25

Hydrogen

Answers to worked examples

WE 25.1 Isotopic substitution (on p. 1164 in *Chemistry*³)

In the infrared spectrum of Ph_2PH, the P–H stretch is observed at 2300 cm⁻¹. At what wavenumber would you expect $\bar{n}(P\text{ - }D)$ to be observed in Ph_2PD?

Strategy

Use Equation 25.2 (p.1164) and the relationship between ν and $\bar{n}$ to predict $\bar{n}(P–D)$.

Solution
From Equation 25.2,

$$\frac{\bar{n}_D}{\bar{n}_H} = \left(\frac{1}{2}\right)^{\frac{1}{2}} = 0.707$$

Therefore $\bar{n}(P–D) = 0.707 \times 2300$ cm⁻¹
$$= 1630 \text{ cm}^{-1}$$

Answers to boxes

Box 25.1 The hydrogen economy (on p. 1141 in *Chemistry*³)

The enthalpy change of combustion for methane is –890 kJ mol⁻¹ at 298 K. Use this to calculate the energy density for methane and compare it to the value given for hydrogen.

Strategy

The energy density (as defined in Box 25.1, p.1141) is the energy released per unit mass of fuel. The value for H_2 (143 $kJ\ g^{-1}$) for the comparison is also given in Box 25.1. Therefore to answer this question you need to calculate the energy released per gram of methane.

Solution

$M_r(CH_4) = 12.011 + (4 \times 1.008) = 16.04$.

$$\text{Energy released on burning 1 g } CH_4 = \frac{890\ kJ\ mol^{-1}}{16.04\ g\ mol^{-1}}$$

$$= 55\ kJ\ g^{-1}$$

This is much lower than the value for hydrogen (143 $kJ\ g^{-1}$).

Box 25.3 Hydrogen storage (on p. 1147 in *Chemistry*[3])

The alloys Mg_2Ni, FeTi and $LaNi_5$ absorb hydrogen to form the metallic hydrides Mg_2NiH_4, $FeTiH_2$ and $LaNi_6H_6$, respectively. Work out the percentage of its own mass of hydrogen that each alloy absorbs. Do these compounds meet the US Department of Energy's target?

Strategy

For this comparison, the US Department of Energy's target is required. The value is given in Box 25.2 (p.1147) as 7.5%. For each compound, a calculation of the percentage mass of hydrogen by unit mass of compound is required for the comparison.

Solution

$M_r(Mg_2Ni) = 107.3$; $M_r(FeTi) = 103.7$; $M_r(LaNi_5) = 432.4$.

1 mol Mg_2Ni absorbs 4 hydrogen atoms, which corresponds to $\dfrac{(4 \times 1.008)\ g\ mol^{-1}}{107.3\ g\ mol^{-1}}$

$= 0.038$ (3.8% of its own mass).

1 mol FeTi absorbs 2 hydrogen atoms, which corresponds to $\dfrac{(2 \times 1.008)\ \text{g mol}^{-1}}{103.7\ \text{g mol}^{-1}} =$

0.020 (2.0% of its own mass).

1 mol LaNi$_5$ can absorb 6 hydrogen atoms, which corresponds to

$\dfrac{(6 \times 1.008)\ \text{g mol}^{-1}}{432.4\ \text{g mol}^{-1}} = 0.014$ (1.4% of its own mass).

None of these compounds meet the US Department of Energy's target.

Box 25.4 Hydrofluoric acid (on p. 1154 in *Chemistry*^{3})

Bearing in mind the reactivity of hydrofluoric acid, how would you expect it to be stored in the laboratory?

Strategy

The danger of HF is not in the strength of the acid but its extremely high reactivity. The reason HF is so reactive is that X–F bonds are very strong providing a large driving force for the reaction. Therefore, the only compounds that can resist the action of HF must be those which already have X–F bonds.

Solution

Hydrofluoric acid cannot be stored in glass bottles as the Si–O bonds in glass are unstable to the action of the acid and react to form Si–F bonds. Solutions are normally stored in containers made of PTFE (poly(tetrafluoroethene), marketed as Teflon).

Box 25.5 Hydrogen bonding and life (on p. 1158 in *Chemistry*^{3})

Why does cytosine form hydrogen bonds with guanine and not with adenine or thymine?

