

Solubility Data for Na₂CO₃ and K₂CO₃ Dissolved in Molten NaNO₃/KNO₃ Eutectic

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Abstract

Relatively little is known about the basic physical chemistry of even simple molten salt systems. This communication reports data for the solubilities of Na₂CO₃ and K₂CO₃ in molten sodium nitrate/potassium nitrate eutectic at temperatures between 520 and 620 K. Values of the Gibb's free energy, enthalpy and entropy of solution have been calculated from these results.

The saturated solubilities of Na₂CO₃ and K₂CO₃ were measured at temperatures in the range from 523 to 613 K by equilibrating the melts with excess of solid carbonate in a Pyrex vessel heated in a tube furnace. Its temperature was maintained to ± 0.1 K by means of a proportional controller working with a sensor immersed in the melt.

Table 1. Thermodynamic and solubility data for Na₂CO₃ and K₂CO₃ in molten NaNO₃/KNO₃ eutectic
m, molal solubility. $\Delta G_{\text{sol}}^{\circ}$ in kJ mol⁻¹, $\Delta S_{\text{sol}}^{\circ}$ in kJ mol⁻¹ K⁻¹

| T (K) | Na ₂ CO ₃ in molten NaNO ₃ /KNO ₃ eutectic | | | | K ₂ CO ₃ in molten NaNO ₃ /KNO ₃ eutectic | | | | |
|--|--|----------------|------------------------|--|---|-----------------|------------------------|------------------------|--|
| | 10 ² m | $\ln K_{sp}^A$ | ΔG_{sol}° | ΔS_{sol}° | 10 ² m | $\ln K_{sp}^A$ | ΔG_{sol}° | ΔS_{sol}° | |
| 523 | 2.57±0.3 | -9.6 (-9.63) | 41.9 | 0.12 | 2.16±0.2 | -10.12 (-10.35) | 45 | 0.12 | |
| | | | | | 2.15 | -10.12 | | | |
| 525 | 2.33±0.3 | -9.89 (-9.54) | 41.6 | 0.12 | | | | | |
| 533 | 3.27±0.3 | -8.78 (-9.18) | 40.7 | 0.12 | 2.37±0.2 | -9.84 (-9.89) | 43.8 | 0.12 | |
| | 3.67 | -8.53 | | | | | | | |
| 543 | 3.95±0.4 | -8.31 (-8.75) | 39.5 | 0.12 | 2.84±0.2 | -9.3 (-9.45) | 42.7 | 0.12 | |
| 548 | 3.25±0.4 | -8.9 (-8.54) | 38.9 | 0.12 | | | | | |
| 553 | 3.84±0.4 | -8.39 (-8.33) | 38.3 | 0.12 | 3.11±0.3 | -9.03 (-9.01) | 41.4 | 0.12 | |
| 563 | 4.66±0.5 | -7.81 (-7.92) | 37.1 | 0.12 | 3.70±0.4 | -8.51 (-8.60) | 40.3 | 0.12 | |
| 573 | 4.40±0.5 | -7.99 (-7.54) | 35.9 | 0.12 | 4.20±0.4 | -8.13 (-8.20) | 39.1 | 0.12 | |
| | 4.70 | -7.79 | | | 4.65 | -7.82 | | | |
| 583 | 4.45±0.5 | -7.95 (-7.16) | 34.7 | 0.12 | 4.67±0.5 | -7.81 (-7.82) | 37.9 | 0.12 | |
| | 5.64 | -7.24 | | | | | | | |
| 593 | 6.50±0.6 | -6.81 (-6.8) | 33.5 | 0.12 | 4.80±0.5 | -7.73 (-7.44) | 36.7 | 0.12 | |
| | 6.71 | -6.72 | | | 5.50 | -7.32 | | | |
| 603 | 7.33±0.7 | -6.45 (-6.45) | 32.3 | 0.12 | | | | | |
| | 8.71 | -5.94 | | | | | | | |
| 613 | 8.06±0.8 | -6.17 (-6.11) | 31.14 | 0.12 | 7.86±0.8 | -6.24 (-6.74) | 34.3 | 0.12 | |
| | 8.82 | -5.9 | | | | | | | |
| $\Delta H_{sol}^\circ = 104 \text{ kJ mol}^{-1}$ | | | | $\Delta H_{sol}^\circ = 106.8 \text{ kJ mol}^{-1}$ | | | | | |

^A Values of ln *K*_{sp}(exp), with values of ln *K*_{sp}(calc) in parentheses calculated from the regression line obtained by the method of least squares from the values of ln *K*_{sp}(exp).

A portion of the solution was filtered by suction through a glass sinter, and a sample of the filtrate was taken for analysis by means of a weighed glass tube fitted with a rubber pipette-filler. The solidified salt was dissolved in distilled water and the carbonate content was estimated by titration.

Assuming activity coefficients to be unity in these dilute solutions and that complete dissociation occurs, we calculated values of the solubility product K_{sp} . The enthalpy of solution, ΔH_{sol}° , was obtained from the slope of the straight-line plot of $\ln K_{sp}$ against reciprocal temperature, the method of least squares being used to obtain the equation to the line of best fit. 'Smoothed' values of $\ln K_{sp}$ were then calculated and used to calculate the Gibb's free energy and entropy of solution, ΔG_{sol}° and ΔS_{sol}° , in the usual way. These data are recorded in Table 1. The product moment correlation coefficients for the fit of the original data to straight lines were 0.96 for Na_2CO_3 and 0.99 for K_2CO_3 . As might be suspected from the nature of these solutions the thermodynamic quantities are rather similar in the two cases. The low solubility of both solutes is surprising.

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