

## Solid/Liquid Phase Diagram of the Ammonium Sulfate/Malic Acid/Water System

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**Table 1S.** Raw DSC data for the  $(\text{NH}_4)_2\text{SO}_4/\text{C}_4\text{H}_6\text{O}_5/\text{H}_2\text{O}$  system. Water activities and activity coefficients determined at the depressed ice melting point and are calculated using equation 4 from the text.

| $[(\text{NH}_4)_2\text{SO}_4]$<br>Wt% | $[\text{C}_4\text{H}_6\text{O}_5]$<br>Wt% | $[\text{H}_2\text{O}]$ Wt% | Final Melting<br>Temperature<br>(K) | Mole<br>Fraction<br>$\text{H}_2\text{O}$ | Water<br>Activity | $\gamma_1$ |
|---------------------------------------|-------------------------------------------|----------------------------|-------------------------------------|------------------------------------------|-------------------|------------|
| 0.00                                  | 0.00                                      | 100.00                     | 273.15                              | 1.0000                                   | 1.0000            | 1.0000     |
| 1.01                                  | 0.00                                      | 98.99                      | 274.70                              | 0.9959                                   | 1.0151            | 1.0193     |
| 2.62                                  | 0.00                                      | 97.39                      | 273.92                              | 0.9891                                   | 1.0075            | 1.0185     |
| 5.01                                  | 0.00                                      | 94.99                      | 272.30                              | 0.9789                                   | 0.9918            | 1.0132     |
| 5.08                                  | 0.00                                      | 94.92                      | 272.16                              | 0.9786                                   | 0.9905            | 1.0121     |
| 7.52                                  | 0.00                                      | 92.48                      | 270.83                              | 0.9678                                   | 0.9778            | 1.0103     |
| 7.53                                  | 0.00                                      | 92.47                      | 271.15                              | 0.9678                                   | 0.9808            | 1.0135     |
| 10.03                                 | 0.00                                      | 89.97                      | 270.52                              | 0.9564                                   | 0.9748            | 1.0193     |
| 10.10                                 | 0.00                                      | 89.90                      | 270.23                              | 0.9561                                   | 0.9721            | 1.0168     |
| 14.96                                 | 0.00                                      | 85.04                      | 268.47                              | 0.9329                                   | 0.9556            | 1.0244     |
| 15.10                                 | 0.00                                      | 84.90                      | 268.39                              | 0.9322                                   | 0.9549            | 1.0243     |
| 20.01                                 | 0.00                                      | 79.99                      | 266.39                              | 0.9072                                   | 0.9364            | 1.0322     |
| 20.06                                 | 0.00                                      | 79.94                      | 266.74                              | 0.9069                                   | 0.9396            | 1.0361     |
| 20.06                                 | 0.00                                      | 79.94                      | 266.45                              | 0.9069                                   | 0.9370            | 1.0332     |
| 25.00                                 | 0.00                                      | 75.00                      | 263.74                              | 0.8800                                   | 0.9125            | 1.0369     |
| 25.00                                 | 0.00                                      | 75.00                      | 263.63                              | 0.8800                                   | 0.9115            | 1.0358     |
| 30.03                                 | 0.00                                      | 69.97                      | 260.98                              | 0.8507                                   | 0.8882            | 1.0441     |
| 30.03                                 | 0.00                                      | 69.97                      | 260.32                              | 0.8507                                   | 0.8825            | 1.0374     |
| 30.03                                 | 0.00                                      | 69.97                      | 262.15                              | 0.8507                                   | 0.8984            | 1.0561     |
| 34.99                                 | 0.00                                      | 65.01                      | 256.97                              | 0.8196                                   | 0.8540            | 1.0420     |
| 35.00                                 | 0.00                                      | 65.00                      | 257.55                              | 0.8195                                   | 0.8589            | 1.0480     |

