

Unit 7: Energy Balances on reactive systems

Reminders

- Homework 6 will be posted by Monday and due on November 22 (covering unit 6)

Announcements

- “Midterm” is moved to **Wednesday, November 15** during class
 - Cumulative of units 1-5
- No class or office hours on Wednesday, November 22 (leading into break)

Day	Time	Location	Personnel
Monday	4:30- 5:30PM	AW Smith 147	Duval
Tuesday	4 – 5PM	AW Smith 152	TA
Wednesday	7-8PM	Zoom	TA
Thursday	6-7PM	Zoom	Duval

Unit 7: Energy balances on reactive systems

2

After today's lecture, students should be able to:

- Define **exothermic** and **endothermic** reactions
- Explain **heat of reaction**

General Procedure for Energy Balances

3

- Draw and fully label PFD
- Solve material balance OR determine if its solvable
- Write the general E-balance equation (first law)
- Cancel terms & justify why
- **Draw the theoretical path for each species**
- **Write relevant equations for each theoretical step**
- **Look up all thermodynamic constants**
- Solve OR explain how you would solve

First Law of Thermodynamics

4

1st Law, open system $\dot{Q} - \dot{W}_S = \Delta\dot{H} + \Delta\dot{E}_K + \Delta\dot{E}_P$

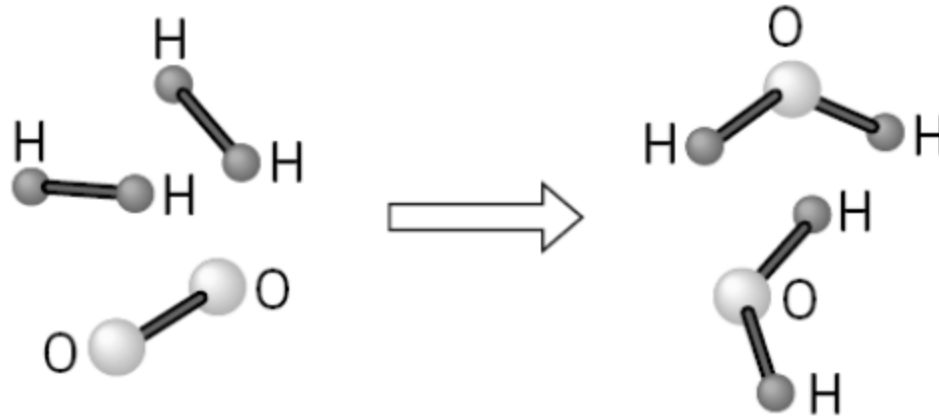
1st Law, closed system $Q - W = \Delta U + \Delta E_K + \Delta E_P$

Remember... $\Delta\dot{H} = \Delta\dot{U} + \Delta P\dot{V}$

- Calculate ΔU and $\Delta\dot{H}$ associated with:
 - ▣ ΔP at constant T and state
 - ▣ ΔT at constant P and state
 - ▣ Phase changes at constant T and P
 - ▣ **Chemical reactions at constant T and P**

Chemical Reactions

5



- **Chemical reaction:** process that involves breaking and forming chemical bonds

Types of reactions

6

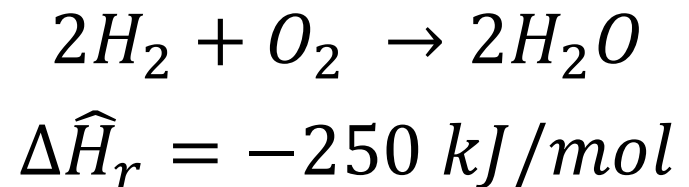
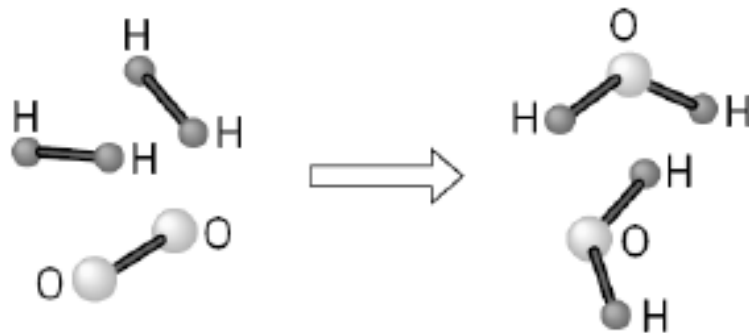
- **Exothermic** reactions
 - ▣ Energy is released
 - Ex: combustion of fuels, Haber process for producing ammonia

