Thermochemistry

Chemical reactions involve changes in energy. **Energy** is the ability to do work or to produce heat. Work is the capacity to move an object over a distance against a resisting force. So, for example, every time you take a breath you are working. As you might think, different types of work require different types and/or amounts of energy.

There are three forms of energy:

1. Radiant energy – energy that moves in waves.
2. Kinetic energy – energy of motion (can be mechanical or thermal).
3. Potential energy – stored energy (energy possessed by objects because of their position or arrangement).

Thermochemistry studies the effects of heat in chemical reactions. Heat can be transferred between the reaction and its surroundings. The amount of energy required to change the temperature of a substance depends upon the nature and the amount of the substance. Heat energy is measured in calories and joules. A **calorie** is the amount heat required to raise the temperature of 1 gram of water 1°C, (1cal. = 1g H_2O X 1°C). 1000 calories can be expressed as a kilocalorie or Calorie. The SI unit for heat is the joule, 1 calorie is equal to 4.184 joules.

Practice: Convert the following measurements.

1. 578 cal. = ? joules __________
2. 4267 cal. = ? joules __________
3. 3.98 joules = ? cal. __________
4. 7.87 joules = ? cal. __________
5. 54.00 Cal. = ? cal. __________
6. 345 Cal. = ? joules __________

When a reaction (system) occurs we measure the heat that is produced or absorbed by the reaction. If the heat is released into the surroundings, (the space and object around the system), the reaction is **exothermic**. If heat is absorbed from the surroundings into the system the reaction is **endothermic**. To observe the changes in heat we measure the temperature of the system and surroundings. **Temperature** is a quantitative measurement of the tendency of heat to flow in a given direction using an arbitrary scale. The three most common temperature scales are **Fahrenheit, Celcius and Kelvin**. The celcius system is based on the freezing and boiling points of water, while the Kelvin system is based on absolute zero. Absolute zero is the point at which all movement stops for all matter. In chemistry we will use celcius and Kelvin. For these two systems the increment of change is identical, making conversion between the two simple addition and subtraction.

°C = K – 273 K= °C + 273 (0K = -273 °C)

- For example: convert 32 °C to K
  32 °C + 273 = 305K

- For example: convert 258K to °C
  258K – 273 = -15 °C

Practice: Complete the following conversions (remember to use the add/subtract rules for sig. figs).

1. 41 °C to K ________ 2. 95 °C to K ________ 3. 409 K to °C ________

The change in the heat of a reaction (accounting for the temperature and pressure of the surroundings) is referred to as the change in **enthalpy (ΔH).** The change in energy for a reaction is the difference between the enthalpy of the products and the enthalpy of the reactants.

$$\Delta H_{reaction} = \Delta H_{products} - \Delta H_{reactants}$$

Calculating the $\Delta H_{reaction}$ can help to determine if a reaction will occur spontaneously or if energy will be needed to activate the reaction (**activation energy**). The temperature and the pressure of the system can effect the results, therefore these must also be monitored. The $\Delta H_{products}$ and $\Delta H_{reactants}$ can be found on the standard enthalpies chart, notice that the enthalpies for single elements and the diatomic molecules are zero.

Sign of ΔH	Process	Heat
Positive	endothermic	absorbed
Negative	exothermic	released

For example:
Determine the $\Delta H_{reaction}$ for C_3H_8 (g) + 5 O_2 (g) → 3 CO_2 (g) + 4 H_2O (g)

$\Delta H_{reaction}$ = [(3 mol)(-393.51kJ/mol)+(4 mol)(-285.83kJ/mol)]-
[(1mol)(-103.85kJ/mol)+(5 mol)(0kJ/mol)]
$\Delta H_{reaction}$ = [-1180.53kJ + -967.2kJ]-[-103.85kJ]
$\Delta H_{reaction}$ = -2043.88kJ

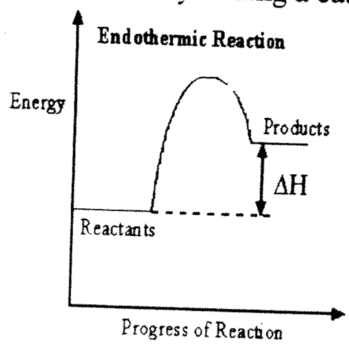
Was this reaction endo or exothermic? The $\Delta H_{reaction}$ is -2043.88kJ therefore the reaction released heat and is exothermic.

