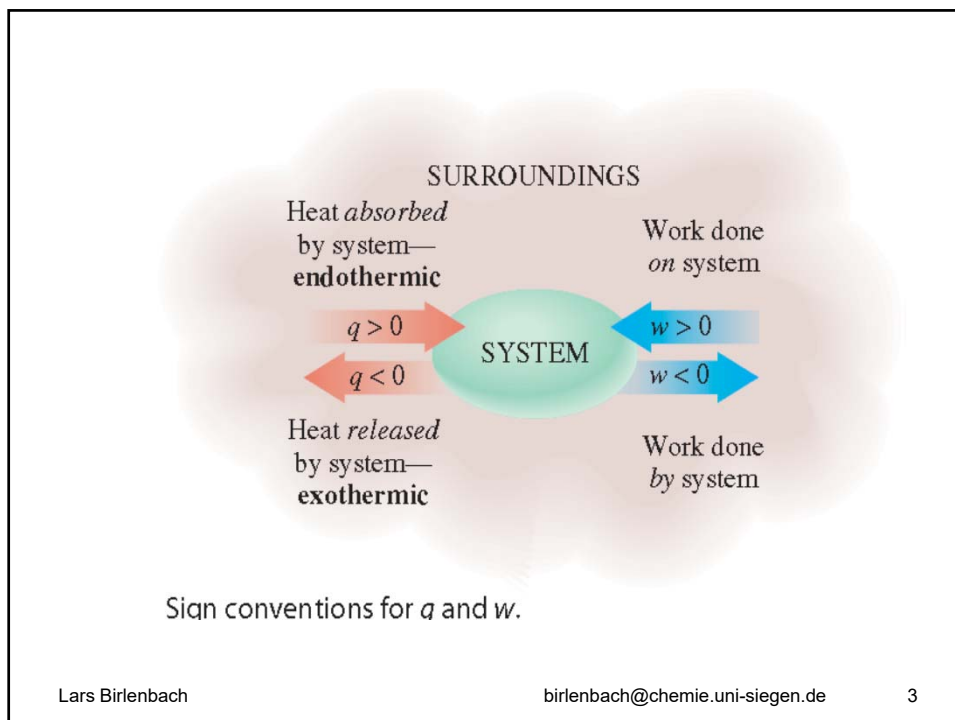
Compression (volume decreases)	Expansion (volume increases)
Work is done *by* the surroundings *on* the system, so the sign of w is positive	Work is done *by* the system *on* the surroundings, so the sign of w is negative
V_2 is less than V_1, so $\Delta V = (V_2 - V_1)$ is negative	V_2 is greater than V_1, so $\Delta V = (V_2 - V_1)$ is positive
$w = -P\,\Delta V$ is positive $(-) \times (+) \times (-) = +$	$w = -P\,\Delta V$ is negative $(-) \times (+) \times (+) = -$
Can be due to a *decrease* in number of moles of gas (Δn negative)	Can be due to an *increase* in number of moles of gas (Δn positive)

$p = 1\ \text{atm}$ $p = 1\ \text{atm}$

Constant pressure,
T of gases > 100°C

Constant temperature bath (heated mineral oil)

2 mol H$_2$ + 1 mol O$_2$

2 mol H$_2$O(g)

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$

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Kolben

Zn

HCl-Lösung

(a)