- **Endothermic** reactions
 - ▣ Energy is absorbed
 - Ex: photosynthesis

Heat of Reaction

7

- **Heat of reaction:** enthalpy change when stoichiometric quantities of reactants at some T and P react to form products at the same T and P



Heat of reaction

8



- Is the reaction **exothermic** or **endothermic**?
- What if we don't have stoichiometric amounts of each reactant? Or what if we don't have 100% conversion?

$$\Delta H = \Delta \hat{H}_r(T, P) \xi$$

*Enthalpy change associated
with a chemical reaction!*

Cool, cool, cool. How does this fit with theoretical process paths?

9

In the “heat of reaction method” the heats of reaction are calculated separately from process paths!

- Enthalpy change (no reactions):

$$\Delta H = \sum n_{i,out} \hat{H}_{i,out} - \sum n_{i,in} \hat{H}_{i,in}$$

- Enthalpy change (single reaction):

$$\Delta H = \xi \Delta \hat{H}_r + \sum n_{i,out} \hat{H}_{i,out} - \sum n_{i,in} \hat{H}_{i,in}$$

Unit 7: Energy balances on reactive systems

Reminders

- HW 6 is posted and is due on November 20
- HW 7 will be assigned on November 20 and is due on Nov 27

Announcements

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- No office hours on Wednesday, November 27

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After today's lecture, students should be able to:

- Finish the problem started last class
- Calculate the heat of reaction ($\Delta\hat{H}_{rxn}$) using:
 - ▣ **Hess's Law and standard heats of formation**

Cool, cool, cool. How does this fit with theoretical process paths?

3

Using the “Heat of Reaction Method” form of the energy balance—heats of reaction are calculated separately from process paths!

- Enthalpy change (no reactions):

$$\Delta H = \sum n_{i,out} \hat{H}_{i,out} - \sum n_{i,in} \hat{H}_{i,in}$$

- Enthalpy change (single reaction):

$$\Delta H = \xi \Delta \hat{H}_r + \sum n_{i,out} \hat{H}_{i,out} - \sum n_{i,in} \hat{H}_{i,in}$$



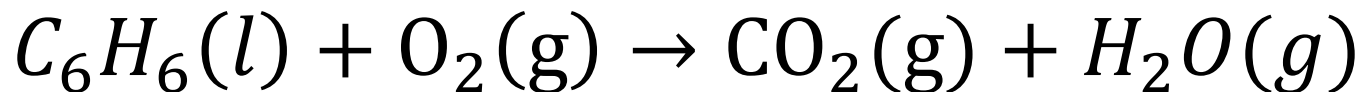
*What do we do if this is not given
in the problem statement?*

Heat of Combustion

4

- **Standard heat of combustion (ΔH_c°):**
Enthalpy change associated with the combustion of 1 mole of a reactant with O_2 to product H_2O and CO_2 at 298K and 1atm

Example: combustion of benzene



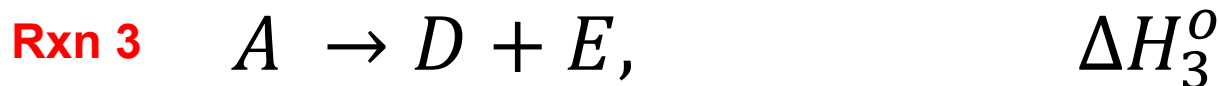
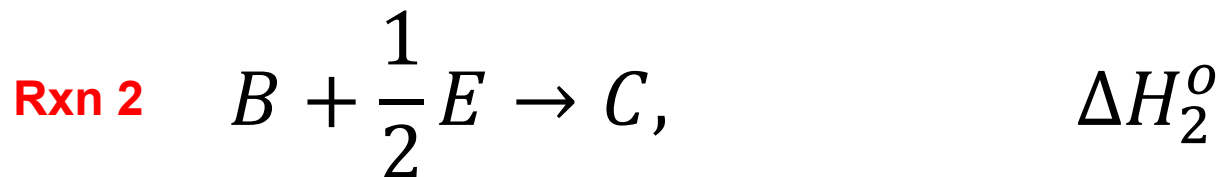
Look it up!
Table B.1