Strategy

In order for a hydrogen-bonded array to form, the sequence in the nucleotides have to match up so the hydrogen bond donors on one nucleotide can match up with the hydrogen bond acceptors on the other nucleotide. Compare the sequence in cytosine

with the other three nucleotides to investigate the match/mis-match between the proton acceptors and the protons.

Solution

Cytosine and guanine interact through three hydrogen bonds – they are complementary as cytosine has a hydrogen bond donor at a position that guanine has a hydrogen bond acceptor. Neither adenine nor thymine has the same arrangement of hydrogen bond donors and acceptors that would allow it to interact with cytosine.

Box 25.6 Burning ice (on p. 1161 in *Chemistry*³)

Methane hydrate has the approximate formula $CH_4 \cdot 6.2H_2O$. What volume of methane could be released from 1 tonne of methane hydrate at 298 K? (1 mol of gas has a volume of 24.5 dm³ at this temperature and 1 atm pressure.)

Strategy

In order to work out the volume of gas released, the number of moles of methane hydrate per tonne has to be calculated. The number of moles multiplied by the volume per mole will then give the total volume.

Solution

The relative atomic mass of methane hydrate is

$$M_r(CH_4 \cdot 6.2H_2O) = 16.04 + (6.2 \times 18.01)$$
$$= 127.70 \text{ g mol}^{-1}$$

Since 1 tonne = 1×10^6 g, so

$$\text{Amount of } CH_4 \cdot 6.2H_2O \text{ in 1 tonne} = \frac{1 \times 10^6 \text{ g}}{127.70 \text{ g mol}^{-1}} = 7831 \text{ mol}$$

Since 1 mol $CH_4 \cdot 6.2H_2O$ releases 1 mol CH_4, 1 tonne of $CH_4 \cdot 6.2H_2O$ releases 7831 mol CH_4.

At 298 K, 1 mol gas occupies 24. 5dm³

The volume of CH_4 = 24.5 dm³ mol⁻¹ × 7831 mol

$$= 192 \text{ dm}^3$$

Box 25.7 Tritium (on p. 1162 in *Chemistry*[3])

Formation of tritium in the atmosphere involves the nuclear reaction of ^{14}N with a neutron. Write the nuclear equation for this process and identify the other product.

Strategy

Use a nuclear equation to add the relative atomic mass and atomic numbers together of $^{14}_{7}$N with a neutron ($^{1}_{0}n$). Remove the nuclear formula of tritium ($^{3}_{1}$H) .

Calculate the remaining relative atomic mass and atomic numbers and use the Periodic Table on the inside front cover to find the element..

Solution

$$^{14}_{7}\text{N} + {}^{1}_{0}n \rightarrow ? + {}^{3}_{1}\text{H}$$
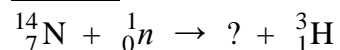
Relative atomic mass of the unknown element = (14+1) − 3 = 12.
Atomic number of the unknown element = (7+0) − 1 = 6

The other product has atomic mass of 12 and an atomic number of 6. From the Periodic Table this element must be carbon (^{12}C).

Answers to end of chapter questions

1. What volume of hydrogen gas (at 298 K and 1 atm) is required for the extraction of 1 kg of copper from a Cu^{2+} (aq) solution? (1 mol gas occupies 24.5 dm^3 at this temperature and pressure.)

Strategy

The extraction of the metal from the solution requires a redox reaction where the aqueous metal cation is reduced to the metal by the hydrogen gas. Therefore the first step is to write a balanced reaction for the formation of Cu(0) from Cu(II) using hydrogen. The next stage is to calculate the number of moles of copper in 1 kg of copper so the generated equation can be used to calculate the number of moles of

hydrogen required. Finally, the volume of hydrogen can be calculated by multiplying the number of moles by the volume occupied by one mole of gas.

Solution
In the reaction between Cu^{2+} (aq) and H_2

$$Cu^{2+} (aq) + H_2 (g) \rightarrow Cu (s) + 2 H^+ (aq)$$
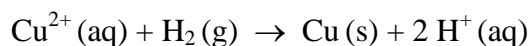
1 mol Cu is generated by 1 mol H_2.