## Supporting Information

|       |       |       |        |        |        |        |
|-------|-------|-------|--------|--------|--------|--------|
| 0.00  | 5.12  | 94.88 | 272.87 | 0.9928 | 0.9973 | 1.0045 |
| 0.00  | 5.12  | 94.88 | 272.72 | 0.9928 | 0.9958 | 1.0031 |
| 5.01  | 5.03  | 89.96 | 271.43 | 0.9706 | 0.9835 | 1.0133 |
| 10.01 | 5.02  | 84.97 | 269.70 | 0.9469 | 0.9671 | 1.0214 |
| 15.01 | 4.99  | 80.00 | 268.00 | 0.9216 | 0.9512 | 1.0322 |
| 19.97 | 5.03  | 75.00 | 265.76 | 0.8945 | 0.9307 | 1.0404 |
| 25.03 | 4.98  | 69.99 | 262.95 | 0.8652 | 0.9055 | 1.0466 |
| 29.99 | 5.07  | 64.94 | 259.57 | 0.8338 | 0.8760 | 1.0507 |
| 35.00 | 5.01  | 59.99 | 256.90 | 0.8001 | 0.8534 | 1.0667 |
| 36.99 | 5.02  | 57.99 | 254.25 | 0.7858 | 0.8316 | 1.0582 |
| 39.95 | 5.04  | 55.00 | 254.33 | 0.7637 | 0.8322 | 1.0897 |
| 39.98 | 5.08  | 54.94 | 255.00 | 0.7633 | 0.8377 | 1.0974 |
| 40.80 | 5.04  | 54.16 | 254.99 | 0.7572 | 0.8376 | 1.1062 |
| 0.00  | 9.98  | 90.02 | 272.35 | 0.9853 | 0.9923 | 1.0071 |
| 0.00  | 10.00 | 90.00 | 271.86 | 0.9853 | 0.9876 | 1.0023 |
| 0.00  | 10.22 | 89.78 | 272.15 | 0.9849 | 0.9904 | 1.0055 |
| 0.00  | 10.22 | 89.78 | 272.45 | 0.9849 | 0.9932 | 1.0084 |
| 0.00  | 10.22 | 89.78 | 272.25 | 0.9849 | 0.9913 | 1.0065 |
| 5.00  | 10.02 | 84.98 | 270.52 | 0.9616 | 0.9748 | 1.0137 |
| 10.02 | 10.04 | 79.94 | 268.66 | 0.9362 | 0.9574 | 1.0226 |
| 10.12 | 9.95  | 79.93 | 268.68 | 0.9359 | 0.9576 | 1.0232 |
| 10.23 | 9.91  | 79.86 | 268.22 | 0.9354 | 0.9533 | 1.0191 |
| 14.97 | 10.16 | 74.87 | 266.76 | 0.9091 | 0.9398 | 1.0338 |
| 20.02 | 10.00 | 69.98 | 264.34 | 0.8801 | 0.9179 | 1.0429 |
| 20.37 | 10.21 | 69.42 | 264.55 | 0.8774 | 0.9198 | 1.0483 |
| 24.97 | 10.05 | 64.98 | 261.26 | 0.8489 | 0.8906 | 1.0491 |
| 30.00 | 10.01 | 59.99 | 257.18 | 0.8150 | 0.8558 | 1.0500 |
| 30.00 | 10.04 | 59.96 | 256.05 | 0.8149 | 0.8464 | 1.0386 |