$$\Delta \hat{H}_c^\circ = -3267.6 \frac{kJ}{mol}$$

Application of Hess's Law

5

Hess's Law: If the stoichiometric equation for rxn 1 can be obtained by algebraic operations on stoichiometric equations for rxns 2, 3, ... then $\Delta H_{rxn,1}^0$ can be obtained by performing the same operations on $\Delta H_{rxn,3}^0$, $\Delta H_{rxn,2}^0$



$$\Delta H_1^0 = 2\Delta H_2^0 + \Delta H_3^0$$

Heat of Formation

6

- **Standard Heat of formation (ΔH_f^0):** Enthalpy change associated with the forming 1 mole of a compound from its elements at 298K and 1atm

Example: formation of benzene



$$\Delta \hat{H}_f^0 = +48.66 \frac{kJ}{mol}$$

Look it up!
Table B.1

Example

7

- Calculate the **heat of reaction** using Hess's Law and standard heats of formation for the following reaction:



Table B.1 (Continued)

Compound	Formula	Mol. Wt.	SG (20°/4°)	$T_m(^{\circ}\text{C})^b$	$\Delta\hat{H}_m(T_m)^{c,j}$ kJ/mol	$T_b(^{\circ}\text{C})^d$	$\Delta\hat{H}_v(T_b)^{e,j}$ kJ/mol	$T_c(\text{K})^f$	$P_c(\text{atm})^g$	$(\Delta\hat{H}_f^{\circ})^{h,j}$ kJ/mol	$(\Delta\hat{H}_c^{\circ})^{i,j}$ kJ/mol
Chloroform	CHCl ₃	119.39	1.489	−63.7	—	61.0	—	536.0	54.0	−131.8(l)	−373(l)
Copper	Cu	63.54	8.92	1083	13.01	2595	304.6	—	—	0(c)	—
Cupric sulfate	CuSO ₄	159.61	3.606 ^{15°}	Decomposes > 600°C						−769.9(c)	—
Cyclohexane	C ₆ H ₁₂	84.16	0.779	6.7	2.677	80.7	30.1	553.7	40.4	−156.2(l) −123.1(g)	−3919.9(l) −3953.0(g)
Cyclopentane	C ₅ H ₁₀	70.13	0.745	−93.4	0.609	49.3	27.30	511.8	44.55	−105.9(l) −77.2(g)	−3290.9(l) −3319.5(g)
<i>n</i> -Decane	C ₁₀ H ₂₂	142.28	0.730	−29.9	—	173.8	—	619.0	20.8	−249.7(l)	−6778.3(l) −6829.7(g)
Diethyl ether	(C ₂ H ₅) ₂ O	74.12	0.708 ^{25°}	−116.3	7.30	34.6	26.05	467	35.6	−272.8(l)	−2726.7(l)
Ethane	C ₂ H ₆	30.07	—	−183.3	2.859	−88.6	14.72	305.4	48.2	−84.67(g)	−1559.9(g)
Ethyl acetate	C ₄ H ₈ O ₂	88.10	0.901	−83.8	—	77.0	—	523.1	37.8	−463.2(l) −426.8(g)	−2246.4(l) —
Ethyl alcohol (Ethanol)	C ₂ H ₅ OH	46.07	0.789	−114.6	5.021	78.5	38.58	516.3	63.0	−277.63(l) −235.31(g)	−1366.91(l) −1409.25(g)
Ethyl benzene	C ₈ H ₁₀	106.16	0.867	−94.67	9.163	136.2	35.98	619.7	37.0	−12.46(l) +29.79(g)	−4564.9(l) −4607.1(g)
Ethyl bromide	C ₂ H ₅ Br	108.98	1.460	−119.1	—	38.2	—	504	61.5	−54.4(g)	—
Ethyl chloride	C ₂ H ₅ Cl	64.52	0.903 ^{15°}	−138.3	4.452	13.1	24.7	460.4	52.0	−105.0(g)	—
3-Ethyl hexane	C ₈ H ₁₈	114.22	0.717	—	—	118.5	34.27	567.0	26.4	−250.5(l) −210.9(g)	−5407.1(l) −5509.8(g)
Ethylene	C ₂ H ₄	28.05	—	−169.2	3.350	−103.7	13.54	283.1	50.5	+52.28(g)	−1410.99(g)
Ethylene glycol	C ₂ H ₆ O ₂	62.07	1.113 ^{19°}	−13	11.23	197.2	56.9	—	—	−451.5(l) −387.1(g)	−1179.5(l) —
Ferric oxide	Fe ₂ O ₃	159.70	5.12	Decomposes at 1560°C						−822.2(c)	—
Ferrous oxide	FeO	71.85	5.7	—	—	—	—	—	—	−266.5(c)	—
Ferrous sulfide	FeS	87.92	4.84	1193	—	—	—	—	—	−95.1(c)	—
Formaldehyde	H ₂ CO	30.03	0.815 ^{−20°}	−92	—	−19.3	24.48	—	—	−115.90(g)	−563.46(g)
Formic acid	CH ₂ O ₂	46.03	1.220	8.30	12.68	100.5	22.25	—	—	−409.2(l) −362.6(g)	−262.8(l) —
Glycerol	C ₃ H ₈ O ₃	92.09	1.260 ^{50°}	18.20	18.30	290.0	—	—	—	−665.9(l)	−1661.1(l)
Helium	He	4.00	—	−269.7	0.02	−268.9	0.084	5.26	2.26	0(g)	—

