

Name: Solutions

Student Number: _____

Faculty of Science and Engineering
Final Examination
CHEM 1000 3.0 – Chemical Structure

December 13, 2010

9:00 – 11:00 a.m.

2 hours
100 marks

- Calculators are permitted but may not be shared.
- All cell phones must be turned off and placed out of reach.
- The last three pages containing a periodic table, constants, equations and other useful data may be removed. (Notes and/or other study aids are not permitted).
- Atomic masses are located on the periodic table.
- Extra paper for rough work is not permitted.
- Write your answers in the space provided. Answers may not be submitted on the periodic table or other reference pages.

Q#5
continues →
on
Pg. 657

Page	Mark
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13	
Total	

1. Iron(III) oxide (Fe_2O_3 , M.M. $159.69 \text{ g mol}^{-1}$) can be decomposed to give the mixed Iron(II,III) oxide (Fe_3O_4 , M.M. $231.53 \text{ g mol}^{-1}$) and oxygen.



Determine the mass of Fe_2O_3 that must be decomposed to produce oxygen that fills a 3.95 L vessel to a pressure of 120 kPa at -73°C .

moles of O_2 : $PV = nRT$

$$\frac{120 \times 10^3}{1.013 \times 10^5} \cdot 3.95 = n \cdot 0.08206 \cdot 200.15$$

$$n = \underline{0.285 \text{ moles}}$$

1 mole O_2 requires 6 moles Fe_2O_3 i.e. 1.71 moles

$$\therefore \text{mass } \text{Fe}_2\text{O}_3 = 1.71 \times 159.69$$

$$= \underline{\underline{273 \text{ g}}}$$

- 6] 2. You have a container of ice at 0.0°C . What is the minimum mass of ice that must be added to 150.0 g of liquid water at 15.0°C to lower its temperature to 0.0°C ?

$$\text{heat lost by water} = m c \Delta T$$

$$= 150.0 \cdot 4.184 \cdot 15$$

$$= \underline{\underline{9414 \text{ J}}}$$

heat must be absorbed by melting ice at 0.0°C .

$$q = n \Delta H_{\text{fus}}$$

$$= \frac{m}{18.011} \times 6.01 \times 10^3 \text{ J}$$

$$\Rightarrow 9414 = \frac{m}{18.011} \times 6.01 \times 10^3 \Rightarrow \underline{\underline{m = 28.2 \text{ g}}}$$

- [15] 3. A sample of 1.28 g of solid naphthalene ($C_{10}H_8$, M.M. $128.17 \text{ g mol}^{-1}$) is reacted with excess oxygen in a constant volume bomb calorimeter to give $CO_2(g)$ and $H_2O(l)$. The heat capacity of the calorimeter has been determined to be $10.3 \text{ kJ } ^\circ\text{C}^{-1}$ and the temperature of the calorimeter rises by $5.15 \text{ }^\circ\text{C}$.

a. write the balanced equation for this reaction



b. calculate the change in internal energy for this reaction

Constant volume so $\Delta U = q_v$

$$q = C \Delta T = 10.3 \times 5.15 = +53.0 \text{ kJ (released)}$$

$$\therefore \Delta U = \underline{-53.0 \text{ kJ}} \text{ or per mole } \Delta U = \frac{-53.0}{1.28/128.17} = \underline{-5387 \text{ kJ mol}^{-1}}$$

c. calculate the standard enthalpy change for this reaction in kJ mol^{-1}

$$\Delta H = \Delta U + \Delta n RT \quad \Delta n = 10 - 12 = -2$$

$$\Delta H = -5387 - 2 \cdot 8.314 \cdot 298.15 \times 10^{-3} = \underline{-5392 \text{ kJ mol}^{-1}}$$

d. calculate the standard enthalpy of formation of naphthalene given

$$\Delta H_f^\circ(CO_2(g)) = -393.51 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(H_2O(l)) = -285.83 \text{ kJ mol}^{-1}$$

