25
Hydrogen

Answers to worked examples

WE 25.1 Isotopic substitution

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

Strategy

Use Equation 25.2 (p.1155) and the relationship between ν and $\bar{\nu}$ to predict $\bar{\nu}(P-D)$.

Solution

From Equation 25.2,

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

Therefore $\bar{\nu}(P-D) = 0.707 \times 2300\ cm^{-1}$

$= 1630\ cm^{-1}$

Answers to boxes

Box 25.1 The hydrogen economy

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.1133) is the energy released per unit mass of fuel. The data for H_2 (143 kJ kg^{-1}) for the comparison are given in the same paragraph. Therefore all that is required is answer this question is to calculate the energy released per gram of methane.

Solution

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

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

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

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

Box 25.3 Hydrofluoric acid

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 M–F 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 M–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 Burning ice

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 dm^3 at this temperature and 1 atm pressure.)

<u>Strategy</u>

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.

<u>Solution</u>

The RAM 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

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

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. 5dm^3

$$\text{The volume of } CH_4 = 24.5 \text{ dm}^3 \text{ mol}^{-1} \times 7831 \text{ mol}$$
$$= 192 \text{ dm}^3$$

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 × 24.5 dm^3 mol^{-1} = 386 dm^3

3. 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

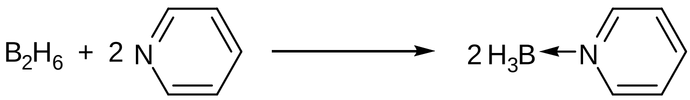
Write balanced equations for the reactions, considering in each case the type of acid/base reaction occurring.

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.

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

5. 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 as polymers.

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. Elements lying towards the top of the groups tend to show covalency in their bonding.

Solution

(a) BeH_2 is a covalent hydride with a polymeric structure (beryllium is at the top of Group 2).

(b) PH_3 is a covalent hydride with a molecular structure.

(c) KH is an ionic hydride.

(d) HCl is a covalent hydride with a molecular structure.

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

7. In the infrared spectrum of hydrogen iodide, the HI absorption is observed at 2310 cm^{-1}. Predict the value for the deuterated molecule.

Strategy

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

Solution

Using Equation 25.2

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

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