Table B.2 Heat Capacities^a

**Physical Property
database**
Quickly integrates
tabulated heat
capacities

$$\text{Form 1: } C_p[\text{kJ}/(\text{mol}\cdot^\circ\text{C})] \text{ or } [\text{kJ}/(\text{mol}\cdot\text{K})] = a + bT + cT^2 + dT^3$$

$$\text{Form 2: } C_p[\text{kJ}/(\text{mol}\cdot^\circ\text{C})] \text{ or } [\text{kJ}/(\text{mol}\cdot\text{K})] = a + bT + cT^{-2}$$

Example: $(C_p)_{\text{acetone(g)}} = 0.07196 + (20.10 \times 10^{-5})T - (12.78 \times 10^{-8})T^2 + (34.76 \times 10^{-12})T^3$, where T is in $^\circ\text{C}$.

Note: The formulas for gases are strictly applicable at pressures low enough for the ideal gas equation of state to apply.

Compound	Formula	Mol. Wt.	State	Form	Temp. Unit	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$	Range (Units of T)
Acetone	CH_3COCH_3	58.08	l	1	$^\circ\text{C}$	123.0	18.6			−30–60
			g	1	$^\circ\text{C}$	71.96	20.10	−12.78	34.76	0–1200
Acetylene	C_2H_2	26.04	g	1	$^\circ\text{C}$	42.43	6.053	−5.033	18.20	0–1200
Air		29.0	g	1	$^\circ\text{C}$	28.94	0.4147	0.3191	−1.965	0–1500
			g	1	K	28.09	0.1965	0.4799	−1.965	273–1800
Ammonia	NH_3	17.03	g	1	$^\circ\text{C}$	35.15	2.954	0.4421	−6.686	0–1200
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	132.15	c	1	K	215.9				275–328
Benzene	C_6H_6	78.11	l	1	$^\circ\text{C}$	126.5	23.4			6–67
			g	1	$^\circ\text{C}$	74.06	32.95	−25.20	77.57	0–1200
Isobutane	C_4H_{10}	58.12	g	1	$^\circ\text{C}$	89.46	30.13	−18.91	49.87	0–1200
<i>n</i> -Butane	C_4H_{10}	58.12	g	1	$^\circ\text{C}$	92.30	27.88	−15.47	34.98	0–1200
Isobutene	C_4H_8	56.10	g	1	$^\circ\text{C}$	82.88	25.64	−17.27	50.50	0–1200
Calcium carbide	CaC_2	64.10	c	2	K	68.62	1.19	-8.66×10^{10}	—	298–720
Calcium carbonate	CaCO_3	100.09	c	2	K	82.34	4.975	-12.87×10^{10}	—	273–1033
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	74.10	c	1	K	89.5				276–373
Calcium oxide	CaO	56.08	c	2	K	41.84	2.03	-4.52×10^{10}		273–1173
Carbon	C	12.01	c	2	K	11.18	1.095	-4.891×10^{10}		273–1373
Carbon dioxide	CO_2	44.01	g	1	$^\circ\text{C}$	36.11	4.233	−2.887	7.464	0–1500
Carbon monoxide	CO	28.01	g	1	$^\circ\text{C}$	28.95	0.4110	0.3548	−2.220	0–1500