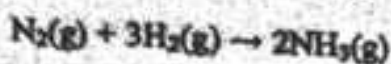
$$\Delta H_{\text{comb}} = \sum \Delta H_f^\circ(\text{pr}) - \sum \Delta H_f^\circ(\text{react})$$

$$= 10 \cdot \Delta H_f^\circ(CO_2) + 4 \Delta H_f^\circ(H_2O) - \Delta H_f^\circ(C_{10}H_8) - 12 \Delta H_f^\circ(O_2)$$

$$\therefore -5392 = 10(-393.51) + 4(-285.83) - \Delta H_f^\circ(C_{10}H_8) - 12 \cdot 0$$

$$\Delta H_f^\circ(C_{10}H_8) = \underline{-313 \text{ kJ mol}^{-1}}$$

4. The following reaction is used to generate ammonia (NH_3 , M.M. $17.031 \text{ g mol}^{-1}$)



In performing the reaction, the following masses of reagents and products are reached when the total pressure is 210 atm.

Mass $\text{NH}_3 = 149 \text{ g}$, Mass $\text{N}_2 = 765 \text{ g}$, Mass $\text{H}_2 = 164 \text{ g}$

What is the partial pressure of NH_3 ?

Here we simply need to recognize that

$$\frac{P_i}{P_T} = \frac{n_i}{n_T} \quad @ \text{ constant } V, T.$$

So need # of moles.

$$n_{\text{NH}_3} = \frac{149}{17.03}$$

$$= 8.75 \text{ mol}$$

$$n_{\text{N}_2} = \frac{765}{28.014}$$

$$= 27.31 \text{ mol}$$

$$n_{\text{H}_2} = \frac{164}{2.016}$$

$$= 81.35$$

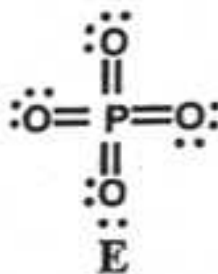
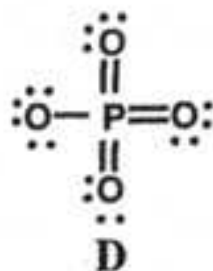
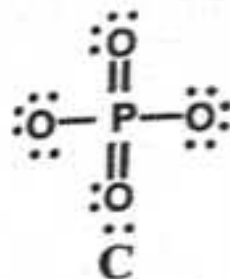
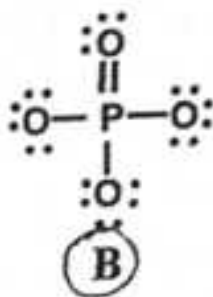
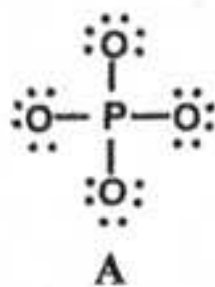
$$n_{\text{Total}} = 117.41$$

$$\therefore \frac{P_i}{P_T} = \frac{n_i}{n_T} \quad \text{becomes} \quad \frac{P_{\text{NH}_3}}{210} = \frac{8.75}{117.41}$$