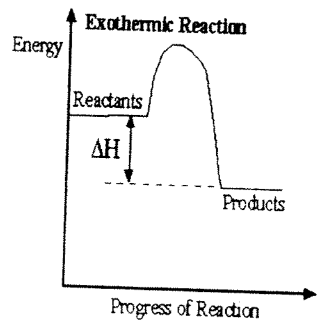
Practice: Calculate the $\Delta H_{reaction}$ for the following problems.

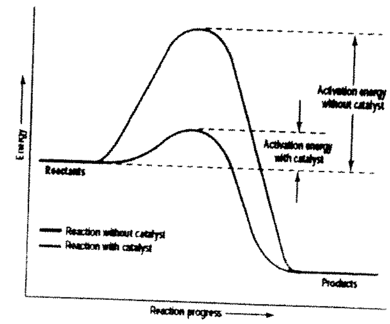
1. 2 KBr (s) + I_2 (g) → 2 KI (s) + Br_2 (g)

2. 2 HCl (g) + 2 AgCl (s) → 2 AgCl (s) + H_2 (g)

We can graphically represent the heat transfer of a reaction in a reaction profile. This graph allows us to observe the changes in enthalpy throughout the reaction. If any activation energy is required it can be measured by finding the energy of the peak and subtracting the energy of the reactants. The transitional state, or activation complex, is the period of time in which the bonds of the reactants are breaking and the bonds are reforming to create the products. The activation energy required for some reactions can be lowered by adding a catalyst.

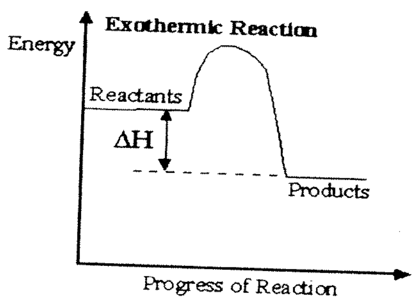






Example: For the reaction:

C_3H_8 (g) + 5 O_2 (g) → 3 CO_2 (g) + 4 H_2O (g)



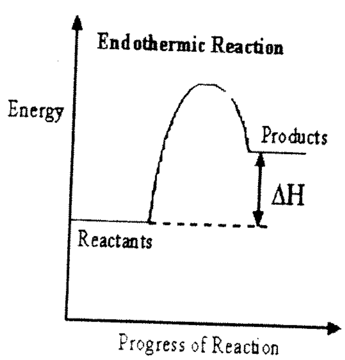
Reactants: (1 mol)(-103.85kJ) + (5 mol)(0kJ)
-103.85kJ

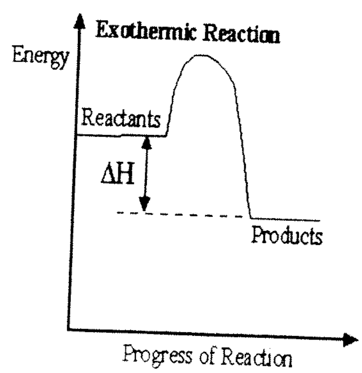
Products: (3 mol)(-393.51kJ) + (4 mol)(-285.83kJ)
-2147.73kJ

ΔH = -2043.88kJ (exothermic)