H$_2$-Gas plus Anfangs-atmosphäre

Zn   HCl-Lösung
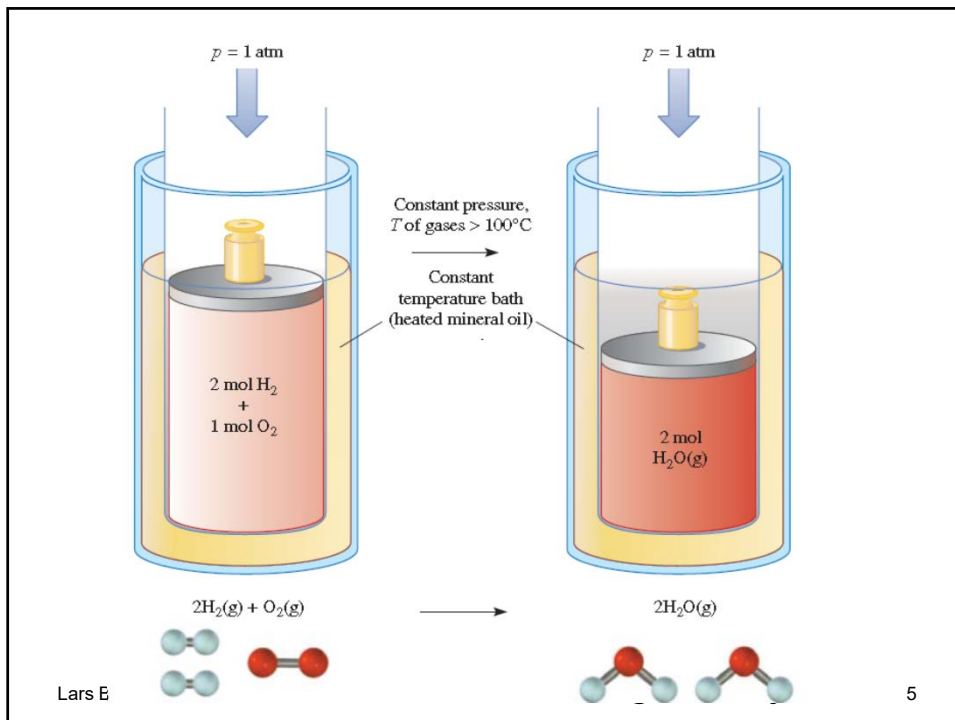
(b)

Work $\qquad W = -p\Delta V$

reactions which produce Gas:

energy ΔE when V = const.

enthalpie ΔH when p = const.

$\text{Zn} + 2\ \text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2\uparrow$

$$\Delta H = \Delta E + p\Delta V$$

aus:: Mortimer, Chemie, 10. Auflage Thieme Verlag

15-11 Relationship Between ΔH and ΔE

The fundamental definition of enthalpy, H, is

$$H = E + PV$$

For a process at constant temperature and pressure,

$$\Delta H = \Delta E + P\,\Delta V \qquad \text{(constant } T \text{ and } P)$$

From Section 15-10, we know that $\Delta E = q + w$, so

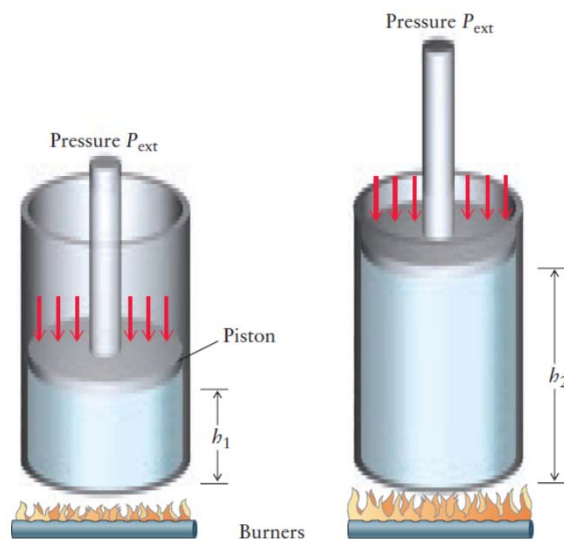$$\Delta H = q + w + P\,\Delta V \qquad \text{(constant } T \text{ and } P)$$