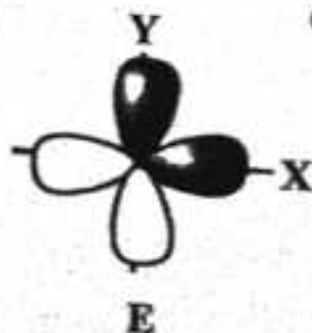
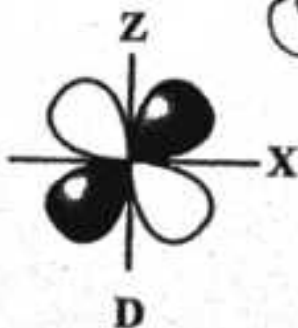
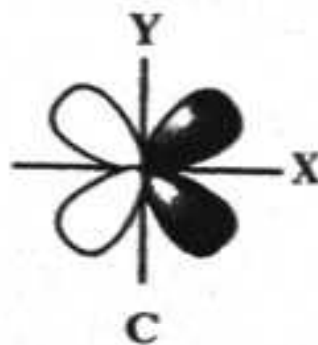
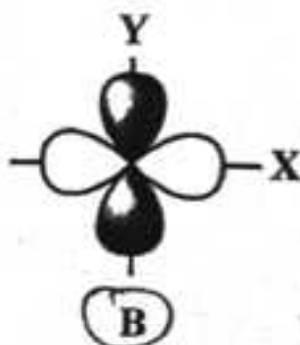
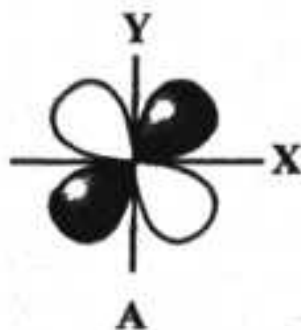
$$P_{\text{NH}_3} = \underline{\underline{15.6 \text{ atm}}}$$

{15} 5. For the following nine questions circle the correct answer. Questions i), iii) to v), viii) and ix) are worth 2 marks the others one mark.

i) Which of the following is the best Lewis structure for phosphate ion, PO_4^{3-} ?



ii) Which of the following represents the angular function of a $d_{x^2-y^2}$ atomic orbital?



Questions iii) and iv) pertain to the molecule sulfur tetrafluoride, SF_4 .

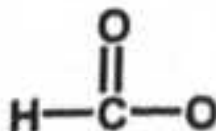
iii) The hybridization of the sulfur atom is

- a. sp^2
- b. sp^3
- c. sp^3d
- d. sp^3d^2
- e. sp^2d^2

iv) Given the electronegativities of S and F, respectively are 2.6 and 4.0, the charge on the sulfur atom as calculated by Allen's method is

- a. 0
- b. +6
- c. +1.40
- d. +0.52
- e. +0.85

v) In the valence bond interpretation of the electronic structure of the formate ion (HCOO^-) shown below, the π -system consists of



- a. 3 orbitals and 4 electrons
- b. 4 orbitals and 3 electrons
- c. 2 orbitals and 4 electrons
- d. 3 orbitals and 3 electrons
- e. 2 orbitals and 2 electrons

vi) When light is absorbed by an atom in the ground state the energy of the electromagnetic wave

- a) needs to exceed slightly the energy of the transition for a transition to take place.
- b) needs to be equal or smaller than the energy of the excited state in which the electron will be transfer.
- c) can have any values $h\nu$ as long as it is bigger than the largest allowed transition.
- d) Can only be equal to the difference in energy involved in the transition otherwise the electron remains in the ground state.
- e) the photon can have any value, it does not matter at all.

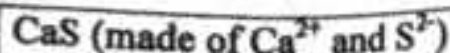
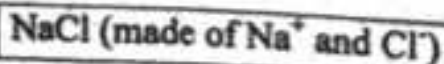
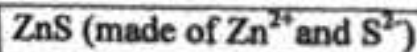
vii) Which of these statements are true about the Bohr Model (more than one answer maybe correct)

- a) It is first model to introduce quantization to explain the atomic spectra of hydrogen.
- b) In this model the energy is independent of n , it only depends on the mass of the electron.
- c) This model is valid only for the hydrogen atom, i.e., an atom with one electron and one proton.
- d) This model was used successfully to explain the effect of the magnetic field on gas phase atoms.
- e) In this model only classical physics is used to describe the motion of the electron.

viii) Which of the following substance has the highest polarizability? Circle your answer.



ix) Place these three ionic solids in increasing order of lattice energy



a) $\text{ZnS} = \text{CaS} < \text{NaCl}$

b) $\text{NaCl} < \text{ZnS} = \text{CaS}$

c) $\text{NaCl} < \text{CaS} < \text{ZnS}$

d) $\text{NaCl} < \text{ZnS} < \text{CaS}$

e) $\text{ZnS} = \text{NaCl} = \text{CaS}$

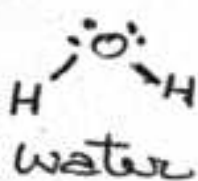
- [5] 6. a) The boiling points of anhydrous hydrogen halides are: HF, 19°C; HCl, -85°C; HBr, -67°C; HI, -34°C. Explain any trends in the data, as well as any deviations from that trend.