1 kg (1000 g) of Cu, where $A_r(Cu) = 63.55$ g mol^{-1}, contains $\dfrac{1000 \text{ g}}{63.55 \text{ g mol}^{-1}} = 15.74$ mol

Therefore 15.74 mol H_2 are required to generate 1 kg Cu.

Since 1 mol of gas occupies 24.5 dm^3 at 298 K, the volume of H_2 required is
15.74 mol $\times$ 24.5 dm^3 mol^{-1} = 386 dm^3

2.   Using Table 25.1 (p.1145), which of the following metals would you expect to react with dilute acid to generate H_2: (a) Sn; (b) Ag; (c) Ba; (d) Ni; (e) Hg? Explain your answers.
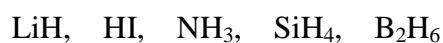
Strategy
The reference (0 V) for the standard reduction potentials given in Table 25.1 is the reduction of the H_3O^+ cation to water and hydrogen. If the metal ion has a negative reduction potential, the metal will be oxidised by the acid to give hydrogen and the metal ion in solution. If however, the potential is positive the metal ions will not be affected by the acid.

Solution
In Table 25.1, Sn, Ba and Ni all have negative standard electrode potentials, so would be expected to displace hydrogen from dilute acids. Ag and Hg have positive standard electrode potentials, so would not react.

3.   Assign oxidation states to the elements in the following hydride compounds

$$LiH, \quad HI, \quad NH_3, \quad SiH_4, \quad B_2H_6$$

Strategy

Compare the electronegativity of hydrogen to that of the other element. If hydrogen is the more electronegative element its oxidation state is –1, whereas if it is the more electropositive element its oxidation state is +1. Use this together with the number of hydrogen atoms to work out the oxidation state of the other element.

Solution

Hydrogen (χ^P 2.20) is more electronegative than lithium (χ^P 0.98). The oxidation state of hydrogen is –1, and the oxidation state of lithium is +1.

Hydrogen (χ^P 2.20) is less electronegative than iodine (χ^P 2.66). The oxidation state of hydrogen is +1, and the oxidation state of iodine is –1.

Hydrogen (χ^P 2.20) is less electronegative than nitrogen (χ^P 3.04). The oxidation state of hydrogen is +1, and since there are three hydrogen atoms to one nitrogen atom the oxidation state of nitrogen is –3.

Hydrogen (χ^P 2.20) is more electronegative than silicon (χ^P 1.90). The oxidation state of hydrogen is –1, and since there are four hydrogen atoms to one silicon atom the oxidation state of silicon is +4.

Hydrogen (χ^P 2.20) is more electronegative than boron (χ^P 2.04). The oxidation state of hydrogen is –1, and since there are three hydrogen atoms to one boron atom the oxidation state of boron is +3.

4.   Predict the products and write balanced equation for the following reactions:
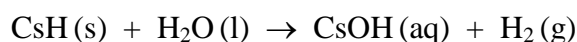(a) CsH + water
(b) B_2H_6 + pyridine
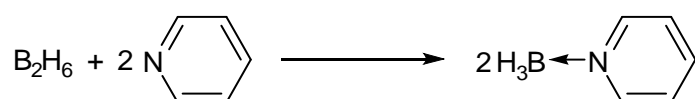(c) Si_2H_6 + oxygen
(d) N_2H_4 + HNO_3 (aq)

Strategy

Write balanced equations for the reactions, considering in each case the type of acid/base reaction occurring.

Solution

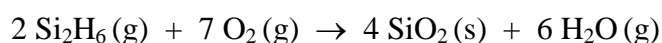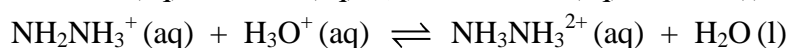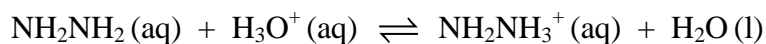(a)   CsH reacts with water to generate H_2 and an alkaline solution of CsOH

$$CsH\,(s)\; +\; H_2O\,(l)\;\rightarrow\; CsOH\,(aq)\; +\; H_2\,(g)$$

(b) B_2H_6 acts as a Lewis acid and pyridine acts as a Lewis base and they react to form an adduct:

(c) Si_2H_6 combusts in a similar manner to SiH_4 giving SiO_2 and H_2O:

$$2\,Si_2H_6\,(g)\; +\; 7\,O_2\,(g)\;\rightarrow\; 4\,SiO_2\,(s)\; +\; 6\,H_2O\,(g)$$

(d)   Hydrazine acts as a base and is protonated by the acid in two stages to give $NH_2NH_3^+$ (aq) and $NH_3NH_3^{2+}$ (aq). The nitrates are spectator ions.

$$NH_2NH_2\,(aq)\; +\; H_3O^+\,(aq)\;\rightleftharpoons\; NH_2NH_3^+\,(aq)\; +\; H_2O\,(l)$$
$$NH_2NH_3^+\,(aq)\; +\; H_3O^+\,(aq)\;\rightleftharpoons\; NH_3NH_3^{2+}\,(aq)\; +\; H_2O\,(l)$$

5. SF_6 is a stable compound. Suggest why the hydride analogue, SH_6, does not exist.

Strategy

Compounds are only stable if the energy released on forming the product compensates for the breaking of the bonds in the starting materials. If the starting materials are more stable than the products, the reaction would not occur. The alternative way to consider this problem is to determine the likely decomposition pathway.

Solution

SH_6 would decompose exothermically to give H_2S and H_2:

$$SH_6 \rightarrow H_2S + 2 H_2$$
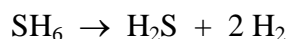
The reaction is highly exothermic due to the formation of strong H–H bonds.

6. Classify the following hydrides as ionic, covalent, or metallic: (a) BeH_2, (b) PH_3, (c) KH; (d) HCl; (e) $FeTiH_{1.8}$. For the covalent hydrides, state whether they exist as discrete molecules or are linked by bridging hydrogen atoms.

Strategy

Covalent bonding involves the sharing of electrons, if the orbitals of the constituent elements are too different in energy/electronegativity the bonding will be ionic in character as electron transfer will occur. Covalent hydrides that are electron deficient tend to form 3-centre 2-electron bonds, and as a consequence these compounds contain bridging hydrogen atoms.

Solution

(a) BeH_2 is a covalent hydride with a polymeric structure (it is electron deficient)

(b) PH_3 is a covalent hydride with a molecular structure (it is electron rich)

(c) KH is an ionic hydride.

(d) HCl is a covalent hydride with a molecular structure (it is electron precise)

(e) $FeTiH_{1.8}$ is a metallic hydride.

7. Suggest reasons why plumbane (PbH_4) is not well characterized.

Strategy

Consider the relative energies of the bonds that need to be broken and formed in forming plumbane from lead and hydrogen.

Solution

The enthalpy of formation of plumbane will be very endothermic, as the H–H bonds which need to be broken are strong but the Pb–H bonds that are formed are weak. This weakness is a consequence of the poor overlap between the hydrogen $1s$ orbital

and the large, diffuse lead orbitals. Furthermore, formation of tetravalent lead compounds is less favourable than for the other Group 14 elements since formation of two additional bonds does not outweigh the promotion energy cost of involving the *s* electrons in the bonding (the inert pair effect).

If plumbane could be made, decomposition into the elements would be highly favourable.

8. Calcium hydride is used at remote locations such as Antarctica as a source of hydrogen (see Section 25.2, p.1146). What mass of CaH_2 is required to fill a 500 dm^3 weather balloon at -50 °C and an atmospheric pressure of 95500 Pa?

Strategy

Use the ideal gas equation (Equation 8.5, Section 8.1, p. 349) to calculate the number of moles of hydrogen required to fill the balloon at this temperature and pressure. Use the balanced equation for the reaction between calcium hydride and water to work out how many moles of calcium hydride are required to generate this amount of hydrogen, and finally use the relative formula mass of CaH_2 to determine what mass this corresponds to.