Carbon tetrachloride	CCl_4	153.84	l	1	K	93.39	12.98			273–343
Chlorine	Cl_2	70.91	g	1	$^\circ\text{C}$	33.60	1.367	−1.607	6.473	0–1200
Copper	Cu	63.54	c	1	K	22.76	0.6117			273–1357

^aAdapted in part from D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, © 1974, Table E.1. Adapted by permission of Prentice-Hall, Inc., Englewood Cliffs, NJ.

Table B.2 (Continued)

Compound	Formula	Mol. Wt.	State	Form	Temp. Unit	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$	Range (Units of T)
10 Cumene (Isopropyl benzene)	C ₉ H ₁₂	120.19	g	1	°C	139.2	53.76	-39.79	120.5	0-1200
Cyclohexane	C ₆ H ₁₂	84.16	g	1	°C	94.140	49.62	-31.90	80.63	0-1200
Cyclopentane	C ₅ H ₁₀	70.13	g	1	°C	73.39	39.28	-25.54	68.66	0-1200
Ethane	C ₂ H ₆	30.07	g	1	°C	49.37	13.92	-5.816	7.280	0-1200
Ethyl alcohol (Ethanol)	C ₂ H ₅ OH	46.07	l	1	°C	103.1				0
			l	1	°C	158.8				100
			g	1	°C	61.34	15.72	-8.749	19.83	0-1200
Ethylene	C ₂ H ₄	28.05	g	1	°C	+40.75	11.47	-6.891	17.66	0-1200
Ferric oxide	Fe ₂ O ₃	159.70	c	2	K	103.4	6.711	-17.72 × 10 ¹⁰	—	273-1097
Formaldehyde	CH ₂ O	30.03	g	1	°C	34.28	4.268	0.0000	-8.694	0-1200
Helium	He	4.00	g	1	°C	20.8				0-1200
<i>n</i> -Hexane	C ₆ H ₁₄	86.17	l	1	°C	216.3				20-100
			g	1	°C	137.44	40.85	-23.92	57.66	0-1200
Hydrogen	H ₂	2.016	g	1	°C	28.84	0.00765	0.3288	-0.8698	0-1500
Hydrogen bromide	HBr	80.92	g	1	°C	29.10	-0.0227	0.9887	-4.858	0-1200
Hydrogen chloride	HCl	36.47	g	1	°C	29.13	-0.1341	0.9715	-4.335	0-1200
Hydrogen cyanide	HCN	27.03	g	1	°C	35.3	2.908	1.092		0-1200
Hydrogen sulfide	H ₂ S	34.08	g	1	°C	33.51	1.547	0.3012	-3.292	0-1500
Magnesium chloride	MgCl ₂	95.23	c	1	K	72.4	1.58			273-991
Magnesium oxide	MgO	40.32	c	2	K	45.44	0.5008	-8.732 × 10 ¹⁰		273-2073
Methane	CH ₄	16.04	g	1	°C	34.31	5.469	0.3661	-11.00	0-1200
			g	1	K	19.87	5.021	1.268	-11.00	273-1500
Methyl alcohol (Methanol)	CH ₃ OH	32.04	l	1	°C	75.86	16.83			0-65
			g	1	°C	42.93	8.301	-1.87	-8.03	0-700
Methyl cyclohexane	C ₇ H ₁₄	98.18	g	1	°C	121.3	56.53	-37.72	100.8	0-1200
Methyl cyclopentane	C ₆ H ₁₂	84.16	g	1	°C	98.83	45.857	-30.44	83.81	0-1200
Nitric acid	NHO ₃	63.02	l	1	°C	110.0				25
Nitric oxide	NO	30.01	g	1	°C	29.50	0.8188	-0.2925	0.3652	0-3500

