

Exercise 1.10. Absorption of competitive species: SO₂ vs. CO₂

A flue gas contains 44,000 ppm of CO₂ and 300 ppm of SO₂; the scrubbing liquor pH is 7. Flue gas stream: 42,500 m³/h (= 11.8 m³/s), at 66 °C. Blow-down: 1.0 m³/h (liquor discharged).

At pH 7: $K_{H(\text{CO}_2)} = 0.2 \text{ M/atm}$; $K_{H(\text{SO}_2)} = 3 \times 10^5 \text{ M/atm}$. (Both: H_{eff} !)

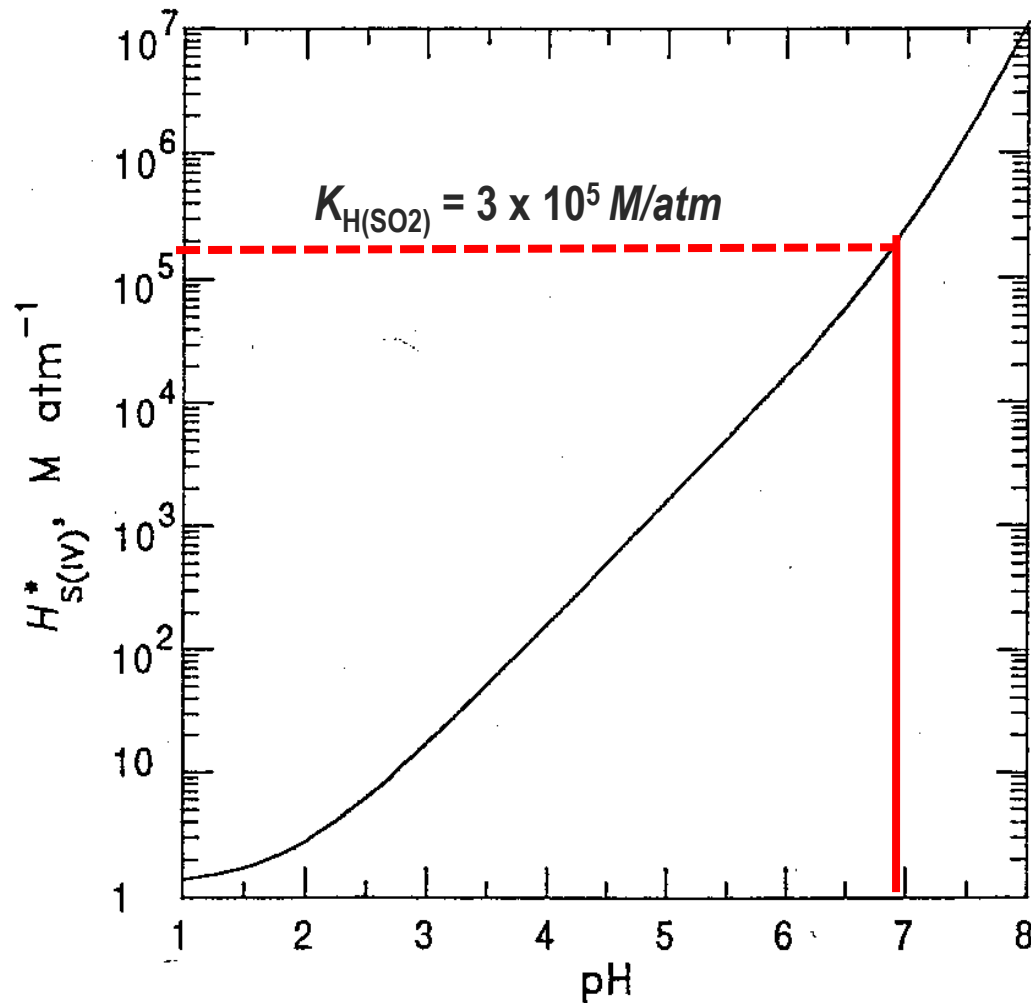
A) Calculate [CO₂]aq.;

B) To keep (SO₂)_g < 5 ppm in the cleaned gas, what can be the max SO₂ concentration in the scrubbing liquor?