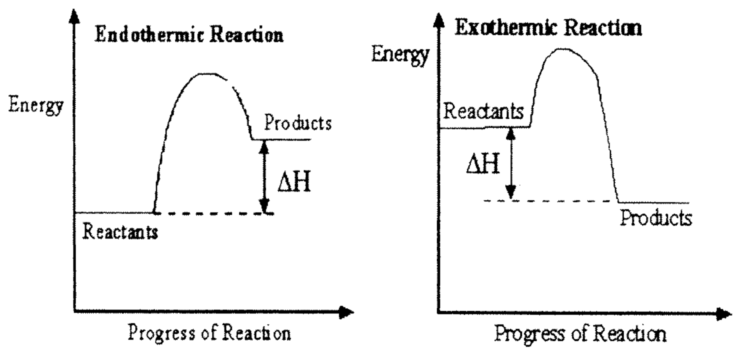
Practice: Complete the following graphs for the data given in the previous practice problems. Choose the proper graph and label it with the data from the reaction.

1. 2 KBr (s) + I_2 (g) →2 KI (s) + Br_2 (g)





2. 2 HCl (g) + 2 AgCl (s) → 2 AgCl (s) + H_2 (g)



Calorimetry

Calorimetry is the study of heat flow and heat measurement. Calorimetry can be used to determine the enthalpy changes of a reaction by making accurate measurements of temperature changes produced by a chemical reaction. These temperature changes are measured in a devise referred to as a calorimeter. The size of the temperature change depends upon the enthalpy of the reaction and the heat capacity of the surroundings. **Specific heat capacity (C_p)** of a substance is the amount of energy required to raise the temperature of 1 gram of any substance by 1°C. The specific heat for water is 1 cal/g °C or 4.184 joules/g °C. (**you must know both of these values!!**) By using a calorimeter we can measure the heat transferred during a reaction, $\mathbf{q_{rxn}}$. The heat transferred is equal and opposite to the heat absorbed by the surroundings: $\mathbf{q_{rxn} = -q_{surr}}$. The heat absorbed by the surroundings can be calculated by the formula:

$$\mathbf{q_{rxn} = (mass)(\Delta T)(C_p)}$$

- For example: How many calories of heat are needed to raise the temperature of 1.00 kg of water from 10.2 °C to 26.8 °C?

  $q_{rxn} = (\text{mass})(T_f - T_i)(C_p)$
  $= (1000g)(26.8\ °C - 10.2\ °C)(1\ \text{cal/g}\ °C)$
  $= 16600$ cal.

- How many joules would that be?

  16600 cal. x $\frac{4.184 \text{ joules}}{1 \text{ cal.}}$ = 68454.4J or 69500J

Practice: Complete the following calculations on a separate piece of paper.

1. How much heat would be absorbed by 55g of copper when heated from 24 °C to 40. °C? (Copper: $C_p = 0.385$ J/g °C)

2. What temperature change will 100 ml of water undergo when it absorbs 325 calories of heat?

3. How much heat is lost when a 4110g metal bar ($C_p = 0.2311$ J/g °C) is cooled from 100.0 °C to 20.00 °C?

4. How much heat (in joules) is required to raise the temperature of 854 g of water from 23.5 °C to 85.0 °C?

5. What was the initial temperature of a 100.0g piece of lead (C_p = 0.158 J/g °C) when placed in 50.0 g of water, the initial temperature of the water was 20.0 °C, the systems final temperature was 34.0 °C?

Enthalpy

The heat absorbed by the surroundings can be used to determine $\Delta H_{reaction}$.

$$\Delta H = \text{mass of given} \times \frac{1\text{mole}}{\text{Molar mass Of given}} \times \frac{q_{rxn}}{\text{\# of moles from balanced Equation}}$$

For example:
How much heat is released when 6.44g of sulfur reacts with excess oxygen gas according to the following equation?

$2\ S + 3\ O_2\ (g) \rightarrow 2\ SO_3$ ΔH_{rxn} = -791.4 kJ

$$\Delta H_{rxn} = 6.44\text{g S} \times \frac{1\text{ mole S}}{32.07\text{g S}} \times \frac{-791.4\text{ kJ}}{2\text{ mol S}} = -79.5\text{kJ}$$

Practice: Complete the following problems.