Nitrogen	N ₂	28.02	g	1	°C	29.00	0.2199	0.5723	−2.871	0–1500
Nitrogen dioxide	NO ₂	46.01	g	1	°C	36.07	3.97	−2.88	7.87	0–1200
Nitrogen tetroxide	N ₂ O ₄	92.02	g	1	°C	75.7	12.5	−11.3		0–300
Nitrous oxide	N ₂ O	44.02	g	1	°C	37.66	4.151	−2.694	10.57	0–1200
Oxygen	O ₂	32.00	g	1	°C	29.10	1.158	−0.6076	1.311	0–1500
<i>n</i> -Pentane	C ₅ H ₁₂	72.15	l	1	°C	155.4	43.68			0–36
			g	1	°C	114.8	34.09	−18.99	42.26	0–1200
Propane	C ₃ H ₈	44.09	g	1	°C	68.032	22.59	−13.11	31.71	0–1200
Propylene	C ₃ H ₆	42.08	g	1	°C	59.580	17.71	−10.17	24.60	0–1200
Sodium carbonate	Na ₂ CO ₃	105.99	c	1	K	121				288–371
Sodium carbonate decahydrate	Na ₂ CO ₃ · 10H ₂ O	286.15	c	1	K	535.6				298
Sulfur	S	32.07	c	1	K	15.2	2.68			273–368
			(Rhombic) c	1	K	18.3	1.84			368–392
			(Monoclinic)							
Sulfuric acid	H ₂ SO ₄	98.08	l	1	°C	139.1	15.59			10–45
Sulfur dioxide	SO ₂	64.07	g	1	°C	38.91	3.904	−3.104	8.606	0–1500
Sulfur trioxide	SO ₃	80.07	g	1	°C	48.50	9.188	−8.540	32.40	0–1000
Toluene	C ₇ H ₈	92.13	l	1	°C	148.8	32.4			0–110
			g	1	°C	94.18	38.00	−27.86	80.33	0–1200
Water	H ₂ O	18.016	l	1	°C	75.4				0–100
			g	1	°C	33.46	0.6880	0.7604	−3.593	0–1500

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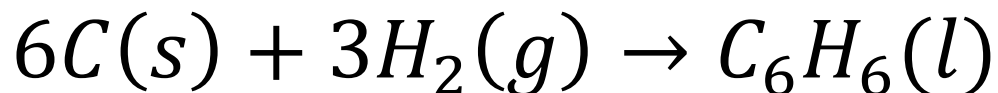
- Use the “**Heat of Formation Energy Balance**” to calculate the enthalpy change in a reactive process

Heat of Formation

3

- **Standard Heat of formation (ΔH_f°):** Enthalpy change associated with the forming 1 mole of a compound from its elements at 298K and 1atm

Example: formation of benzene



$$\Delta \hat{H}_f^\circ = +48.66 \frac{kJ}{mol}$$

Look it up!
Table B.1

Table B.1 (Continued)