Solution
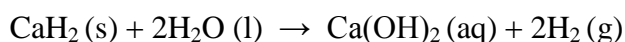
The ideal gas equation (Equation 8.5) is

$$pV = nRT$$

$p = 95500$ Pa $(J\ m^{-3})$, $V = 0.5\ m^3$, $R = 8.314\ J\ K^{-1}\ mol^{-1}$, $T = 223$ K

Rearranging gives

$$n = \frac{pV}{RT}$$

$$n = \frac{95500\ J\ m^{-3}\ \acute{}\ 0.5\ m^3}{8.314\ J\ K^{-1}\ mol^{-1}\ \acute{}\ 223\ K}$$

$$= 25.8\ mol$$

The balanced equation for the reaction is

$$CaH_2\ (s) + 2H_2O\ (l)\ \rightarrow\ Ca(OH)_2\ (aq) + 2H_2\ (g)$$

so 1 mole CaH_2 generates 2 moles H_2.

This means that the mass CaH_2 required is equal to $\dfrac{25.8\ mol}{2} = 12.9\ mol$

The relative formula mass of CaH_2 is $40.078 + (2 \times 1.008) = 42.09\ g\ mol^{-1}$

So the mass CaH_2 required is equal to

$$m = 12.9 \text{ mol} \times 42.09 \text{ g mol}^{-1}$$
$$= 543 \text{ g}$$

9.   Use the following bond dissociation enthalpy data to calculate the enthalpy change of formation for HF (g).

D(H–H) = +436 kJ mol^{-1}

D(F–F) = +159 kJ mol^{-1}
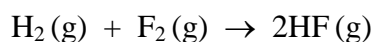
D(H–F) = +570 kJ mol^{-1}

<u>Strategy</u>

Write an equation for the formation of HF from hydrogen and fluorine gas. Construct a thermochemical cycle based on these data to calculate $\Delta_f H^{\ominus}$(HF).

<u>Solution</u>

For the reaction

$$H_2 \text{ (g)} + F_2 \text{ (g)} \rightarrow 2HF \text{ (g)}$$

$2\Delta_f H^{\ominus}$(HF) = D(H–H) + D(F–F) − $2D$(H–F)

          = (+436 kJ mol^{-1}) + (+159 kJ mol^{-1}) − (2 × +570) kJ mol^{-1}

          = −545 kJ mol^{-1}

So $\Delta_f H^{\ominus}$(HF) = (−545 kJ mol^{-1} / 2) = −273 kJ mol^{-1}

10.   Explain the trend in hydrogen bond strengths:

(a)   F–H···F in HF_2^- 220 kJ mol^{-1}

(b)   O–H···O in H_2O 22 kJ mol^{-1}

(c)   S–H···S in H_2S 7 kJ mol^{-1}

<u>Strategy</u>

Consider how the hydrogen bonding strength is affected by the electronegativity and charge of the acceptor.

Solution

D–H⋯A hydrogen bond strengths increase with the increasing electronegativity of D and A. Anionic acceptors such as F^- form stronger hydrogen bonds than neutral acceptors such as H_2O, and the F–H⋯F interaction in HF_2^- can be described as a covalent 3-centre 4-electron interaction with the hydrogen atom located halfway between the fluorine atoms. The hydrogen bond in water is a more common type of hydrogen bond, and the lack of charge on D and A ensures it is weaker, with the hydrogen atom closer to one of the oxygen atoms. S is much less electronegative than O and hence forms much weaker hydrogen bonds.

11. Account for the following observations.
(a) The boiling point of ammonia is higher than that of phosphine.
(b) The melting point of hydrogen selenide is higher than that for hydrogen sulfide.
(c) Water is denser than ice, whereas liquid methane is less dense than solid methane.

Strategy

Consider the intermolecular interactions present in each of the pairs of molecules.

Solution

(a) Ammonia (NH_3) contains strong hydrogen bonds that must be broken to convert ammonia into the gas phase. The boiling point is higher than might be expected because of this, and higher than that of phosphine, which does not contain significant hydrogen bonds.

(b) Neither hydrogen selenide (H_2Se) nor hydrogen sulfide (H_2S) contain strong hydrogen bonds, so in this case the melting point is determined by London dispersion interactions. This means the melting point increases with increasing relative molecular mass.

(c) Normally for a material, the solid is denser than the liquid, and this is true for methane. Water is unusual in that the liquid is denser than the solid. This is because ice has a very open hydrogen bonding structure that partially collapses on converting the solid to the liquid.

12. In the infrared spectrum of hydrogen iodide, $\bar{n}$(HI) absorption is observed at 2310 cm^{-1}. Predict the value of $\bar{n}$(DI) in the deuterated analogue.