1. How much heat will be released when 4.72g of carbon reacts with excess oxygen gas according to the following equation?
   $C + O_2\ (g) \rightarrow CO_2\ (g)$ ΔH_{rxn} = -393.5 kJ

2. How much heat will be absorbed when 38.2g of bromine gas reacts with excess hydrogen gas according to the following equation?
   $Br_2\ (g) + H_2\ (g) \rightarrow 2\ HBr\ (g)$ ΔH_{rxn} = 72.80kJ

3. How much heat will be released when 1.48g of chlorine gas reacts with excess phosphorous according to the following equation?
   $2\ P + 5\ Cl_2\ (g) \rightarrow 2\ PCl_5$ ΔH_{rxn} = -886kJ

Entropy (S): a quantitative measurement of the disorder of a system (randomness)

To calculate the change in entropy (ΔS):
$\Delta S_{total} = \Delta S_{products} - \Delta S_{reactants}$

Gibb's Free Energy (G): a determination of spontaneity
To calculate the change in enthalpy (ΔG):
$\Delta G_{total} = \Delta G_{products} - \Delta G_{reactants}$
- or -
To calculate the change in enthalpy (ΔH):
$\Delta G = \Delta H - T\Delta S$

Use the following chart to determine spontaneity.

ΔG	**Reaction will:**
negative	be spontaneous
positive	not be spontaneous, it will required energy to occur
zero	is at equilibrium

Name: ______________________________ Block: ___ Date: ____________________

Thermochemistry Homework

Match the following terms with their correct definition.

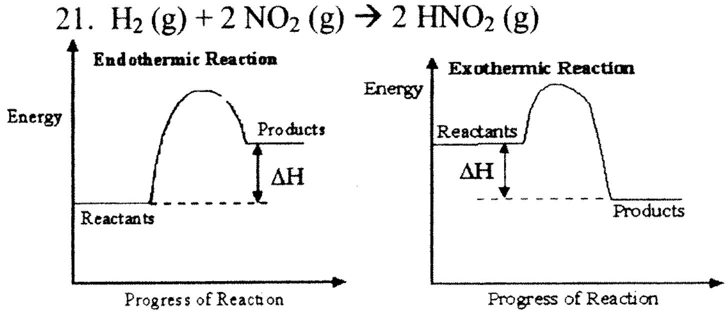
___1. Calorimetry	a. the amount heat required to raise the temperature of 1g of water by 1 °C
___2. Endothermic reaction	b. heat content of a system at a constant pressure
___3. Enthalpy	c. measurement of the amount of heat absorbed or released during a chemical reaction
___4. Exothermic reaction	d. the study of the changes in heat energy during a chemical reaction
___5. Activation energy	e. the amount of heat required to raise the temperature of 1 gram of any substance by 1 °C
___6. Calorie	f. a process that releases heat
___7. Specific heat	g. a process that absorbs heat
___8. Thermochemistry	h. energy will be needed to activate the reaction

Complete the following conversions.

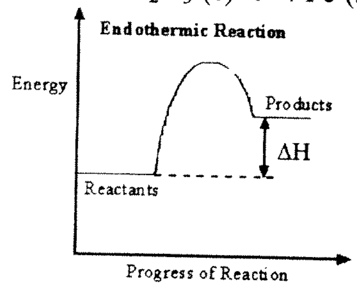
1. 5.42 cal. = ?joules	________	6. 8.02 joules = ?cal.	________
2. 726.0 cal. = ?joules	________	7. 32.3 joules = ?Cal.	________
3. 60.5 joules = ?cal.	________	8. 742 Cal. = ?joules	________
4. 1203 joules = ?cal.	________	9. 12.5 cal. = ?Cal.	________
5. 4140 Cal. = ?cal.	________	10. 33.7 Cal. = ?joules	________
11. 47°C = ?K	________	16. 2410K = ?°C	________
12. 321K = ?°C	________	17. -97°C = ?K	________
13. 1000°C = ?K	________	18. 301K = ?°C	________
14. -20°C = ?K	________	19. 4.9°C = ?K	________
15. 32K = ?°C	________	20. -53.4°C = ?K	________

