CHAPTER 3 SOLUTIONS

3.1

Using the GAMS program in Example 3.2, a method could not be found to locate the repeat units having the second and third lowest values of the objective function, Z. Initially, an attempt was made to place a lower bound on Z, adjusting it upward from Z = 0.0007 (the minimum value) until the solution with the next lowest Z is located. In the solution obtained by GAMS, small fractional numbers of groups were obtained.

Next, n_7 was set equal to zero and the following inequalities were added:

$$373 \le T_g \le 393$$
$$1.25 \le \rho \le 1.75$$

which produced the solution:

```
----   63 VARIABLE  TG.L          =   379.3233
          VARIABLE  RHO.L         =     1.2804
          VARIABLE  W.L           =     0.0244
          VARIABLE  n1.L          =     7.0000
          VARIABLE  n2.L          =     2.0000
          VARIABLE  n3.L          =     0.0000
          VARIABLE  n4.L          =     7.0000
          VARIABLE  n5.L          =     0.0000
          VARIABLE  n6.L          =     0.0000
          VARIABLE  n7.L          =     0.0000
          VARIABLE  Z.L           =    15.0395
```

For this repeat unit, -$(CH_2)_7(CO)_2(O)_7$-, the glass transition temperature is close to 383 K, but significant differences are associated with the specified density (1.5 g/cm^3) and water adsorption (0.005 g H_2O/g polymer).

Using the inequalities:

$$373 \le T_g \le 393$$
$$1.0 \le \rho \le 2.0$$

another solution is obtained:

```
       63 VARIABLE  TG.L          =   385.7143
          VARIABLE  RHO.L         =     1.0323
          VARIABLE  W.L           =     0.0177
          VARIABLE  n1.L          =     6.0000
```

VARIABLE n2.L	=	1.0000
VARIABLE n3.L	=	0.0000
VARIABLE n4.L	=	0.0000
VARIABLE n5.L	=	0.0000
VARIABLE n6.L	=	0.0000
VARIABLE n7.L	=	0.0000
VARIABLE Z.L	=	6.5595

For this repeat unit, $-(CH_2)_6CO-$, the glass transition temperature is close to 383 K, the difference associated with the specified density (1.5 g/cm^3) is increased, and that associated with the water adsorption (0.005 g H_2O/g polymer) is decreased.

Note that better solutions could not be found. When the seventh group is included, only the solution in Example 3.2 is obtained.

These results can be reproduced by modifying the GAMS program listed in the file, EXER3-2.doc, in the GAMS folder associated with the Solution Manual on the Wiley web site for this book.

3.2

This solution is obtained by eliminating the seventh group, -CHCl-, from the GAMS program in Example 3.2. The resulting GAMS program and solution are:

```
VARIABLES
      n1, n2, n3, n4, n5, n6, TG, RHO, W, H, V, Y, M, STG, SRHO, SW, Z;

POSITIVE VARIABLES
      STG, SRHO, SW, W, H, V, Y, TG, M, RHO;

INTEGER VARIABLES
      n1, n2, n3, n4, n5, n6;

      n1.LO = 0;    n1.UP = 7;
      n2.LO = 0;    n2.UP = 7;
      n3.LO = 0;    n3.UP = 7;
      n4.LO = 0;    n4.UP = 7;
      n5.LO = 0;    n5.UP = 7;
      n6.LO = 0;    n6.UP = 7;

      M.LO = 14;
      V.LO = 10;
      H.LO = 3.3E-5;
      Y.LO = 2700;

      W.LO   = 0;              W.UP   = 0.18;
      TG.LO  = 298;            TG.UP  = 673;
      RHO.LO = 1;              RHO.UP = 1.5;

      STG.L = 383;  SRHO.L = 1.50;  SW.L = .005;

EQUATIONS
      SPEC1, SPEC2, SPEC3, MOLWEIGHT, GLASSTMP, YTOT, HTOT, VTOT, DENSITY,
      ABSORBANCE, OBJ;
```

```
OBJ..           Z     =E=  ((SQR((STG - TG)/STG)) + (SQR((SRHO - RHO)/SRHO)) + (SQR((SW -
                           W)/SW)));

SPEC1..         SRHO   =E=  1.5;
SPEC2..         STG    =E=  383;
SPEC3..         SW     =E=  .005;
MOLWEIGHT..     M      =E=  n1*(14) + n2*(28) + n3*(44) + n4*(16) + n5*(43) + n6*(30);
YTOT..          Y      =E=  n1*(2700) + n2*(27000)+ n3*(8000) + n4*(4000) + n5*(12000) +
                            n6*(13000);
HTOT..          H      =E=  n1*(3.3E-5) + n2*(0.11)+ n3*(0.075) + n4*(0.02) + n5*(0.75) +
                            n6*(0.75);
VTOT..          V      =E=  n1*(15.85) + n2*(13.40)+ n3*(23) + n4*(10) + n5*(24.9) +
                            n6*(19.15);
GLASSTMP..      TG     =E=  (Y/M);
DENSITY..       RHO    =E=  (M/V);
ABSORBANCE..    W      =E=  ((18*H)/M)

MODEL GROUPS /ALL/;
SOLVE GROUPS USING MINLP MINIMIZING Z;
OPTION DECIMALS = 4;
DISPLAY TG.L, RHO.L, W.L, n1.L, n2.L, n3.L, n4.L, n5.L, n6.L, Z.L;

*----    62 VARIABLE  TG.L          =    364.2857
*           VARIABLE  RHO.L         =      1.0133
*           VARIABLE  W.L           =      0.0157
*           VARIABLE  n1.L          =      7.0000
*           VARIABLE  n2.L          =      1.0000
*           VARIABLE  n3.L          =      0.0000
*           VARIABLE  n4.L          =      0.0000
*           VARIABLE  n5.L          =      0.0000
*           VARIABLE  n6.L          =      0.0000
*           VARIABLE  Z.L           =      4.7278
```