C) the amount of SO₂ to be removed in mol/h, and kg/h;

D) [SO₂]aq in the scrubbing liquor (= blow-down conc.!).

Effective Henry's Law Constant of SO₂ as a Function of pH



H_{eff} increases with pH

FIGURE 6.6 Effective Henry's law constant for SO₂ as a function of solution pH at 298 K.

Effective Henry's Law Constant of CO₂ as a Function of pH

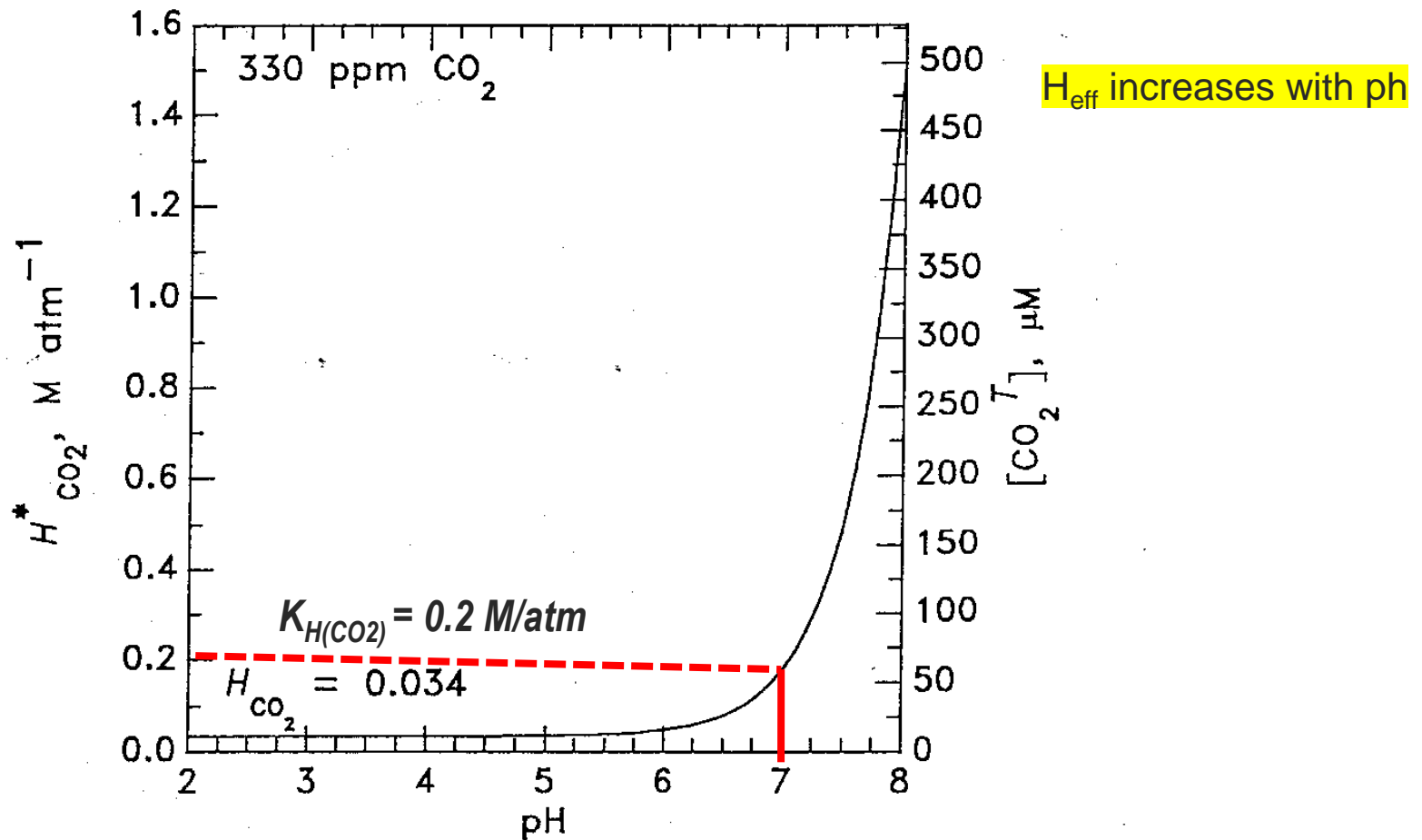
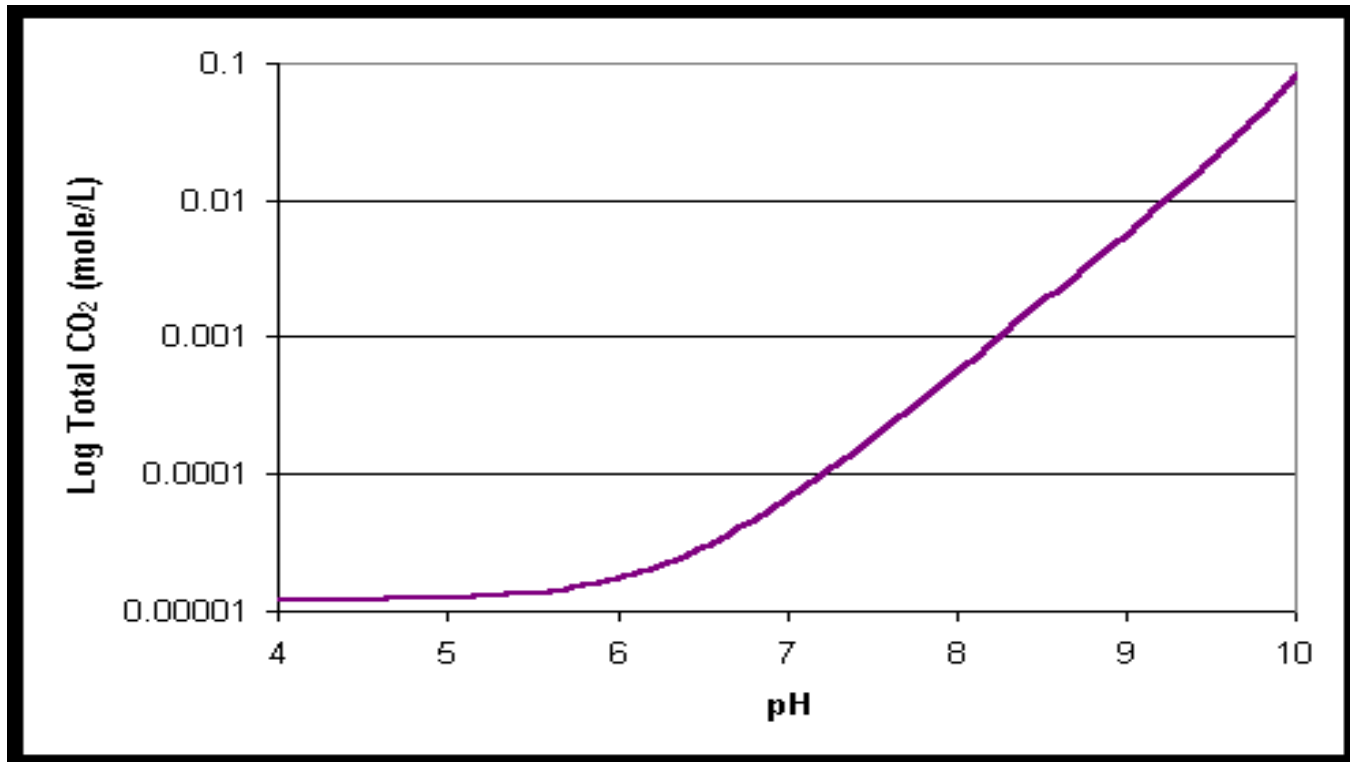


FIGURE 6.4 Effective Henry's law constant for CO₂ as a function of the solution pH. Also shown is the corresponding equilibrium total dissolved CO₂ concentration $[CO_2^T]$ for a CO₂ mixing ratio of 330 ppm.