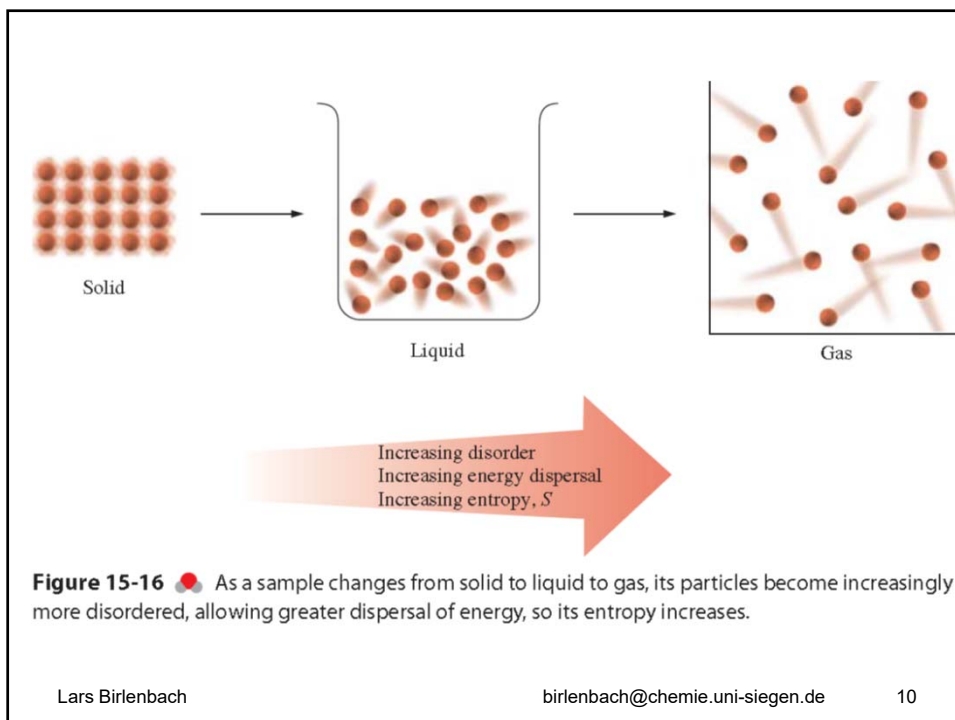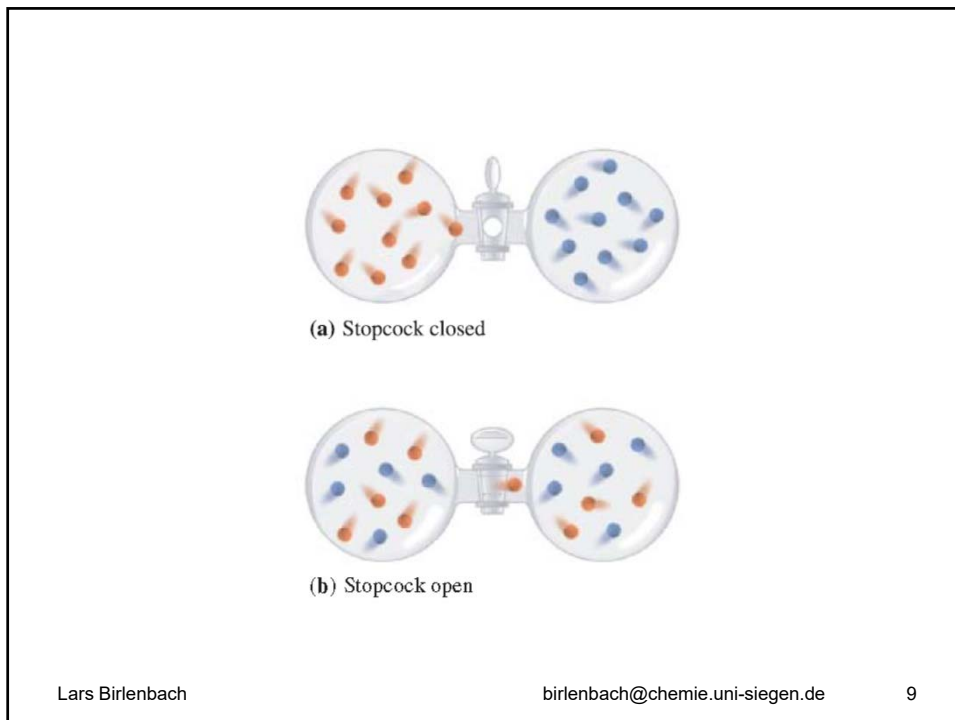At constant pressure, $w = -P\,\Delta V$, so