Compound	Formula	Mol. Wt.	SG (20°/4°)	$T_m(^{\circ}\text{C})^b$	$\Delta\hat{H}_m(T_m)^{c,j}$ kJ/mol	$T_b(^{\circ}\text{C})^d$	$\Delta\hat{H}_v(T_b)^{e,j}$ kJ/mol	$T_c(\text{K})^f$	$P_c(\text{atm})^g$	$(\Delta\hat{H}_f^{\circ})^{h,j}$ kJ/mol	$(\Delta\hat{H}_c^{\circ})^{i,j}$ kJ/mol
Chloroform	CHCl ₃	119.39	1.489	−63.7	—	61.0		536.0	54.0	−131.8(l)	−373(l)
Copper	Cu	63.54	8.92	1083	13.01	2595	304.6	—		0(c)	—
Cupric sulfate	CuSO ₄	159.61	3.606 ^{15°}			Decomposes > 600°C				−769.9(c)	—
Cyclohexane	C ₆ H ₁₂	84.16	0.779	6.7	2.677	80.7	30.1	553.7	40.4	−156.2(l)	−3919.9(l)
Cyclopentane	C ₅ H ₁₀	70.13	0.745	−93.4	0.609	49.3	27.30	511.8	44.55	−123.1(g)	−3953.0(g)
<i>n</i> -Decane	C ₁₀ H ₂₂	142.28	0.730	−29.9	—	173.8	—	619.0	20.8	−105.9(l)	−3290.9(l)
Diethyl ether	(C ₂ H ₅) ₂ O	74.12	0.708 ^{25°}	−116.3	7.30	34.6	26.05	467	35.6	−77.2(g)	−3319.5(g)
Ethane	C ₂ H ₆	30.07	—	−183.3	2.859	−88.6	14.72	305.4	48.2	−249.7(l)	−6778.3(l)
Ethyl acetate	C ₄ H ₈ O ₂	88.10	0.901	−83.8	—	77.0	—	523.1	37.8	—	−6829.7(g)
Ethyl alcohol (Ethanol)	C ₂ H ₅ OH	46.07	0.789	−114.6	5.021	78.5	38.58	516.3	63.0	−426.8(g)	—
Ethyl benzene	C ₈ H ₁₀	106.16	0.867	−94.67	9.163	136.2	35.98	619.7	37.0	−277.63(l)	−1366.91(l)
Ethyl bromide	C ₂ H ₅ Br	108.98	1.460	−119.1	—	38.2	—	504	61.5	−235.31(g)	−1409.25(g)
Ethyl chloride	C ₂ H ₅ Cl	64.52	0.903 ^{15°}	−138.3	4.452	13.1	24.7	460.4	52.0	−12.46(l)	−4564.9(l)
3-Ethyl hexane	C ₈ H ₁₈	114.22	0.717	—	—	118.5	34.27	567.0	26.4	+29.79(g)	−4607.1(g)
Ethylene	C ₂ H ₄	28.05	—	−169.2	3.350	−103.7	13.54	283.1	50.5	−54.4(g)	—
Ethylene glycol	C ₂ H ₆ O ₂	62.07	1.113 ^{19°}	−13	11.23	197.2	56.9	—	—	−105.0(g)	—
Ferric oxide	Fe ₂ O ₃	159.70	5.12			Decomposes at 1560°C				−250.5(l)	−5407.1(l)
Ferrous oxide	FeO	71.85	5.7	—	—	—	—	—	—	−210.9(g)	−5509.8(g)
Hydrogen	H ₂	2.016	—	−259.19	0.12	−252.76	0.904	33.3	12.8	+52.28(g)	−1410.99(g)
Hydrogen bromide	HBr	80.92	—	−86	—	−67	—	—	—	−451.5(l)	−1179.5(l)
Hydrogen chloride	HCl	36.47	—	−114.2	1.99	−85.0	16.1	324.6	81.5	−387.1(g)	—
Hydrogen cyanide	HCN	27.03	—	−14	—	26	—	—	—	−822.2(c)	—
Hydrogen fluoride	HF	20.0	—	−83	—	20	—	503.2	—	−266.5(c)	—