Without the group, –CHCl-, the repeat unit is -$(CH_2)_7$CO-. The glass transition temperature differs significantly from 383 K, and significant differences are associated with the specified density (1.5 g/cm^3) and water adsorption (0.005 g H_2O/g polymer). These results can be reproduced using the GAMS program listed in the file, EXER3-2.doc, in the GAMS folder associated with the Solution Manual on the Wiley web site for this book.

When the following bounds are added,

$$373 \le T_g \le 393$$
$$1.0 \le \rho \le 2.0$$

as in the solution to Exercise 3.1, the following results are obtained:

```
63 VARIABLE  TG.L     =   385.7143
   VARIABLE  RHO.L    =     1.0323
   VARIABLE  W.L      =     0.0177
   VARIABLE  n1.L     =     6.0000
   VARIABLE  n2.L     =     1.0000
   VARIABLE  n3.L     =     0.0000
   VARIABLE  n4.L     =     0.0000
   VARIABLE  n5.L     =     0.0000
   VARIABLE  n6.L     =     0.0000
   VARIABLE  n7.L     =     0.0000
   VARIABLE  Z.L      =     6.5595
```

For this repeat unit, $-(CH_2)_6CO-$, the glass transition temperature is close to 383 K, the difference associated with the specified density (1.5 g/cm^3) is similar, and that associated with the water adsorption (0.005 g H_2O/g polymer) is increased.

3.3

The GAMS program in Example 3.2 is resolved with the glass transition temperature specified at 423 K. To obtain a glass transition temperature in the vicinity of 423 K, it was necessary to include the inequality constraint:

TG.LO = 415

The results are:

```
63 VARIABLE  TG.L      =   420.8000
   VARIABLE  RHO.L     =     1.4828
   VARIABLE  W.L       =     0.0096
   VARIABLE  n1.L      =     4.0000
   VARIABLE  n2.L      =     1.0000
   VARIABLE  n3.L      =     0.0000
   VARIABLE  n4.L      =     0.0000
   VARIABLE  n5.L      =     0.0000
   VARIABLE  n6.L      =     0.0000
   VARIABLE  n7.L      =     6.0000
   VARIABLE  Z.L       =     0.8489
```

The polymer repeat unit is: $-(CH_2)_4(CO)(CHCl)_6-$. Its glass transition temperature, 420.8 K, and density, 1.48 g/cm^3, are close to their specifications. However, the water absorption, 0.0096 g H_2O/g polymer, is nearly double its specification.

These results can be reproduced by modifying the GAMS program listed in the file, EXER3-2.doc, in the GAMS folder associated with the Solution Manual on the Wiley web site for this book.