Strategy

Use Equation 25.2 and the corresponding $\bar{n}$(HI) to calculate the absorption for DI.

Solution

Using Equation 25.2

$$\frac{\bar{n}_D}{\bar{n}_H} \approx \left(\frac{1}{2}\right)^{1/2} = 0.707$$

$$\bar{n}(DI) \approx 0.707 \times \bar{n}(HI) = 0.707 \times 2310 \text{ cm}^{-1} = 1630 \text{ cm}^{-1}$$

13. In the IR spectrum of HCl, $\bar{n}$(HCl) is observed at 2990 cm^{-1}. Predict a value for $\bar{n}$ (TCl) in the tritiated analogue.

Strategy

Using the same approach as developed for comparing $\bar{n}$(HX) and $\bar{n}$(DX) (p.1163)

$$\frac{\bar{n}_T}{\bar{n}_H} = \left(\frac{m_H}{m_T}\right)^{\frac{1}{2}}$$

Since $\left(\dfrac{m_H}{m_T}\right)^{\frac{1}{2}} \approx \left(\dfrac{1}{3}\right)^{\frac{1}{2}}$

$$\bar{n}_T = \left(\frac{1}{3}\right)^{\frac{1}{2}} \times \bar{n}_H$$

Solution

$$\bar{n}_T = \left(\frac{1}{3}\right)^{\frac{1}{2}} \times 2990 \text{ cm}^{-1}$$

$$= 1730 \text{ cm}^{-1}$$

14. The energy density of hydrogen is 143 $kJ\ g^{-1}$.

    (a) How much energy is released on combustion of 1 m^3 hydrogen at 298 K and 1 atm?

    (b) Given that the alloy Mg_2Ni reversibly absorbs hydrogen to form Mg_2NiH_4, what mass of Mg_2Ni would be required to absorb 1 m^3 hydrogen at 298 K and 1 atm?

    (1 mol gas occupies 24.5 dm^3 at 298 K and 1 atm).

Strategy

(a) Use the volume occupied by a mole of gas to work out how many moles of hydrogen are present in 1 m^3 of the gas. Then use the relative molecular mass of hydrogen to work out the mass this corresponds to. Finally use the energy density of hydrogen to work out the energy released on combustion of this mass of hydrogen.

(b) 1 mol Mg_2Ni absorbs 2 mol H_2 to form Mg_2NiH_4. From part (a) you know that 1 m^3 H_2 at 298 K and 1 atm is 40.8 mol, so you can use the stoichiometry of the reaction to work out how many moles of Mg_2Ni are required. Finally, use the relative formula mass of Mg_2Ni to work out what mass this corresponds to.

Solution

(a) First convert the molar gas volume into m^3: 1 dm^3 = 1 × 10^{-3} m^3.

Since 1 mol gas occupies 24.5 × 10^{-3} m^3 at 298 K and 1 atm, the number of moles in 1 m^3 is given by:

$$n = \frac{1\ m^3}{24.5\ \acute{}\ 10^{-3}\ m^3\ mol^{-1}}$$

$$= 40.8\ mol.$$

The relative molecular mass of H_2 is 2 × 1.008 = 2.016 $g\ mol^{-1}$

Therefore, mass of hydrogen = 40.8 mol × 2.016 $g\ mol^{-1}$

$$= 82.3\ g$$

Since the energy density is 143 $kJ\ g^{-1}$, the energy given off by burning 82.3 g is equal to

$$E = 143\ kJ\ g^{-1} × 82.3\ g$$

$$= 11\ 800\ kJ\ (= 11.8\ MJ)$$

(b) Since 1 mol Mg_2Ni absorbs 2 mol H_2, and 1 m^3 contains 40.8 mol H_2, the amount of Mg_2Ni required is

$$n = \left(\frac{40.8 \text{ mol}}{2} \right)$$

$$= 20.4 \text{ mol}$$

The relative formula mass of $Mg_2Ni = (24.305 \times 2) + 58.693 = 107.3 \text{ g mol}^{-1}$

The mass required is therefore equal to

$$m = 20.4 \text{ mol} \times 107.3 \text{ g mol}^{-1}$$

$$= 2190 \text{ g} = (2.19 \text{ kg})$$