OIV-MA-AS323-04C Sulfur dioxide

Type IV method

1. Definitions

Free sulfur dioxide is defined as the sulfur dioxide present in the must or wine in the following forms: H_2SO_3, HSO_3, whose equilibrium as a function of pH and temperature is:

$$H_2SO_3 \rightleftarrows H^+ + HSO_3$$

H_2SO_3 represents molecular sulfur dioxide.

Total sulfur dioxide is defined as the total of all the various forms of sulfur dioxide present in the wine, either in the free state or combined with their constituents.

2. Molecular Sulfur Dioxide

2.1. Principle of the Method

The percentage of molecular sulfur dioxide, H_2SO_3, in free sulfur dioxide, is calculated as a function of pH, alcoholic strength and temperature.

For a given temperature and the alcoholic strength:

$$H_2SO_3 \rightleftarrows H^+ + HSO_3$$

$$[H_2SO_3] = \frac{L}{10^{(pH-pk_m)} + 1} \quad (1)$$

where

L = $[H_2SO_3] + [HSO_3]$

pk_M = pk_T □ $\frac{A\sqrt{I}}{I + B\sqrt{I}}$

I = ionic strength

A & B = Coefficients which vary according to temperature and alcoholic strength.

k_T = Thermodynamic dissociation constant; the value of pk_T is given in Table 1 for various alcoholic strengths and temperatures.

k_M = Mixed dissociation constant

Taking a mean value 0.038 for the ionic strength I, Table 2 gives the values of pk_M for various temperatures and alcoholic strengths.

The molecular sulfur dioxide content calculated by the relationship given in (1) is presented in Table 3 for various values of pH, temperature and alcoholic strength.

2.2. Calculations

Knowing the pH of wine and its alcoholic strength, the percentage of molecular sulfur dioxide is given in Table 3 for a temperature t °C. Let this be X %.

The amount of molecular sulfur dioxide in mg/L is given by:X · C

C = the free sulfur dioxide in mg/L

Table I

Values of the thermodynamic constant pk_T

Alcohol % by volume	Temperature °C				
	20	25	30	35	40
0	1.798	2.000	2.219	2.334	2.493
5	1.897	2.098	2.299	2.397	2.527
10	1.997	2.198	2.394	2.488	2.606
15	2.099	2.301	2.503	2.607	2.728
20	2.203	2.406	2.628	2.754	2.895

Table II

Values of the Mixed Dissociation Constant pk_M (I= 0.038)

Alcohol % by volume	Temperature °C				
	20	25	30	35	40
0	1.723	1.925	2.143	2.257	2.416
5	1.819	2.020	2.220	2.317	2.446
10	1.916	2.116	2.311	2.405	2.522

15	2.014	2.216	2.417	2.520	2.640
20	2.114	2.317	2.538	2.663	2.803

Table III

Molecular Sulfur Dioxide as a Percentage of Free Sulfur Dioxide (I=0.038)

pH	T = 20 °C Alcohol % by volume				
		0	10	15	20
2.8	7.73	9.46	11.55	14.07	17.09
2.9	6.24	7.66	9.40	11.51	14.07
3.0	5.02	6.18	7.61	9.36	11.51
3.1	4.03	4.98	6.14	7.58	9.36
3.2	3.22	3.99	4.94	6.12	7.58
3.3	2.58	3.20	3.98	4.92	6.12
3.4	2.06	2.56	3.18	3.95	4.92
3.5	1.64	2.04	2.54	3.16	3.95
3.6	1.31	1.63	2.03	2.53	3.16
3.7	1.04	1.30	1.62	2.02	2.53
3.8	0.83	1.03	1.29	1.61	2.02
T = 25 °C					
2.8	11.47	14.23	17.15	20.67	24.75
2.9	9.58	11.65	14.12	17.15	22.71

3.0	7.76	9.48	11.55	14.12	17.18
3.1	6.27	7.68	9.40	11.55	14.15
3.2	5.04	6.20	7.61	9.40	11.58
3.3	4.05	4.99	6.14	7.61	9.42
3.4	3.24	4.00	4.94	6.14	7.63
3.5	2.60	3.20	3.97	4.94	6.16
3.6	2.07	2.56	3.18	3.97	4.55
3.7	1.65	2.05	2.54	3.18	3.98
3.8	1.32	1.63	2.03	2.54	3.18
T = 30 °C					
2.8	18.05	20.83	24.49	29.28	35.36
2.9	14.89	17.28	20.48	24.75	30.29
3.0	12.20	14.23	16.98	20.71	25.66
3.1	9.94	11.65	13.98	17.18	21.52
3.2	8.06	9.48	11.44	14.15	17.88
3.3	6.51	7.68	9.30	11.58	14.75
3.4	5.24	6.20	7.53	9.42	12.08
3.5	4.21	4.99	6.08	7.63	9.84
3.6	3.37	4.00	4.89	6.16	7.98
3.7	2.69	3.21	3.92	4.95	6.44

3.8	2.16	2.56	3.14	3.98	5.19

Table III (continued)

Molecular Sulfur Dioxide as a Percentage of Free Sulfur Dioxide (I=0.038)

pH	T=35 °C Alcohol % by volume				
	0	5	10	15	20
2.8	22.27	24.75	28.71	34.42	42.18
2.9	18.53	20.71	24.24	29.42	36.69
3.0	15.31	17.18	20.26	24.88	31.52
3.1	12.55	14.15	16.79	20.83	26.77
3.2	10.24	11.58	13. 82	17.28	22.51
3.3	8.31	9.42	11.30	14.23	18.74
3.4	6.71	7.63	9.19	11.65	15.49
3.5	5.44	6.16	7.44	9.48	12.71
3.6	4.34	4.95	6.00	7.68	10.36
3.7	3.48	3.98	4.88	6.20	8.41
3.8	2.78	3.18	3.87	4.99	6.80
T = 40 °C					
2.8	29.23	30.68	34.52	40.89	50.14
2.9	24.70	26.01	29.52	35.47	44.74
3.0	20.67	21.83	24.96	30.39	38.85

3.1	17.15	18.16	20.90	25.75	33.54
3.2	14.12	14.98	17.35	21.60	28.62
3.3	11.55	12.28	14.29	17.96	24.15
3.4	9.40	10.00	11.70	14.81	20.19
3.5	7.61	8.11	9.52	12.13	16.73
3.6	6.14	6.56	7.71	9.88	13.77
3.7	4.94	5.28	6.22	8.01	11.25
3.8	3.97	4.24	5.01	6.47	9.15

Bibliography

Molecular sulfur dioxide:

- BEECH F.W. & TOMAS Mme S., *Bull. O.I.V.,* 1985, **58,** 564-581.
- USSEGLIO-TOMASSET L. & BOSIA P.D., *F.V., O.I.V.,* 1984, n° 784.