3.4

A GAMS program is presented below that utilizes the property estimation equations in Example 3.3. This program is listed in the file, EXER3-4.doc, in the GAMS folder associated with the Solution Manual on the Wiley web site for this book.

```
VARIABLES

      n1, n2, n3, n4, Tb, Tc, sigt, sumn, sigpc, Pc, Tbr, h, G, k, Pl, Ph,
      Tlr, Thr, cpl, M, Svb, Hvb, n, Hv, Z;

POSITIVE VARIABLES

       Pc, Tbr, M, cpl, Hv, Pl, Ph;

       Pc.LO = 20;
       G.LO = 0.4835;
       Tlr.LO = 0.001;
       Thr.LO = 0.001;
       M.LO = 0.001;
       cpl.LO = 18.4;
       Hv.LO = 18.4;
       Pl.LO = 1.4;  Pl.UP = 7;
       Ph.LO = 7;  Ph.UP = 14;

INTEGER VARIABLES

      n1, n2, n3, n4;                  {n1 (CH3), n2 (CH), n3 (F), n4 (S)}

      n1.LO = 0; n1.UP = 4;
      n2.LO = 0; n2.UP = 4;
      n3.LO = 0; n3.UP = 10;
      n4.LO = 0; n4.UP = 10;

      Tb.LO = 195;
      Tc.LO = 325;

EQUATIONS

      OCTET, SPEC1, SPEC2, SPEC3, SPEC4,
      BOILPT, DEFsigt, CRITTEMP, DEFsumn, DEFsigpc, CRITPRES,
      DEFTbr, DEFh, DEFG, DEFk, DEFPlr, DEFPhr, PRESSLOW, PRESSHIGH,
      HEATCAP, MOLWEIGHT, DEFSvb, DEFHvb, DEFN, DEFHv, OBJ;

OCTET..                    n1*(1) + n2*(-1) + n3  =E= 2;

SPEC1..                    n1 + n2 + n3 + n4 =G= 2;

SPEC2..                    n1 + n2 + n3 + n4 =G= 2*n2 + 2;

SPEC3..                    n1 + n2 + n3 + n4 =G= n4 + 2;

SPEC4..                    n1 + n2 =L= 4;
```

```
BOILPT..        Tb =E= 198.2 + (n1*23.58) + (n2*21.74) + (n3*(-0.03)) + (n4*68.78);

DEFsigt..       sigt =E=  n1*0.0141 + n2*0.0164 + n3*0.0111 + n4*0.0119;

CRITTEMP..      Tc =E= Tb/(0.584 + 0.965*sigt - sigt*sigt);

DEFsumn..       sumn =E= n1 + n2 + n3 + n4;

DEFsigpc..      sigpc =E= n1*(-0.0012)+ n2*0.002 + n3*(-0.0057) + n4*0.0049;

CRITPRES..      Pc =E= Tb / (0.113 + 0.0032*sumn - sigpc)**2;

DEFTbr..        Tbr =E= Tb/Tc;

DEFh..          h =E=  Tbr * LOG(Pc/(1-Tbr));

DEFG..          G =E= 0.4835 + 0.4605*h;

DEFk..          k =E= (h/G - (1 + Tbr)) / ((3 + Tbr)*SQR(1 - Tbr));

DEFTlr..        Tlr =E= 253/Tc;

DEFThr..        Thr =E= 305/Tc;

PRESSLOW..      Pl =E=  Pc*EXP( (-G*(1-SQR(Tlr) + k*(3 + Tlr)*(1 - (Tlr))**3))/Tlr);

PRESSHIGH..     Ph =E=  Pc*EXP( (-G*(1 - SQR(Thr) + k*(3 + Thr)*(1 - Thr)**3))/Thr);

HEATCAP..       cpl =E=  0.239 * (n1*36.8 + n2*21 + n3*17 + n4*33);

MOLWEIGHT..     M =E=  n1*15.04 + n2*13.02 + n3*19 + n4*32.07;

DEFSvb..        Svb =E=  44.367 + 15.33*LOG10(Tb) + 0.39137*Tb/M + 0.00433*SQR(Tb)/M -
                0.000005627*(Tb)**(3)/M;

DEFHvb..        Hvb =E= Svb*Tb;

DEFN..          n =E= (0.00264*Hvb/(8.31*Tb) + 0.8794)**(10);

DEFHv..         Hv =E= Hvb*((1 - 253/Tc)/(1 - Tb/Tc))**(n);

OBJ..           Z =E= Hv;

Model groups /all/;
solve groups using minlp maximizing Z;
Option decimals = 3;
Display Z.L, n1.L, n2.L, n3.L, n4.L, Tc.L, Pc.L, Pl.L, Ph.L, Svb.L, Hv.L, cpl.L, M.L, Tb.L;
```

