SULPHURIC ACID DEW POINT

1. Introduction

Calculating the Acid Dew Point (ADP) is essential in industries where acid components are present in the fuel. The acid dew point is the temperature at which acidic components in a gas mixture begin to condense into liquid form. This process can lead to corrosion of equipment and significant loss of efficiency in industrial processes.

To calculate the acid dew point, several correlations have been proposed. The key components include the composition of the gas mixture, the total pressure, and the partial pressures of individual acidic gases. Typically, sulfuric acid (H_2SO_4) is a major concern in industries dealing with flue gases from combustion processes.

In summary, calculating the acid dew point is a critical aspect of industrial safety and equipment maintenance. Understanding the composition of gas mixtures and employing appropriate methods to determine the acid dew point helps industries prevent corrosion and ensure the efficient and safe operation of their processes.

2. Sulphuric Acid Dew Point

The acid dew point is the stage at which gaseous sulfuric acid undergoes condensation, transitioning into a liquid state. This phenomenon can be expressed through the following formula:

$$SO_2(g) + \frac{1}{2}O_2(g) \leftrightarrow SO_3(g) \rightarrow H_2O\,(g) + SO_3(g) \rightarrow H_2SO_4(g) \rightarrow H_2SO_4(g) \xrightarrow{ADP} H_2SO_4(l)$$

Due to its high hygroscopic nature, sulfuric acid has a propensity to attract additional water, forming an aqueous solution:

$$H_2SO_4(l) + H_2O\,(g) \rightarrow H_2SO_4(aq)$$

3. Conversion of SO_2 to SO_3

The equilibrium curve for the reaction between sulphur dioxide (SO_2) and sulphur trioxide (SO_3) is typically represented graphically in the context of chemical thermodynamics. The reaction is as follows:

$$2SO_2(g) \leftrightarrow 2SO_3(g)$$

This reaction is an example of a reversible reaction, meaning it can proceed in both the forward and reverse directions. The equilibrium constant (K_{eq}) for this reaction is expressed as:

$$K_{eq} = \frac{[SO_3]^2}{[SO_2]^2}$$

The equilibrium curve shows how the concentrations of SO_2 and SO_3 at equilibrium change with temperature and pressure.

The equilibrium curve for the SO_2-SO_3 reaction is influenced by Le Chatelier's principle, which states that if a system at equilibrium is subjected to a change in temperature, pressure, or concentration of reactants/products, the system will adjust to counteract that change and restore a new equilibrium.

For the SO_2-SO_3 system:

Effect of Temperature:
The reaction is exothermic (releases heat). According to Le Chatelier's principle, an increase in temperature will shift the equilibrium position to the left, favouring the reverse reaction (SO_3 to SO_2).

Effect of Pressure:
Since the number of moles of gas does not change in the balanced equation, changes in pressure do not have a significant effect on the position of the equilibrium.

In summary, the equilibrium curve for the SO_2-SO_3 reaction would show how the concentrations of SO_2 and SO_3 at equilibrium change with temperature, and it would be influenced by the principles of chemical equilibrium. Graphically, you would observe shifts in the equilibrium position based on changes in temperature and pressure.

4. Conversion of SO_3 to H_2SO_4

The reaction between sulphur trioxide (SO_3) and water (H_2O) to form sulfuric acid (H_2SO_4) is an example of an acid-catalysed reaction. The balanced chemical equation for this reaction is:

$$SO_3(g) + H_2O\ (g) \leftrightarrow H_2SO_4(g)$$

This reaction is also reversible, and the equilibrium constant (K_{eq}) can be expressed as:

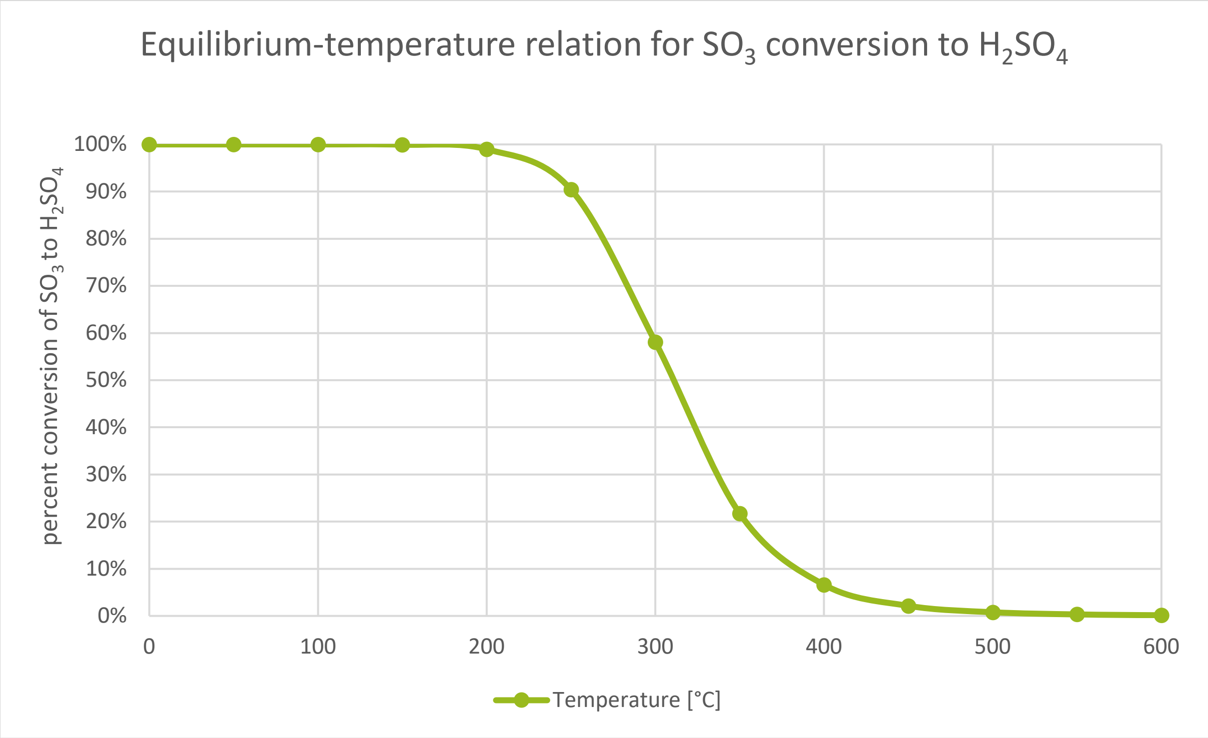
$$K_{eq} = \frac{[H_2SO_4]}{[SO_3][H_2O]}$$

Now, let's discuss the equilibrium conditions and the factors that affect the equilibrium position:

Effect of Temperature:
This reaction is exothermic. According to Le Chatelier's principle, an increase in temperature will shift the equilibrium position to the left, favouring the reverse reaction (breakdown of H_2SO_4 into SO_3 and H_2O). On the other hand, a decrease in temperature will favour the forward reaction, leading to the formation of more H_2SO_4.

Effect of Pressure:
The reaction involves gases (SO_3) and a liquid (H_2O). Changes in pressure may not have a significant impact on the position of the equilibrium, especially if the reaction involves a liquid or a solid. However, high pressures may influence the solubility of gases in the liquid phase.