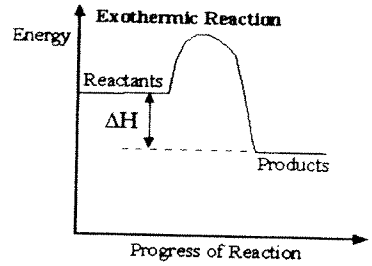
Calculate the $\Delta H_{reaction}$ and complete the appropriate graph for the following problems.

21. $H_2(g) + 2\ NO_2(g) \rightarrow 2\ HNO_2(g)$

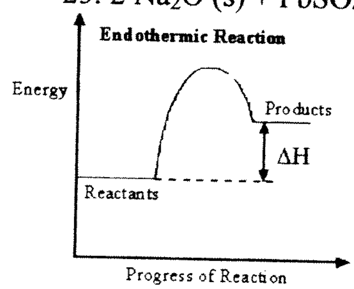


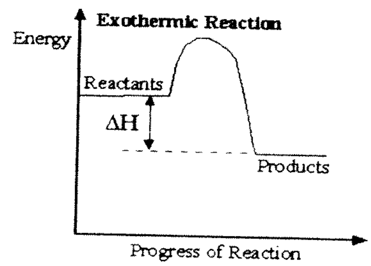
22. Fe_2O_3 (s) → 4 Fe (s) + 3 O_2 (g)





23. 2 Na_2O (s) + $PbSO_4$ (s) → 2 Na_2SO_4 (s) + PbO_2 (s)





Complete the following calculations.

24. Haw many calories are required to raise the temperature of 1.00kg of water from 23.5°C to 50.0 °C?

25. How many joules would required for problem #24?

26. Was question #24 endothermic or exothermic?

27. How much heat is required to raise the temperature of 96.7g phosphorous trichloride (C_p = 0.874 J/g °C) from 31.7 °C to 69.2 °C?

28. How much heat is required to raise the temperature of 10.35g carbon tetrachloride (C_p = 0.856 J/g °C) from 32.1 °C to 56.4 °C?

29. Calculate the heat in joules required to raise the temperature of 275g of water 46.8 °C?

30. What is the specific heat of aluminum if the temperature of a 28.4g sample of aluminum is increased by 8.1 °C when 207*J* of heat is absorbed?

31. What is the specific heat of silicon if the temperature of a 4.11g sample of silicon is increased by 3.8 °C when 11.1*J* of heat is added?

32. How much heat will be released when 11.8g of iron reacts with excess oxygen according to the reaction:
$3\ Fe + 2\ O_2\ (g) \rightarrow Fe_3O_4$ $\Delta H = -1120.84kJ$

33. How much heat will be released when 18.6g of hydrogen gas reacts with excess oxygen according to the reaction:
$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g)$ $\Delta H = -571.6kJ$

34. How much heat will be transferred when 14.9g of ammonia reacts with excess oxygen gas according to the reaction:
$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$ $\Delta H = -1170kJ$

35. How much heat will be transferred when 5.81g of graphite reacts with excess hydrogen gas according to the reaction:
$6\ C\ (s) + 3\ H_2\ (g) \rightarrow C_6H_6$ $\Delta H = 49.03kJ$