Boiling point increases with increasing mass of the compound.

Exception: HF has hydrogen bonding.

Magnitude of London forces is the most important factor. Dipole-dipole interactions are not that important here since e.g. H-Cl dipole moment is larger than H-Br but the latter boils at a lower T_b .

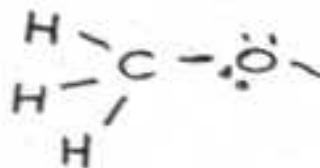
- b) Both water and methanol (H_3C-O-H) have anomalously high boiling points due to hydrogen bonding, but the boiling point of water is higher than that of methanol despite its lower molecular mass. Explain why? (Hint: it might be helpful to draw Lewis structures)



water

water can form 4 hydrogen bonds per water molecule

water molecule



methanol can form fewer H-H-bonds (2 lone pairs and one O-H bond)

(2 lone pairs and one O-H bond)

- [4] 7. Using the data provided and your knowledge of ionic solids order the following solids in increasing size of the holes created by the anions.

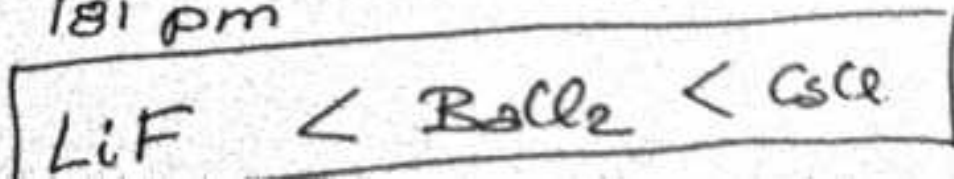
LiF (made of Li^+ and F^-)	CsCl (made of Cs^+ and Cl^-)	$BaCl_2$ (made of Ba^{2+} and Cl^-)
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Ion	Ionic radius (pm)
Ba^{2+}	135
Cl^-	181
Cs^+	167
F^-	133
Li^+	59

$$\frac{r_{Li^+}}{R_{F^-}} = \frac{59 \text{ pm}}{133 \text{ pm}} = 0.4436$$

$$\frac{r_{Cs^+}}{R_{Cl^-}} = \frac{167 \text{ pm}}{181 \text{ pm}} = 0.9227$$

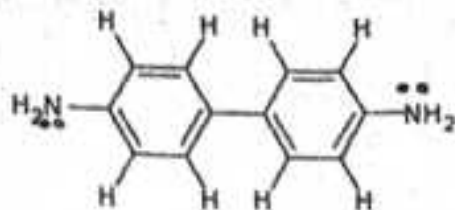
$$\frac{r_{Ba^{2+}}}{R_{Cl^-}} = \frac{135 \text{ pm}}{181 \text{ pm}} = 0.7459$$



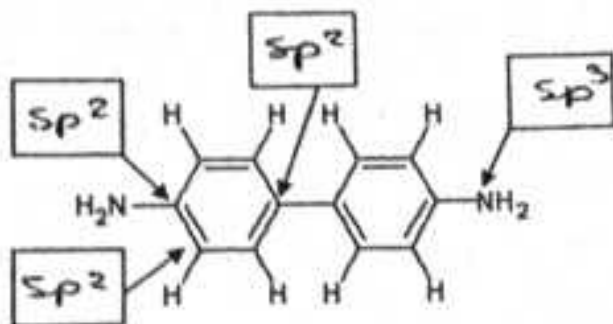
8. Use Lewis structures and VSEPR to complete the table below for the following molecules and ions. All lone pairs must be provided in the Lewis structures.