RESULTS:

```
G e n e r a l   A l g e b r a i c   M o d e l i n g   S y s t e m
E x e c u t i o n


----     98 VARIABLE  Z.L                    =      26.053
```

VARIABLE n1.L	=	0.000
VARIABLE n2.L	=	4.000
VARIABLE n3.L	=	6.000
VARIABLE n4.L	=	0.000
VARIABLE Tc.L	=	410.577
VARIABLE Pc.L	=	49.435
VARIABLE Pl.L	=	6.166
VARIABLE Ph.L	=	14.000
VARIABLE Svb.L	=	84.004
VARIABLE Hv.L	**=**	**26.053**
VARIABLE cpl.L	=	44.454
VARIABLE M.L	=	166.080
VARIABLE Tb.L	=	284.980

The optimal refrigerant is $(CH)_4F_6$. For this molecule:

$$\Delta H^v\{-20°C\} = 26.1\,\text{kJ/mol}$$
$$P^s\{-20°C\} = 6.17\,\text{bar}$$
$$P^s\{32°C\} = 14.0\,\text{bar}$$
$$c_{pl}\{6°C\} = 44.5\,\text{kJ/mol}$$

Hence, all constraints are satisfied.

3.5

Using an EXCEL spreadsheet, in the file EXER3-5.xls in the EXCEL folder associated with the Solution Manual on the Wiley web site for this book, the following results are obtained.

	Methyl propyl ketone $CH_3(CH_2)_2COCH_3$	Methyl butyl ketone $CH_3(CH_2)_3COCH_3$	Methyl isobutyl ketone $(CH_3)_2(CH_2)_2COCH_3$
ΔH^v, KJ/mol	39.2	43.9	43.4
T_b, K	376.3	404.2	403.2
T_m, K	202.1	214.5	208.5
δ_D, MPa$^{1/2}$	10.87	11.61	11.89
δ_P, MPa$^{1/2}$	8.31	7.21	6.69
δ_H, Ma$^{1/2}$	4.31	4.02	3.87
LHS Eq. (3.15)	636.7	565.3	540.7
$\log_{10} K_{ow}$	2.37	3.15	3.38

Note that for the three compounds, all of the constraints in the solution to Example 3.5 are satisfied; that is: $T_b > 323$ K, $T_m < 223$ K, $\delta_P > 6.3$ MPa$^{1/2}$, and $\log_{10} K_{ow} < 4.0$. However, with $R^* = 19.8$ MPa$^{1/2}$, $(R^*)^2 = 392$ MPa. Consequently, the left-hand side of Eq. (3.15) exceeds $(R^*)^2 = 392$ MPa, and hence, the solubility constraint is violated for the three compounds.

3S.1

Calculations for all four salts are made in the manner as in Example 3S.2. For the 50°C case, solubilities at 50°C are estimated by a linear extrapolation of the given data at 40°C and data below at 30°C, taken from the book by Mullin, referenced on page 673. The water of crystallization at 50°C is assumed to be the same as that at 20 and 40°C.

Physical property data:

Salt	Waters of Crystallization	MW of Anhydrous	MW of Hydrous	Heat of Crystallization, 20°C, kmol/mol
Na acetate	3	82.0	136.1	-4.7
Na thiosulfate	5	158.1	248.2	-11.4
Ca nitrate	4	164.1	236.2	-8
Pb acetate	3	325.3	379.3	-5.9

Salt	Solubility, 20°C, g anhy/100 g water	Solubility, 40°C, g anhy/100 g water	Solubility, 30°C, g anhy/100 g water	Estimated Solubility, 50°C, g anhy/100 g water	Kopp's Specific Heat, cal/g-C	Wenner's Specific Heat, cal/g-C
Na acetate	46.5	65.5	54.5	76.5	0.398	0.470
Na thiosulfate	70	103	84	122	0.346	0.316
Ca nitrate	129	196	153	239	0.346	0.366
Pb acetate	44.1	116	69.5	162.5	0.191	0.212

Results of calculations on the basis of 100 grams of water in the solution at the end of crystallization. Water will also be contained in the crystals as water of crystallization.