Appendix 2 Thermodynamic Properties of Various Substances

Compound	$\Delta_f H^\circ$ (at 298 K, in kJ/mol)	$\Delta_f G^\circ$ (at 298 K, in kJ/mol)	S° [at 29[illegible] in J/([illegible]
Ag (s)	0	0	42.5[illegible]
AgBr (s)	−100.37	−96.90	107.1[illegible]
AgCl (s)	−127.01	−109.80	96.2[illegible]
Al (s)	0	0	28.3[illegible]
Al_2O_3 (s)	−1675.7	−1582.3	50.9[illegible]
Ar (g)	0	0	1[illegible]
Au (s)	0	0	[illegible]
$BaSO_4$ (s)	−1473.19	−1362.3	132.2
Bi (s)	0	0	56.5[illegible]
Br_2 (ℓ)	0	0	152.21
C (s, diamond)	1.897	2.90	2.3[illegible]
C (s, graphite)	0	0	5.[illegible]
CCl_4 (ℓ)	−128.4	−62.6	214.39
CH_2O (g)	−115.90	−109.9	218.9[illegible]
$CH_3COOC_2H_5$ (ℓ)	−480.57	−332.7	259.4
CH_3COOH (ℓ)	−483.52	−390.2	158.0
CH_3OH (ℓ)	−238.4	−166.8	127.19
CH_4 (g)	−74.87	−50.8	188.66
CO (g)	−110.5	−137.16	197.66
CO_2 (g)	−393.51	−394.35	213.78[illegible]
CO_3^{2-} (aq), 1 M	−413.8	−386.0	117.6
C_2H_5OH (ℓ)	−277.0	−174.2	159.86
C_2H_6 (g)	−83.8	−32.8	229.1
C_6H_{12} (ℓ)	−157.7	26.7	203.89
$C_6H_{12}O_6$ (s)	−1277	−910.4	209.19
C_6H_{14} (ℓ)	−198.7	−3.8	296.06
$C_6H_5CH_3$ (ℓ)	12.0	113.8	220.96
C_6H_5COOH (s)	−384.8	−245.3	165.71
C_6H_6 (ℓ)	48.95	124.4	173.26
$C_{10}H_8$ (s)	77.0	201.0	217.59
$C_{12}H_{22}O_{11}$ (s)	−2221.2	−1544.7	392.40
Ca (s)	0	0	41.59
Ca^{2+} (aq), 1 M	−542.83	−553.54	−53.1
$CaCl_2$ (s)	−795.80	−748.1	104.62
$CaCO_3$ (s, arag)	−1207.1	−1127.8	92.9
$CaCO_3$ (s, calc)	−1206.9	−1128.8	88.7
Cl (g)	121.30	105.3	165.19
Cl^- (aq), 1 M	−167.2	−131.3	56.4
Cl_2 (g)	0	0	223.08
Cr (s)	0	0	23.62
Cr_2O_3 (s)	−1134.70	105.3	80.65
Cs (s)	0	0	85.15
Cu (s)	0	0	33.17
D_2 (g)	0	0	144.96
D_2O (ℓ)	−249.20	−234.54	198.34
F^- (aq), 1 M	−332.63	−278.8	−13.8
F_2 (g)	0	0	202.791
Fe (s)	0	0	27.3
$Fe_2(SO_4)_3$ (s)	−2583.00	−2262.7	307.46