The equilibrium curve for the SO_3 to H_2SO_4 reaction would illustrate how the concentrations of SO_3, H_2O, and H_2SO_4 at equilibrium change with temperature. It would show how changes in temperature affect the equilibrium position, with higher temperatures favouring the reverse reaction and lower temperatures favouring the forward reaction. Graphically, the equilibrium curve might depict these shifts in equilibrium concentrations based on changes in temperature, as follows:

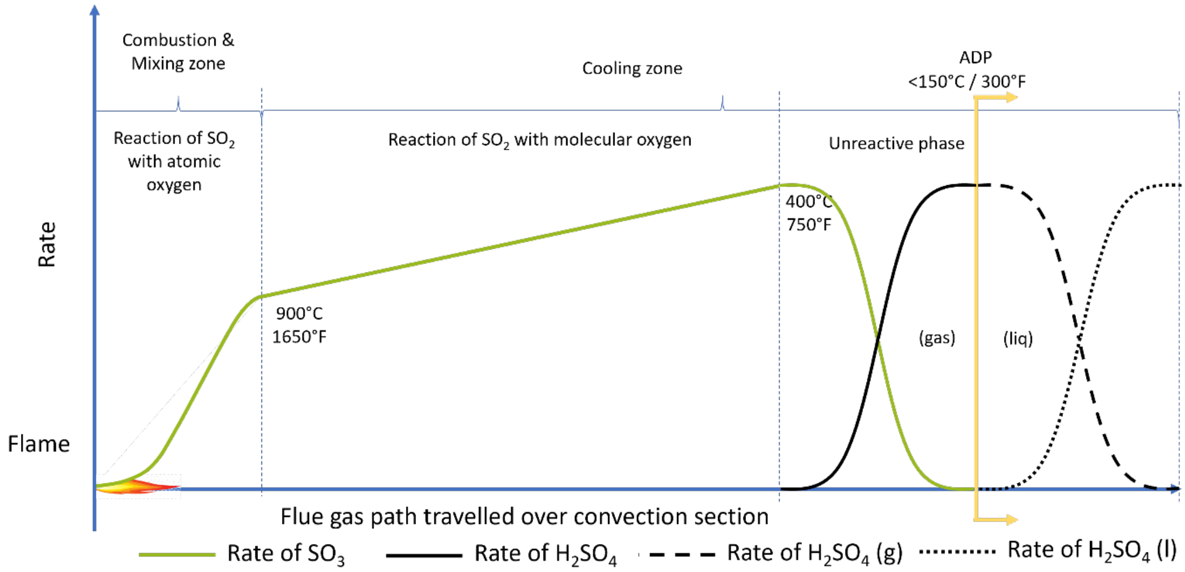


Knowing that the above favours H_2SO_4 at the lower temperatures and that more or less all SO_3 has been converted to H_2SO_4 below 200°C (400°F), technically the Acid Dew Point should be calculated using the amount of H_2SO_4, but as the conversion is 1mol to 1 mol, practically the amount of SO_3 can be used.

5. Formation of SO_2 to Condensation of H_2SO_4

Important is to understand where and how the SO_2, SO_3 and H_2SO_4 is formed and how the Acid Dew Point is influenced over the complete temperature range from fire box to stack.

This can be expressed in the following graph:



As the ADP is the temperature where the sulphuric acid starts condensing, it can be concluded from the above graph that when an heat exchanger condenses acid, the ADP at the outlet of the exchanger is lower than at the inlet. It is therefore beneficial to condense as much as possible when designing a condensing heat exchanger, because the flue gas leaving the exchanger will be less corrosive, which is beneficial for all downstream equipment.