## Supporting Information

|       |       |       |        |        |        |        |
|-------|-------|-------|--------|--------|--------|--------|
| 30.01 | 9.96  | 60.03 | 256.35 | 0.8152 | 0.8489 | 1.0413 |
| 35.00 | 10.01 | 54.99 | 252.97 | 0.7783 | 0.8212 | 1.0551 |
| 35.00 | 10.01 | 54.99 | 252.97 | 0.7783 | 0.8212 | 1.0551 |
| 35.02 | 9.99  | 54.99 | 253.24 | 0.7783 | 0.8234 | 1.0580 |
| 37.00 | 9.99  | 53.01 | 253.26 | 0.7629 | 0.8236 | 1.0795 |
| 39.82 | 9.99  | 50.19 | 252.88 | 0.7401 | 0.8205 | 1.1087 |
| 0.00  | 15.19 | 84.81 | 271.27 | 0.9765 | 0.9820 | 1.0056 |
| 5.02  | 15.04 | 79.94 | 269.40 | 0.9515 | 0.9643 | 1.0134 |
| 9.99  | 14.99 | 75.02 | 267.52 | 0.9248 | 0.9468 | 1.0238 |
| 15.00 | 15.02 | 69.98 | 265.11 | 0.8957 | 0.9248 | 1.0325 |
| 20.00 | 15.00 | 65.00 | 262.62 | 0.8644 | 0.9026 | 1.0441 |
| 25.01 | 15.00 | 59.99 | 259.09 | 0.8305 | 0.8719 | 1.0499 |
| 29.99 | 15.00 | 55.01 | 254.70 | 0.7939 | 0.8353 | 1.0521 |
| 34.79 | 14.98 | 50.23 | 251.91 | 0.7557 | 0.8128 | 1.0756 |
| 34.79 | 14.98 | 50.23 | 251.93 | 0.7557 | 0.8129 | 1.0758 |
| 37.00 | 14.99 | 48.01 | 251.67 | 0.7368 | 0.8109 | 1.1005 |
| 37.97 | 14.99 | 47.04 | 251.72 | 0.7284 | 0.8113 | 1.1138 |
| 0.00  | 20.00 | 80.00 | 271.12 | 0.9675 | 0.9805 | 1.0135 |
| 0.00  | 20.00 | 80.00 | 270.28 | 0.9675 | 0.9726 | 1.0052 |
| 0.00  | 20.16 | 79.84 | 270.98 | 0.9672 | 0.9792 | 1.0124 |
| 0.00  | 20.16 | 79.84 | 270.23 | 0.9672 | 0.9721 | 1.0051 |
| 0.00  | 20.01 | 79.99 | 270.08 | 0.9675 | 0.9707 | 1.0033 |
| 5.00  | 20.03 | 74.97 | 268.06 | 0.9406 | 0.9518 | 1.0119 |
| 10.01 | 19.99 | 70.00 | 266.12 | 0.9117 | 0.9340 | 1.0244 |
| 10.24 | 20.09 | 69.67 | 266.04 | 0.9100 | 0.9332 | 1.0255 |
| 14.98 | 20.06 | 64.96 | 263.63 | 0.8804 | 0.9115 | 1.0353 |
| 19.85 | 20.02 | 60.13 | 260.71 | 0.8476 | 0.8859 | 1.0451 |
| 19.98 | 20.10 | 59.92 | 260.59 | 0.8464 | 0.8848 | 1.0454 |