Compound	$\Delta_f H^\circ$ (at 298 K, in kJ/mol)	$\Delta_f G^\circ$ (at 298 K, in kJ/mol)	S° [at 298 K, in J/(mol·K)]
Fe_2O_3 (s)	−825.5	−743.5	87.4
Ga (s)	0	0	40.83
H^+ (aq), 1 M	0	0	0
HBr (g)	−36.29	−53.51	198.70
HCl (g)	−92.31	−95.30	186.90
HCO_3^- (aq), 1 M	−691.99	−586.85	91.2
HD (g)	0.32	−1.463	143.80
HF (g)	−273.30	−274.6	173.779
HI (g)	26.5	1.7	114.7
HNO_2 (g)	−76.73	−41.9	249.41
HNO_3 (g)	−134.31	−73.94	266.39
HSO_4^- (aq), 1 M	−909.27	−744.63	20.1
H_2 (g)	0	0	130.68
H_2O (g)	−241.8	−228.61	188.83
H_2O (ℓ)	−285.83	−237.14	69.91
H_2O (s)	−292.72	—	—
He (g)	0	0	126.04
Hg (ℓ)	0	0	75.90
Hg_2Cl_2 (s)	−265.37	−210.5	191.6
I (g)	106.76	70.18	180.787
I_2 (s)	0	0	116.14
K (s)	0	0	64.63
KBr (s)	−393.8	−380.7	95.9
KCl (s)	−436.5	−408.5	82.6
KF (s)	−567.3	−537.8	66.6
KI (s)	−327.9	−324.9	106.3
Li (s)	0	0	29.09
Li^+ (aq), 1 M	−278.49	−293.30	13.4
LiBr (s)	−351.2	−342.0	74.3
LiCl (s)	−408.27	−372.2	59.31
LiF (s)	−616.0	−587.7	35.7
LiI (s)	−270.4	−270.3	86.8
Mg (s)	0	0	32.67
Mg^{2+} (aq), 1 M	−466.85	−454.8	−138.1
MgO (s)	−601.60	−568.9	26.95
NH_3 (g)	−45.94	−16.4	192.77
NO (g)	90.29	86.60	210.76
NO_2 (g)	33.10	51.30	240.04
NO_3^- (aq), 1 M	−207.36	−111.34	146.4
N_2 (g)	0	0	191.609
N_2O (g)	82.05	104.2	219.96
N_2O_4 (g)	9.08	97.79	304.38
N_2O_5 (g)	11.30	118.0	346.55
Na (s)	0	0	153.718
Na^+ (aq), 1 M	−240.12	−261.88	59.1
NaBr (s)	−361.1	−349.0	86.8
NaCl (s)	−385.9	−365.7	95.06
NaF (s)	−576.6	−546.3	51.1
NaI (s)	−287.8	−286.1	—
$NaHCO_3$ (s)	−950.81	−851.0	101.7
NaN_3 (s)	21.71	93.76	96.86
Na_2CO_3 (s)	−1130.77	−1048.01	138.79

Compound	$\Delta_f H°$ (at 298 K, in kJ/mol)	$\Delta_f G°$ (at 298 K, in kJ/mol)	$S°$ [at 298 K, in J/(mol·K)]
Na_2O (s)	−417.98	−379.1	75.04
Na_2SO_4 (s)	−331.64	−303.50	35.89
Ne (g)	0	0	146.328
Ni (s)	0	0	29.87
O_2 (g)	0	0	205.14
O_3 (g)	142.67	163.2	238.92
OH^- (aq), 1 M	−229.99	−157.28	−10.75
PH_3 (g)	22.89	30.9	210.24
P_4 (s)	0	0	41.08
Pb (s)	0	0	64.78
$PbCl_2$ (s)	−359.41	−314.1	135.98
PbO_2 (s)	−274.47	−215.4	71.78
$PbSO_4$ (s)	−919.97	−813.20	148.50
Pt (s)	0	0	25.86
Rb (s)	0	0	76.78
S (s)	0	0	32.054
SO_2 (g)	−296.81	−300.13	248.223
SO_3 (g)	−395.77	−371.02	256.77
SO_3 (ℓ)	−438	−368	95.6
SO_4^{2-} (aq), 1 M	−909.3	−744.6	20.1
Si (s)	0	0	18.82
U (s)	0	0	50.20
UF_6 (s)	−2197.0	−2068.6	227.6
UO_2 (s)	−1085.0	−1031.8	77.03
Xe (g)	0	0	169.68
Zn (s)	0	0	41.6
Zn^{2+} (aq), 1 M	−153.89	−147.03	−112.1
$ZnCl_2$ (s)	−415.05	−369.45	111.46

Source: Data from National Institute of Standards and Technology's Chemistry Webbook (available online at webbook.nist.gov/chemistry); D. R. Lide, ed., *CRC Handbook of Chemistry and Physics*, 82nd ed., CRC Press, Boca Raton, Fla., 2001; J. A. Dean, ed., *Lange's Handbook of Chemistry*, 14th ed., McGraw-Hill, New York, 1992.