Molecules	Lewis Structure	Name the shape of the molecule
BrF ₃		T-Shape
SF ₄		see saw
XeF ₂		linear
PF ₆ ⁻		Octahedral

9. Until recently, benzidine (structure shown below) was used in forensic medicine to detect the presence of human blood; when mixed with human blood, benzidine turns a characteristic blue color. Because benzidine has recently been identified as a carcinogen, it has been replaced by other indicators. a) Complete the structure by drawing ALL lone pairs of electrons.



- b) Indicate in the appropriate boxes the hybrid orbitals used by the carbon and nitrogen atoms indicated by arrows.



- c) Indicate the bond angles for the bonds shown below.

- 1) H - N - H bond angle is 103 degrees.
- 2) N - C - C bond angle is 120 degrees.
- 3) H - C = C bond angle is 120 degrees.

- d) How many σ and π bonds are present in this molecule? Fill in the blanks.

There are 27 σ bonds and 6 π bonds.

- e) Is the molecule planar? YES or (NO) Explain your answer.

The geometry around N's is sp^3
and not rigid around C-C central bond.

10. An unknown liquid has a boiling point of 75.5°C at 0.910 atm and a boiling point of 37.3°C at 0.430 atm. Use the data in the table provided below to identify the liquid. Show ALL your work clearly on this page.

simple Clausius Clapeyron application

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_v}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \left(\frac{0.91}{0.43} \right) = -\frac{\Delta H_v}{8.314} \left(\frac{1}{348.95} - \frac{1}{330.35} \right)$$

$$\underline{\underline{\Delta H_v = +38.6 \text{ kJ mol}^{-1}}}$$

from below the compound is ethanol.

Melting and boiling points and enthalpies of fusion and vaporization for selected substances

Substance	Melting Point, °C	ΔH_{fus} , kJ/mol	Boiling Point, °C	ΔH_{vap} , kJ/mol
N ₂	-210.0	0.71	-195.8	5.6
HO	-114.2	2.00	-85.1	16.2
Br ₂	-7.2	10.6	58.9	30.0
CO ₂	-22.6	2.56	76.8	29.8
CH ₃ CH ₂ OH (ethanol)	-114.1	4.93	78.3	38.6
CH ₃ (CH ₂) ₄ CH ₃ (n-hexane)	-95.4	13.1	68.7	28.9
H ₂ O	0	6.01	100	40.7
Fe	97.8	1.6	883	97.4
Hg	396	33.4	1794	176.1

11. Complete the table below (a - f) and calculate the enthalpy of formation of CaO(s).

a) - Lattice Energy	$\text{Ca}^{2+}(\text{g}) + \text{O}^{2-}(\text{g}) \rightarrow \text{CaO}(\text{s})$	-3414 kJ/mol	①
Enthalpy of sublimation of Ca(s)	b) $\text{Ca}(\text{s}) \rightarrow \text{Ca}(\text{g})$	178 kJ/mol	②
Bond Energy of $\text{O}_2(\text{g})$	c) $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$	498 kJ/mol	③
First ionization energy of Ca(g)	$\text{Ca}(\text{g}) \rightarrow \text{Ca}^+(\text{g}) + e$	590 kJ/mol	④
Second ionization energy of Ca(g)	d) $\text{Ca}^+(\text{g}) \rightarrow \text{Ca}^{2+} + e$	1145 kJ/mol	⑤
Electron Affinity of O(g)	e) $\text{O}(\text{g}) + e \rightarrow \text{O}^-(\text{g})$	-141 kJ/mol	⑥
f) 2nd electron affinity of O	$\text{O}^-(\text{g}) + e \rightarrow \text{O}^{2-}(\text{g})$	744 kJ/mol	⑦
Enthalpy of formation of CaO(s)	$\text{Ca}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s})$	To be calculated	⑧

if we take ① + ② + $\frac{1}{2}$ ③ + ④ + ⑤ + ⑥ + ⑦ we get ⑧

$$\therefore \Delta H_f^\circ(\text{CaO}) = \underline{\underline{-649 \text{ kJ mol}^{-1}}}$$

- (10) 12. The density of an unknown metal is 12.3 g/cm^3 and its atomic radius is 0.134 nm . It has a face-centered cubic lattice. Find the atomic mass of this metal.