$$\Delta H = q + (-P\,\Delta V) + P\,\Delta V$$

$$\Delta H = q_p \qquad \text{(constant } T \text{ and } P)$$

The difference between ΔE and ΔH is the amount of expansion work ($P\,\Delta V$ work) that the system can do. Unless there is a change in the number of moles of gas present, this difference is extremely small and can usually be neglected. For an ideal gas, $PV = nRT$. At constant temperature and constant pressure, $P\,\Delta V = (\Delta n)RT$, a work term. Substituting gives

$$\Delta H = \Delta E + (\Delta n)RT \qquad \text{or} \qquad \Delta E = \Delta H - (\Delta n)RT \qquad \text{(constant } T \text{ and } P)$$

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(a) Stopcock closed

(b) Stopcock open

Solid

Liquid

Gas

Increasing disorder
Increasing energy dispersal
Increasing entropy, S

Figure 15-16 As a sample changes from solid to liquid to gas, its particles become increasingly more disordered, allowing greater dispersal of energy, so its entropy increases.

Figure 15-19 When water, H_2O, and propyl alcohol, $CH_3CH_2CH_2OH$ (*left*) are mixed to form a solution (*right*), disorder increases. $\Delta S > 0$ for the mixing of any two molecular substances.

▌**Table 15-6** Entropy Effects Associated with Melting and Freezing

| Change | Temperature | Sign of | | (Magnitude of ΔS_{sys}) Compared with (Magnitude of ΔS_{surr}) | $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$ | Spontaneity |
		ΔS_{sys}	ΔS_{surr}			
1. Melting	> mp	+	−	>	> 0	Spontaneous
(solid → liquid)	= mp	+	−	=	= 0	Equilibrium
	< mp	+	−	<	< 0	Nonspontaneous
2. Freezing	> mp	−	+	>	< 0	Nonspontaneous
(liquid → solid)	= mp	−	+	=	= 0	Equilibrium
	< mp	−	+	<	> 0	Spontaneous

$$G = H - TS$$

$$\Delta G = \Delta H - T\,\Delta S \qquad \text{(constant } T \text{ and } P\text{)}$$

ΔG	Spontaneity of Reaction (constant T and P)
ΔG is positive	Reaction is nonspontaneous (reactant-favored)
ΔG is zero	System is at equilibrium
ΔG is negative	Reaction is spontaneous (product-favored)

$-$ 0 $+$

$\Delta G < 0$	$\Delta G > 0$
Reaction is spontaneous	Reaction is not spontaneous
Product-favored reaction	Reactant-favored reaction
Forward reaction is favored	Reverse reaction is favored

Lars

15-17 The Temperature Dependence

of Spontaneity

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\,\Delta S_{\text{rxn}} \qquad \text{or} \qquad 0 = \Delta H_{\text{rxn}} - T\,\Delta S_{\text{rxn}}$$

$$\Delta H_{\text{rxn}} = T\,\Delta S_{\text{rxn}} \qquad \text{or} \qquad T = \frac{\Delta H_{\text{rxn}}}{\Delta S_{\text{rxn}}} \qquad \text{(at equilibrium)}$$

$$\Delta G = \Delta H - T\,\Delta S \qquad \text{(constant temperature and pressure)}$$

1. $\Delta H = -$ (favorable) $\Delta S = +$ (favorable)   Reactions are product-favored at all temperatures

2. $\Delta H = -$ (favorable) $\Delta S = -$ (unfavorable)   Reactions become product-favored below a definite temperature

3. $\Delta H = +$ (unfavorable) $\Delta S = +$ (favorable)   Reactions become product-favored above a definite temperature

4. $\Delta H = +$ (unfavorable) $\Delta S = -$ (unfavorable)   Reactions are reactant-favored at all temperatures