<u>Case 1, 40°C final temperature</u>

Salt	Grams of salt dissolved	Total grams of solution	Grams of hydrous crystals	Total grams	Supersaturation ratio, *S*
Na acetate	65.5	165.5	98.2	263.7	1.93
Na thiosulfate	103	203	68	271	1.68
Ca nitrate	196	296	127.4	423.4	1.59
Pb acetate	116	216	212.5	428.5	5.19

<u>Case 2, 50°C final temperature</u>

Salt	Grams of salt dissolved	Total grams of solution	Grams of hydrous crystals	Total grams	Supersaturation ratio, *S*
Na acetate	76.5	176.5	136.1	312.6	2.21
Na thiosulfate	122	222	88.8	310.8	1.93
Ca nitrate	239	339	196.8	535.8	1.82
Pb acetate	162.5	262.5	309.2	571.7	6.73

For the above two cases, it appears that the supersaturation ratio of lead acetate is much too high to be feasible. Both the thiosulfate and nitrate have supersaturation ratios that are lower than sodium acetate and, therefore, would appear to be possible candidates.

Another comparison that might be made is based on the heat per gram of mixture that is liberated as the mixture cools back down from 40^{o}C (or 50^{o}C) to, say, 20^{o}C, taking into account the additional amount of crystals that will formed because of the decreased solubility at the lower temperature. For example, if sodium acetate is used, 4,700 calories is liberated per mole of crystals formed. With a crystal MW of 136.1, this gives 34.53 cal/g of crystals formed. Now consider the 40^{o}C case. For 98.2 g of crystals, this gives (98.2)(34.53) = 3,391 cal. At 40^{o}C, the amount of crystals, from above, is 98.2 grams, based on a solubility of 65.5 g/100 g of water. But at 20^{o}C, the solubility is only 46.5 g/100 g of water. To calculate the additional amount of crystals formed, carry out material balance calculations. Let y = the grams of water in the solution at 20^{o}C. The mixture is:

Water = 100 + 98.2[(136.1-82)/136.1)] = 139.0 g
Sodium acetate = 263.7 – 139 = 124.7 g

Then, at equilibrium at 20^{o}C,

Total solution = $y + 46.5(y/100)$
Total crystals = $(139 – y)[136.1/(136.1 – 82)]$
Total solution + Total crystals = 263.7

Solving gives y = 82.1 g. The total solution = 120.3 g. The amount of crystals = 263.7 – 120.3 = 143.4 g. This is an additional 143.4 – 98.2 = 45.2 g. The additional heat liberated is 45.2(34.53) = 1,561 cal. Thus, the total heat liberated = 3391 + 1561 = 4,952 calories. From above, the total grams of mixture are 263.7 g. Therefore, the heat liberated in cooling is 4952/263.7 = 18.8 cal/g mixture.

Similar calculations for the 50^{o}C and the other salts gives:

Salt	Heat liberated, 40^{o}C case, cal/g mixture	Heat liberated, 50^{o}C case, cal/g mixture
Na acetate	18.8	23.0
Na thiosulfate	26.1	33.2
Ca nitrate	28.0	33.9
Pb acetate	11.0	12.5

For this criterion, both the thiosulfate and nitrate appear superior to sodium acetate because of higher heat liberation (on the order of 40% higher). However, the detailed calculations for calcium nitrate, for the 50^{o}C case, show that only solids will be present at equilibrium at 20°C, resulting in a loss of flexibility of the hand warmer. This may or may not be a problem.

These results show that sodium thiosulfate may be superior to sodium acetate. However, experiments are necessary to verify the assumption that it can achieve a supersaturation ratio in the range of 1.68 to 1.93. If so, then tests are also required to:

(1) Confirm the ability of a triggering method to initiate crystallization,
(2) Verify that more heat will be liberated by crystallization of sodium thiosulfate than with sodium acetate,
(3) Determine the ease of regeneration and the number of regeneration cycles possible,
(4) Determine the best ratio of salt to water to use since this will affect the temperature that will be achieved.

Marketing studies also need to be carefully carried out because the competing non-regenerative hand warmers are very inexpensive, dependable, and popular.