Face centred cubic

$$\# \text{ atoms per unit cell} = 4$$

$$\therefore \text{mass of unit cell} = \frac{4 \times AM}{6.023 \times 10^{23}} \text{ g.} \quad (AM \equiv \text{Atomic Mass})$$

$$\text{volume of unit cell} = l^3$$

$$\text{but } 4r = l\sqrt{2}$$

$l \equiv$ length of side of the cube

$r =$ radius of atom.

$$\therefore l = \frac{4r}{\sqrt{2}}$$

$$= \frac{4 \times 0.134 \times 10^{-7} \text{ cm}}{\sqrt{2}}$$

$$= 3.79 \times 10^{-8} \text{ cm.}$$

$$\therefore V = l^3 = 5.444 \times 10^{-23} \text{ cm}^3.$$

$$\therefore \text{density} = \frac{m}{V}$$

$$12.3 = \frac{4 \times AM}{6.023 \times 10^{23}} \div 5.444 \times 10^{-23}$$

$$\underline{\underline{AM = 100.8 \text{ g mol}^{-1}}}$$

THE END

F10 CHEM 1000 Reference Sheet

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$c = 2.9979 \times 10^8 \text{ m s}^{-1}$$

$$R_H = 2.179 \times 10^{-18} \text{ J}$$

$$a_0 = 53 \text{ pm}$$

$$R = 8.314472 \text{ JK}^{-1} \text{ mol}^{-1} = 0.0820574 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$k = 1.38066 \times 10^{-23} \text{ J K}^{-1}$$

$$1 \text{ standard atmosphere} = 1.013 \times 10^5 \text{ Pa} = 760 \text{ torr (mm Hg)}$$

$$1 \text{ mL} = 1 \text{ cm}^3$$

$$\text{Avogadro's number } N_A = 6.02214199 \times 10^{23} \text{ molecules mol}^{-1}$$

$$0^\circ\text{C} = 273.15 \text{ K}$$

$$\text{Specific heat of water} = 4.184 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$$

$$\text{Specific heat of ice} = 2.11 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$$

$$\text{Heat of vaporization of water} = 44.0 \text{ kJ mol}^{-1}$$

$$\text{Heat of fusion of water} = 6.01 \text{ kJ mol}^{-1}$$

$$u_m = \sqrt{\frac{2RT}{M}}; \quad u_{rms} = \sqrt{\frac{3RT}{M}}; \quad u_{av} = \sqrt{\frac{8RT}{\pi M}}$$

$$Z_w = \frac{1}{4} \frac{N}{V} u_{av}; \quad Z_A = \sqrt{2} \pi d^2 \frac{N}{V} u_{av}; \quad Z_{AA} = \frac{1}{2} Z_A \frac{N}{V}; \quad \lambda = \frac{u_{av}}{Z_A}$$

$$d = \frac{PM}{RT}; \quad Z = \frac{PV}{nRT}; \quad \left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

$$E = \frac{-Z^2 R_H}{n^2}; \quad r = \frac{n^2 a_0}{Z^2}$$

$$E = h\nu; \quad c = \nu\lambda$$

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right); \quad \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$q_A = G - N \cdot \sum_{B \neq A} \frac{EN_A}{EN_A + EN_B} N_{AB}$$