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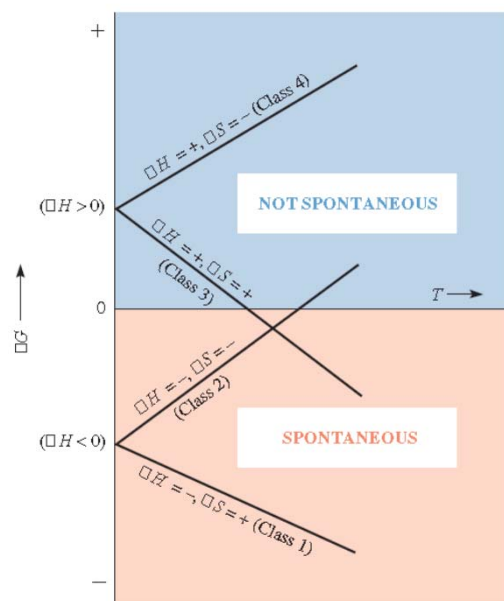
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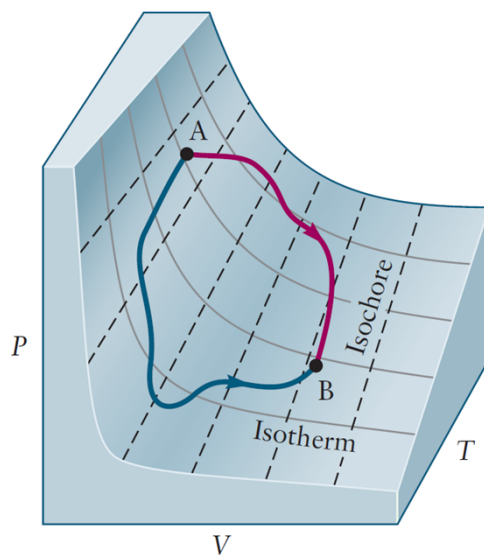
Table 15-7 Thermodynamic Classes of Reactions

Class	Examples	ΔH (kJ/mol)	ΔS (J/mol · K)	Temperature Range of Spontaneity
1	$2H_2O_2(\ell) \longrightarrow 2H_2O(\ell) + O_2(g)$	−196	+126	All temperatures
	$H_2(g) + Br_2(\ell) \longrightarrow 2HBr(g)$	−72.8	+114	All temperatures
2	$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$	−176	−285	Lower temperatures (< 619 K)
	$2H_2S(g) + SO_2(g) \longrightarrow 3S(s) + 2H_2O(\ell)$	−233	−424	Lower temperatures (< 550 K)
3	$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$	+176	+285	Higher temperatures (> 619 K)
	$CCl_4(\ell) \longrightarrow C(graphite) + 2Cl_2(g)$	+135	+235	Higher temperatures (> 517 K)
4	$2H_2O(\ell) + O_2(g) \longrightarrow 2H_2O_2(\ell)$	+196	−126	Nonspontaneous, all temperatures
	$3O_2(g) \longrightarrow 2O_3(g)$	+285	−137	Nonspontaneous, all temperatures

C(graphite) + O_2(g)

-110.5 kJ

CO(g) + $\frac{1}{2}O_2$(g)

-393.5 kJ

-283.0 kJ

CO_2(g)
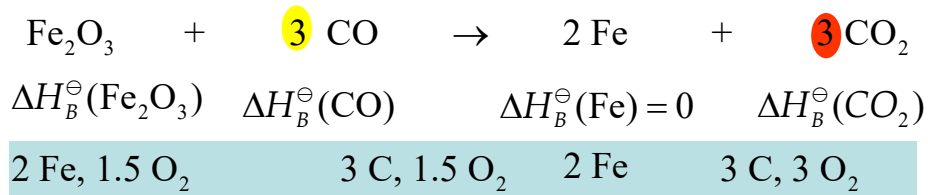
Above is a schematic representation of
the enthalpy changes for the reaction
C(graphite) + $\frac{1}{2}O_2$(g) $\longrightarrow$ CO(g).
The ΔH value for each step is based
on the number of moles of each
substance indicated.