## Supporting Information

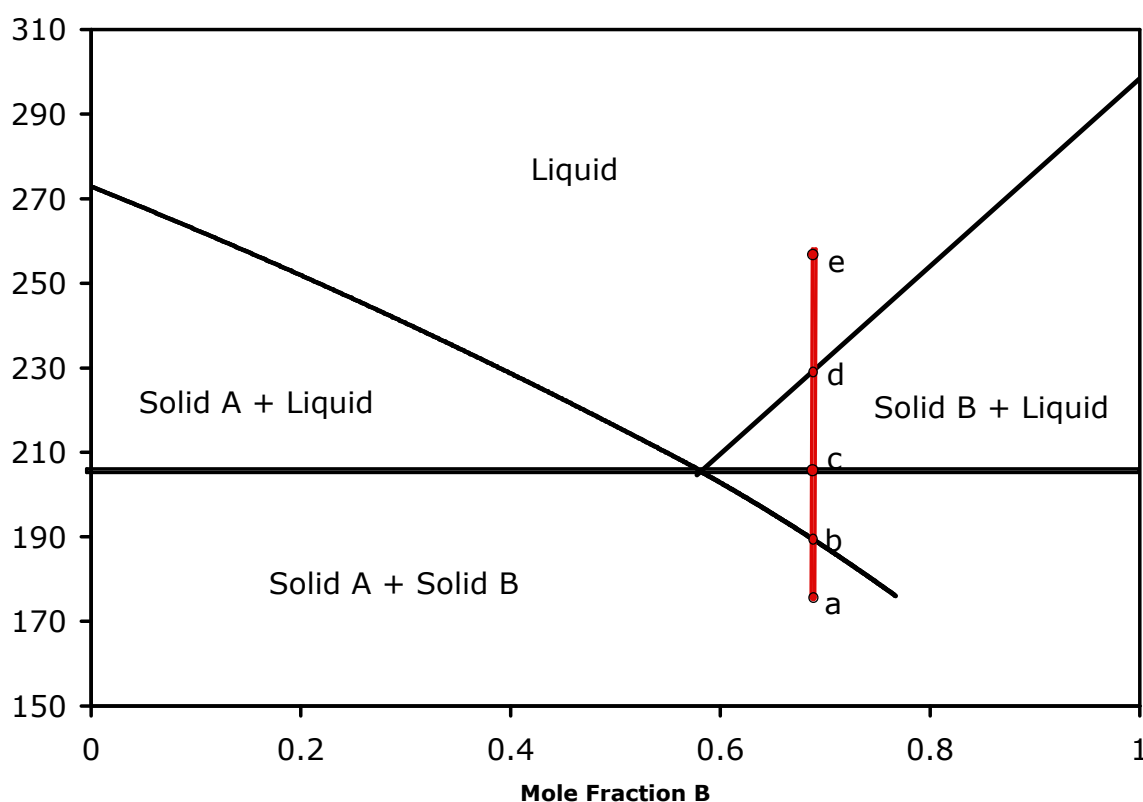
|       |       |       |        |        |        |        |
|-------|-------|-------|--------|--------|--------|--------|
| 20.06 | 20.04 | 59.90 | 260.77 | 0.8461 | 0.8864 | 1.0476 |
| 24.97 | 20.01 | 55.02 | 256.97 | 0.8101 | 0.8540 | 1.0543 |
| 30.01 | 19.98 | 50.01 | 252.22 | 0.7698 | 0.8152 | 1.0591 |
| 29.98 | 20.02 | 50.00 | 252.20 | 0.7698 | 0.8151 | 1.0588 |
| 34.90 | 19.99 | 45.11 | 250.24 | 0.7268 | 0.7996 | 1.1002 |
| 0.00  | 25.00 | 75.00 | 268.79 | 0.9571 | 0.9586 | 1.0015 |
| 5.04  | 24.98 | 69.98 | 266.74 | 0.9281 | 0.9396 | 1.0124 |
| 9.99  | 25.00 | 65.01 | 264.45 | 0.8973 | 0.9189 | 1.0241 |
| 15.01 | 24.98 | 60.01 | 261.79 | 0.8634 | 0.8953 | 1.0369 |
| 19.99 | 24.97 | 55.04 | 258.41 | 0.8268 | 0.8661 | 1.0476 |
| 25.01 | 24.99 | 50.00 | 254.33 | 0.7863 | 0.8322 | 1.0584 |
| 30.01 | 24.99 | 45.00 | 248.67 | 0.7422 | 0.7875 | 1.0610 |
| 0.00  | 29.98 | 70.02 | 268.13 | 0.9456 | 0.9524 | 1.0072 |
| 5.01  | 29.97 | 65.02 | 265.11 | 0.9145 | 0.9248 | 1.0112 |
| 10.02 | 29.98 | 60.00 | 262.64 | 0.8807 | 0.9028 | 1.0250 |
| 10.26 | 29.93 | 59.81 | 262.82 | 0.8792 | 0.9043 | 1.0286 |
| 15.01 | 30.01 | 54.98 | 259.70 | 0.8439 | 0.8772 | 1.0394 |
| 19.98 | 30.05 | 49.97 | 255.88 | 0.8036 | 0.8450 | 1.0514 |
| 20.03 | 30.02 | 49.95 | 255.94 | 0.8034 | 0.8455 | 1.0524 |
| 24.74 | 30.02 | 45.24 | 251.86 | 0.7617 | 0.8124 | 1.0665 |
| 29.70 | 29.75 | 40.55 | 246.47 | 0.7152 | 0.7708 | 1.0777 |
| 0.00  | 34.97 | 65.03 | 265.35 | 0.9326 | 0.9270 | 0.9939 |
| 4.98  | 34.91 | 60.11 | 263.08 | 0.8994 | 0.9066 | 1.0081 |
| 9.99  | 36.03 | 53.98 | 260.19 | 0.8581 | 0.8814 | 1.0271 |
| 10.00 | 34.99 | 55.01 | 261.09 | 0.8622 | 0.8892 | 1.0313 |
| 10.01 | 34.95 | 55.04 | 260.34 | 0.8623 | 0.8827 | 1.0236 |
| 15.01 | 35.99 | 49.00 | 256.77 | 0.8170 | 0.8524 | 1.0432 |
| 15.02 | 35.00 | 49.98 | 257.17 | 0.8217 | 0.8557 | 1.0414 |