$$\Delta H = \Delta U + \Delta PV$$

TABLE 11.3 Some Average Bond Energies^a

Bond	Bond Energy, kJ/mol	Bond	Bond Energy, kJ/mol	Bond	Bond Energy, kJ/mol
H—H	436	C—C	347	N—N	163
H—C	414	C=C	611	N=N	418
H—N	389	C≡C	837	N≡N	946
H—O	464	C—N	305	N—O	222
H—S	368	C=N	615	N=O	590
H—F	565	C≡N	891	O—O	142
H—Cl	431	C—O	360	O=O	498
H—Br	364	C=O	736 ^b	F—F	159
H—I	297	C—Cl	339	Cl—Cl	243
				Br—Br	193
				I—I	151

^a Although all data are listed with about the same precision (three significant figures), some values are actually known more precisely. Specifically, the values for the diatomic molecules: H₂, HF, HCl, HBr, HI, N₂ (N≡N), O₂ (O=O), F₂, Cl₂, Br₂, and I₂ are actually bond-dissociation energies, rather than average bond energies.

^b The value for the C=O bonds in CO₂ is 799 kJ/mol.

Vapor Pressure of Water at Various Temperatures

T (°C)	P (mmHg)	T (°C)	P (mmHg)	T (°C)	P (mmHg)	T (°C)	P (mmHg)
13.0	11.23	19.0	16.48	25.0	23.76	31.0	33.70
14.0	11.99	20.0	17.54	26.0	25.21	32.0	35.66
15.0	12.76	21.0	18.65	27.0	26.74	33.0	37.73
16.0	13.63	22.0	19.83	28.0	28.36	34.0	39.90
17.0	14.53	23.0	21.07	29.0	30.04	35.0	42.18
18.0	15.48	24.0	22.38	30.0	31.82	36.0	44.56

WebElements: the periodic table on the world-wide web
<http://www.webelements.com/>

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1 H 1.00794	2 He 4.002602	3 Li 6.941	4 Be 9.012182	5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180	11 Na 22.989	12 Mg 24.305	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948	
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 52.004	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80	
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc 98	44 Ru 101.07	45 Rh 102.91	46 Pd 106.36	47 Ag 107.868	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.6	53 I 126.905	54 Xe 131.29	
55 Cs 132.905	56 Ba 137.327	57-70 Lanthanoids	71 Lu 174.967	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.222	78 Pt 195.084	79 Au 196.967	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po 209	85 At 210	86 Rn 222
87 Fr 223	88 Ra 226	89-102 Actinoids	103 Lr 260	104 Rf 261	105 Db 262	106 Sg 263	107 Bh 264	108 Hs 265	109 Mt 266	110 Ds 271	111 Uuu 272	112 Uub 277	114 Uuq 289					

atomic number
symbol
atomic weight (standard atomic weight)

71 La 138.905	72 Ce 140.12	73 Pr 140.908	74 Nd 144.24	75 Pm 145	76 Sm 150.36	77 Eu 151.964	78 Gd 157.25	79 Tb 158.925	80 Dy 162.50	81 Ho 164.930	82 Er 167.259	83 Tm 168.930	84 Yb 173.054	85 Lu 174.967
87 Ac 227	88 Th 232.038	89 Pa 231	90 U 238.029	91 Np 237	92 Pu 244	93 Am 243	94 Cm 247	95 Bk 247	96 Cf 251	97 Es 252	98 Fm 257	99 Md 288	100 No 289	

*lanthanoids
**actinoids

Symbols and names: The symbols and names of the elements are those recommended by the International Union of Pure and Applied Chemistry (IUPAC). Names here are in the proposed form for the most recently discovered elements 111-112 and 114 as those used by IUPAC's working group. Symbols in bold face are those of elements which are not yet named. Symbols in italics are those of elements which have not yet been discovered. Symbols in bold face are those of elements which are not yet named. Symbols in italics are those of elements which have not yet been discovered. Symbols in bold face are those of elements which are not yet named. Symbols in italics are those of elements which have not yet been discovered.