Hess's Law

- standard enthalpies of formation $\Delta H_B^{\ominus}$

$$\text{Fe}_2\text{O}_3 \quad + \quad 3\,\text{CO} \quad \rightarrow \quad 2\,\text{Fe} \quad + \quad 3\,\text{CO}_2$$

$\Delta H_B^{\ominus}(\text{Fe}_2\text{O}_3) \quad \Delta H_B^{\ominus}(\text{CO}) \qquad \Delta H_B^{\ominus}(\text{Fe}) = 0 \quad \Delta H_B^{\ominus}(CO_2)$

2 Fe, 1.5 O_2 3 C, 1.5 O_2 2 Fe   3 C, 3 O_2

$$\Delta H_R = 3 \cdot \Delta H_B^{\ominus}(CO_2) - 3 \cdot \Delta H_B^{\ominus}(\text{CO}) - \Delta H_B^{\ominus}(\text{Fe}_2\text{O}_3)$$

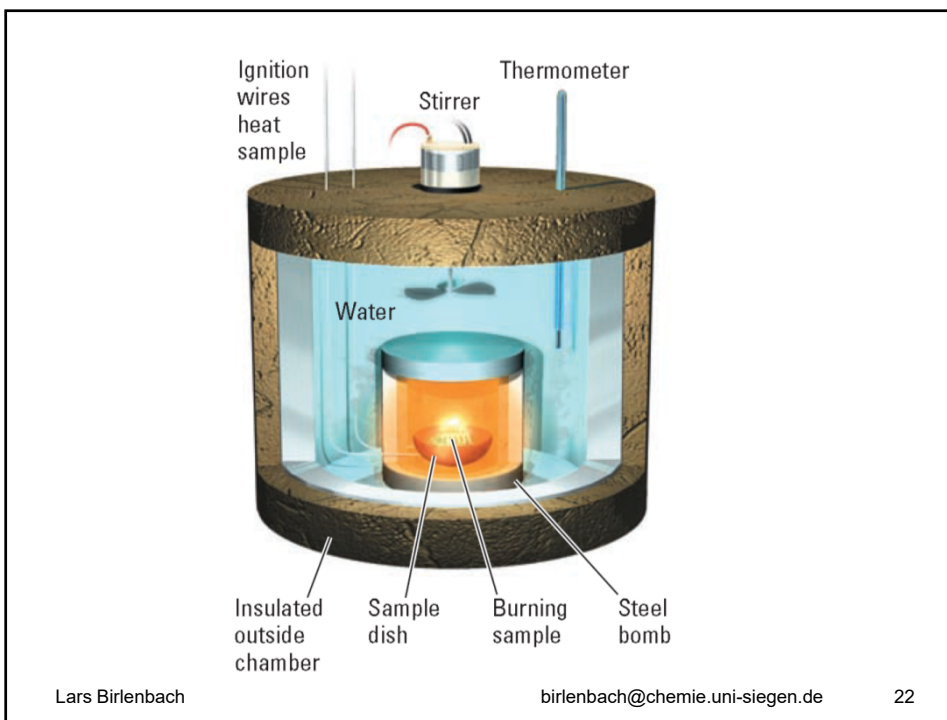$$\Delta H_R = 3 \cdot -393{,}5 - (3 \cdot -110{,}5 - 822{,}5) = -26{,}5 \text{ kJ/mol}$$

Table 15-1 Selected Standard Molar Enthalpies of Formation at 298 K

Substance	ΔH_f^0 (kJ/mol)	Substance	ΔH_f^0 (kJ/mol)
$Br_2(\ell)$	0	HgS(s) red	−58.2
$Br_2(g)$	30.91	$H_2(g)$	0
C(diamond)	1.897	HBr(g)	−36.4
C(graphite)	0	$H_2O(\ell)$	−285.8
$CH_4(g)$	−74.81	$H_2O(g)$	−241.8
$C_2H_4(g)$	52.26	NO(g)	90.25
$C_6H_6(\ell)$	49.03	Na(s)	0
$C_2H_5OH(\ell)$	−277.7	NaCl(s)	−411.0
CO(g)	−110.5	$O_2(g)$	0
$CO_2(g)$	−393.5	$SO_2(g)$	−296.8
CaO(s)	−635.5	$SiH_4(g)$	34.0
$CaCO_3(s)$	−1207.0	$SiCl_4(g)$	−657.0
$Cl_2(g)$	0	$SiO_2(s)$	−910.9