## Supporting Information

|       |       |       |        |        |        |        |
|-------|-------|-------|--------|--------|--------|--------|
| 19.98 | 35.09 | 44.93 | 253.03 | 0.7771 | 0.8217 | 1.0574 |
| 19.99 | 34.96 | 45.05 | 253.26 | 0.7778 | 0.8236 | 1.0589 |
| 20.00 | 36.02 | 43.98 | 252.66 | 0.7716 | 0.8188 | 1.0611 |
| 0.00  | 39.98 | 60.02 | 262.20 | 0.9179 | 0.8989 | 0.9793 |
| 0.00  | 40.00 | 60.00 | 264.43 | 0.9178 | 0.9187 | 1.0010 |
| 5.00  | 39.99 | 55.01 | 260.63 | 0.8812 | 0.8852 | 1.0045 |
| 5.01  | 39.94 | 55.05 | 260.60 | 0.8813 | 0.8849 | 1.0041 |
| 5.01  | 40.03 | 54.96 | 260.57 | 0.8809 | 0.8847 | 1.0042 |
| 10.00 | 40.00 | 50.00 | 257.79 | 0.8408 | 0.8609 | 1.0239 |
| 10.01 | 40.00 | 49.99 | 257.79 | 0.8408 | 0.8609 | 1.0240 |
| 10.03 | 38.97 | 51.00 | 258.27 | 0.8452 | 0.8650 | 1.0233 |
| 10.00 | 39.05 | 50.95 | 258.37 | 0.8451 | 0.8658 | 1.0245 |
| 10.00 | 39.05 | 50.95 | 257.31 | 0.8451 | 0.8569 | 1.0139 |
| 14.99 | 39.99 | 45.02 | 254.19 | 0.7965 | 0.8311 | 1.0435 |
| 14.97 | 40.01 | 45.02 | 252.96 | 0.7966 | 0.8212 | 1.0309 |
| 14.97 | 40.01 | 45.02 | 253.03 | 0.7966 | 0.8217 | 1.0316 |
| 14.98 | 37.97 | 47.05 | 255.81 | 0.8073 | 0.8444 | 1.0459 |
| 20.01 | 40.13 | 39.86 | 248.76 | 0.7459 | 0.7882 | 1.0566 |
| 5.00  | 44.93 | 50.07 | 257.84 | 0.8610 | 0.8613 | 1.0003 |
| 5.00  | 44.96 | 50.04 | 257.82 | 0.8609 | 0.8612 | 1.0003 |
| 5.00  | 44.99 | 50.01 | 257.74 | 0.8608 | 0.8605 | 0.9997 |
| 9.99  | 44.95 | 45.06 | 254.47 | 0.8165 | 0.8334 | 1.0206 |
| 15.00 | 45.05 | 39.95 | 249.35 | 0.7662 | 0.7927 | 1.0346 |
| 19.95 | 44.89 | 35.17 | 243.92 | 0.7125 | 0.7520 | 1.0555 |
| 4.97  | 49.95 | 45.08 | 252.40 | 0.8376 | 0.8167 | 0.9751 |
| 9.92  | 50.04 | 40.05 | 248.36 | 0.7879 | 0.7851 | 0.9964 |
| 14.98 | 50.03 | 35.00 | 242.67 | 0.7315 | 0.7430 | 1.0157 |
| 19.99 | 49.95 | 30.06 | 237.72 | 0.6688 | 0.7086 | 1.0594 |

**Discussion of ‘metastable extensions’ of melting curves and ‘metastable melting.’**

In systems that demonstrate substantial supercooling of one or more components, it is possible to observe partial crystallization of a liquid sample with supercooled solution remaining for long periods of time and/or at extreme conditions. We have observed this condition in the  $(\text{NH}_4)_2\text{SO}_4/\text{C}_4\text{H}_6\text{O}_5/\text{H}_2\text{O}$  system described in this paper. In this situation, the components that have frozen can melt below their equilibrium melting points. To illustrate this, we shall consider a simple binary system with a single eutectic composed of water and a solute as illustrated in Figure 1S, where a temperature vs. composition solid/liquid phase diagram is plotted.



**Figure 1S:** Simple binary phase diagram. Liquidus and eutectic tie lines are solid black lines with the areas of thermodynamic stability for each phase indicated. Dashed curve is a metastable extension of the component A liquidus curve. Red line follows the history of a solution at the composition indicated under various conditions (see text).

The various phase stability regions are given in the Figure. For this discussion we will consider a solution at composition corresponding to the red, vertical line in the figure. At the temperature corresponding to point a, the stable phases are solid A and solid B. If these phases form, then upon warming, solid A and some solid B will melt at point c (eutectic melting).

## Supporting Information

Warming to point d will involve continuous melting of solid B until the final melt at point d. Further warming to point e will result in only liquid being present.

Now let us consider the case that at point a only solid A forms and no solid B because of a high nucleation barrier or kinetic hindrance to growth of solid B. Then, as the sample is warmed along the red, vertical line, solid A will melt at point b where it crosses the *metastable extension* of the liquidus curve for A. This is a *metastable melting* since the system is not in complete thermodynamic equilibrium (solid B did not form). At any temperature between point b and c solid B could form, which would then allow solid A to form. If this occurs, the system is now in a stable state and would follow the warming process described above. If not, only liquid will be present from point b through point e.

This entire discussion can be extended to three component (ternary) systems. In the ternary system, the liquidus line becomes a surface, and the eutectic becomes a phase boundary curve. However, the principle of metastable extension of the liquidus surface and metastable melting at the extension of the surface are the same as that described for a binary system.