Effective Henry's Law Constant of CO₂ as a Function of pH



Exercise 1.10. Absorption of competitive species: SO₂ vs. CO₂ - solution

A) $CO_{2(g)} = 44,000 \text{ ppm} = 4.4\% \text{ v/v}; P_{CO_2} = x_{CO_2} P = 0.044 \times 1 = 0.044 \text{ atm}$

$$[CO_2]_{aq} = K_H P_{CO_2}$$

$$[CO_2]_{aq} = 0.2 \times p_{CO_2} = 0.2 \times 0,044 = \mathbf{8.8 \text{ mM}} (=0.4 \text{ g/L; } CO_2 \text{ absorbed } \approx 1\%)$$

B) $SO_{2(g)} = 5 \text{ ppm}; P_{SO_2} = x_{SO_2} \cdot P = 5 \cdot 10^{-6} \cdot 1 = \mathbf{5.0 \cdot 10^{-6} \text{ atm}}$

$$[SO_2]_{aq} \text{ in eq. with } SO_2 \text{ gas } 5 \text{ ppm} = K_H P_{SO_2}$$

$$[SO_2]_{aq} = 3 \cdot 10^5 \text{ M/atm} \times 5 \cdot 10^{-6} \text{ atm} = \mathbf{1.5 \text{ M}} \text{ (max. conc. in solution in eq. with 5 ppm } SO_2 \text{ in the gas phase)}$$

C) $SO_{2(g)} \text{ to be removed: } (300-5) \text{ ppm} \times 42,500 \text{ m}^3/\text{h} = 12.5 \text{ m}^3/\text{h}$

The flue gas is at 66°C and 1 atm (actual condition). In order to convert to reference conditions ($t=0^\circ\text{C}$; $p=1 \text{ atm}$) you can apply the following expression previously introduced:

$$Q_a = Q_n \frac{P_n \cdot T_a}{P_a \cdot T_n}$$

Therefore,

$$SO_{2(g)} \text{ to be removed: } = 12.5 \text{ m}^3/\text{h} = 10.1 \text{ Nm}^3/\text{h}$$

According to Avogadro's rule at $T=0^\circ\text{C}$ (273 K) and $P=1 \text{ atm}$, 1 mole of any ideal gas has a volume of 22,4 l.

$$SO_{2(g)} \text{ to be removed: } = 10.1 / 22.4 = 0.45 \text{ kmol/h}$$

The MW of SO₂ is 64, then:

$$SO_{2(g)} \text{ to be removed: } = 0.45 \cdot 64 = 28.8 \text{ kg } SO_2/\text{h}$$

Exercise 1.10. Absorption of competitive species: SO₂ vs. CO₂ - solution

D) Concentration of “SO₂” in the liquor:

$$[SO_2]_{aq} \text{ blowdown} = Nr \text{ moles} / \text{Volume} = 0.45 \text{ kmol/h} / 1.0 \text{ m}^3/\text{h} = 0.45 \text{ mol/L} = \mathbf{0.45 \text{ M}}$$

Note 1. **The system can really work!** In fact, the concentration of SO₂ in the blow-down liquor is < than the maximum conc. permitted by Henry law, that is 1.5 M. **If SO₂ conc. in the blow-down is > than 1.5 M, you cannot reduce the SO₂ conc. down to 5 ppm in the cleaned gas ! The higher the blow-down, the lower the pollutants concentrations in the cleaned gas!**

Note 2. At pH 7 there is no SO₂ in the aq. phase, but only HSO₃⁻ (≈70%) and SO₃²⁻ (≈30%) (see Figure in the next slides)

Conclusion: At pH = 7, flue gases can be efficiently desulfurated ,whilst keeping CO₂ absorption at low levels! *What about pH 8? What about pH 6?*