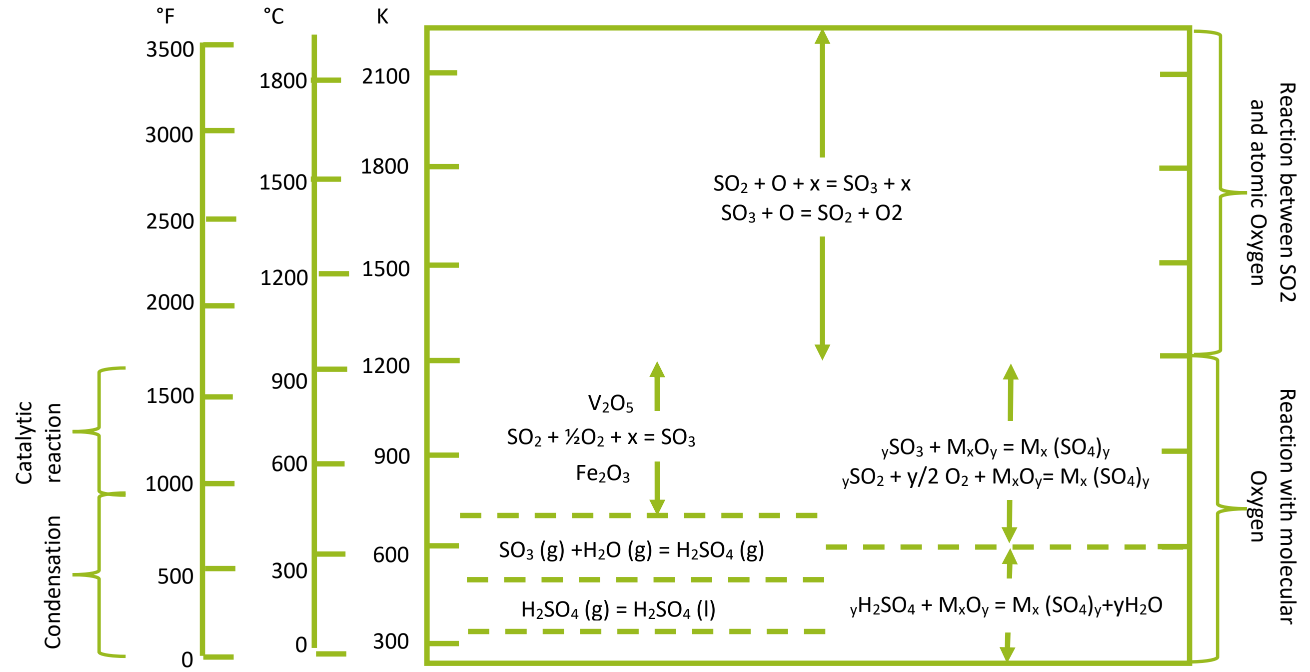
6. Correlations to Calculate the Conversion of SO_2 to SO_3

Conversion of SO_2 to SO_3 can occur due to the following reactions:

- Chemical reactions in fuel beds or coal firing
- Reaction in the combustion chamber between SO_2 and atomic oxygen
- Catalytic oxidation of SO_2 by materials on the convection section surfaces (molecular oxygen)

The reaction in the combustion chamber is normally referred to as the first conversion. Where the reaction due to catalytic oxidation is referred to as the second conversion.

The whole process is shown in the following diagram on the next page.



To determine the amount of SO_3 after the first conversion the equilibrium constant can be defined as follows:

$$K_p = \frac{pSO_3}{pSO_2 \times \sqrt{pO_2}}$$

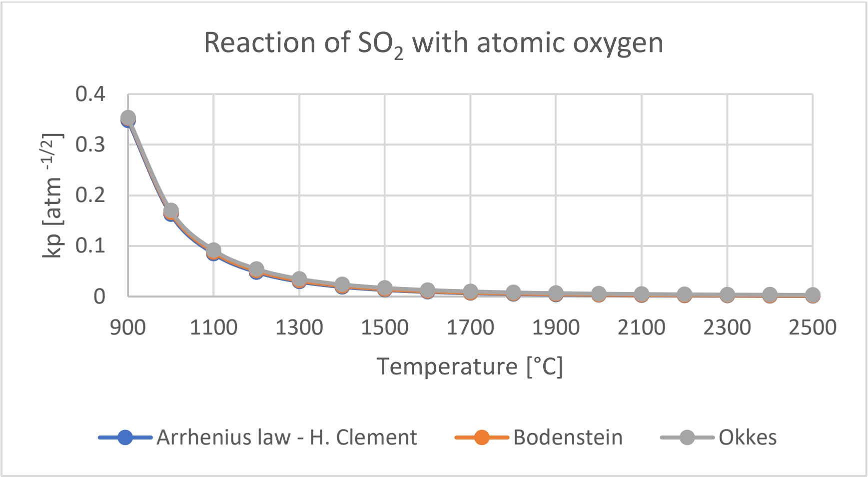
The Kp constant can be obtained by the following equations:

$$K_p = e^{\frac{11373}{T} - 10.75} \qquad T(K)\ acc.\ Arrhenius\ law\ - H.\ Clement\ (1992)$$

$$K_p = 10^{\left(\frac{5186.5}{T} + 0.611 \times log_{10} T - 6.75\right)} \qquad T(K)\ acc.\ Bodenstein$$

$$K_p = e^{\left(\frac{12.12}{T}\right)\left(1 - 0.942 \times T + 0.0702 \times T^2 - 0.0108 \times T \times \ln(1000 \times T) - \frac{0.0031}{T}\right)} \qquad T(K/1000)\ acc.\ Okkes$$

Where T is the temperature of the gas in the firebox, where for fired heaters the temperature is lower compared to steam methane reformers. For Okkes the temperature is set to 1000°C / 1273.15K



7. Correlations to Calculate the Acid Dew Point

Many correlations have been proposed over the years to calculate the sulphuric acid dew point. The following correlations are well known in the industry:

a. Ecoonex BV.

$$ADP = 69.5 + 18.7 \times \log_{10}\left(P_{gas} \times ySO_3\right) + 17.2 \times \log_{10}\left(P_{gas} \times yH_2O\right)$$

Where:
ADP = Acid Dew Point [°C]
ySO_3 = sulphur trioxide, volume fraction
yH_2O = water vapour, volume fraction
P_{gas} = total pressure of the flue gas, pascal abs

b. A.G. Okkes / Mobil Oil Company

$$ADP = 203.25 + 27.6 \times \log_{10}(pH_2O) + 10.83 \times log_{10}(pSO_3) + 1.06 \times [log_{10}(pSO_3) + 8]^{2.19}$$

Where:
ADP = Acid Dew Point [°C]
pSO_3 = Partial pressure of sulphur trioxide , atm
pH_2O = Partial pressure of water vapour, atm

c. R. Pierce

$$\frac{1000}{ADP} = 1.7842 + 0.0269 \times \log_{10}(pH_2O) + 0.1029 \times log_{10}(pSO_3) + 0.0329 \times log_{10}(pH_2O) \times log_{10}(pSO_3)$$

Where:
ADP = Acid Dew Point [K]
pSO_3 = Partial pressure of sulphur trioxide , atm
pH_2O = Partial pressure of water vapour, atm

d. Verhoff F.H. and Banchero J.T. method

$$\frac{1}{ADP} = 0.002276 - 0.00002943\, ln(pH_2O) - 0.0000858 \times \ln(pSO_3) + 0.00000626 \times \ln(pSO_3) \times ln(pH_2O)$$

Where:
ADP = Acid Dew Point [K]
pSO_3 = Partial pressure of sulphur trioxide , mmHg
pH_2O = Partial pressure of water vapour, mmHg

8. Example Calculation

O2 = 1.7 Vol%
H2O = 17 Vol%
SO2 = 20 ppmvol
Pgas = -1000Pa g
Tfirebox = 1000°C

$$K_p = e^{\frac{11373}{(1000+273.15)} - 10.75} = 0.1625$$

$$ySO_3 = 0.1625 \times 0.00002 \times \sqrt{\frac{100325}{101325} \times 0.017} = 0.00000042165$$

$$ADP = 69.5 + 18.7 \times \log_{10}(100325 \times 0.00000042165) + 17.2 \times \log_{10}(100325 \times 0.17) = 116.6°C$$