Phase Diagrams and Thermodynamic Properties of Binary Organic Systems Based on 1,2-, 1,3-, 1,4-Diaminobenzene or Benzidine

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Phase Diagrams and Thermodynamic Properties of Binary Organic Systems Based on 1,2-, 1,3-, 1,4-Diaminobenzene or Benzidine

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The phase diagram data of 47 binary organic systems were critically evaluated with the aid of a computer-coupled thermodynamic/phase diagram analysis. The systems are based upon the three isomeric diaminobenzenes or benzidine, and the second components are compounds such as phenol and substituted phenols, polyhydroxybenzenes, benzoic acid, etc. The results of such an analysis of phase diagram data include the excess Gibbs energies of the liquid phases as well as the Gibbs energies of fusion and formation of intermediate compounds. The quantities were used to calculate a *best* phase diagram for each system. Such phase diagrams conform to necessary thermodynamic constraints and follow from stated evaluative criteria of experimental data.

Key words: phase diagram; thermodynamic properties.

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1. Introduction

Solid-liquid equilibria of organic systems hitherto have received much less attention than those of inorganic systems (alloys, molten salts, ceramics). Interest in binary organic systems has often centered on the formation of intermediate compounds (e.g., as an aid in the identification of an organic substance). More recently the object has been the chemistry and solidification behavior of eutectics, important for the study of materials having controlled two-phase microstructures (in situ composites).¹ As is the case with inorganic systems, binary organic phase diagrams have been investigated by different methods and the results are often in disagreement or are contradictory. In particular, there is sometimes uncertainty concerning the number or stoichiometry of intermediate compounds - illustrated by several cases examined in the present article --- which is crucial for any application involving the formation of new materials from solidification of melts.

The binary systems investigated here are all based on simple diamino compounds: the three isomeric diaminobenzenes, and benzidine (4,4'-diaminobiphenyl). The second components in the binary systems are compounds such as phenol, substituted phenols, di- and trihydroxybenzenes, etc. in which intermediate compounds are often formed. No evaluation of these data has been attempted hitherto and indeed in recent investigations the authors appear to be unaware of previous published work on the same systems.

2. Critique of Experimental Methods

The phase diagrams considered in this article were investigated by three techniques, viz., thermal analysis, the thawmelt method and the microthermal method. Their main features are given here and implications for phase diagram evaluation are discussed in Sec. 4.2.

2.1. Thermal Analysis

This was used by Kremann and co-workers.^{4.5} In this classic method, gram quantities of mixtures were used and temperature-time curves (both heating and cooling modes) were recorded. The sample was stirred and temperature indicated by a thermometer graduated in 0.1°. Both eutectic and liquidus temperatures were detected. Although thermal analysis with organic mixtures frequently encounters serious experimental difficulty (see next section), it was found in the present work that Kremann's results^{4.5} were of equal or better quality than later data derived from other methods. When necessary precautions are taken, thermal analysis carefully done is the preferred method for best results.^{6.7}

2.2. Thaw-Melt Method

This method was used by Dhillon and co-workers,⁸⁻¹⁴ Rai and co-workers¹⁵⁻³⁰ as well as Rastogi et al.³¹ It was developed as an alternative to thermal analysis which, when applied to organic substances, displayed several inconveniences.³² Chief among these is severe supercooling, which may amount to 10° for unstirred samples.³³ This is aggravated by the low thermal conductivity of the sample, which sometimes can be quite viscous. The thaw-melt method is a refinement of the procedure used by organic chemists to determine melting points of synthesized compounds.³⁴⁻³⁶ The mixture is first premelted, cooled and ground to a fine powder in a mortar. A milligram quantity is inserted into a thin-bore melting point tube and, if necessary, protected from the atmosphere in some way. The tube is attached to a mercury thermometer, usually calibrated in 0.1°, and immersed in a liquid bath, the temperature of which is slowly raised. Phase changes and the corresponding temperatures are noted visually. The temperature of first appearance of liquid in the sample is the eutectic temperature (thaw); the temperature at which the last solid disappears is taken as the liquidus temperature (melt).

This method is both simpler and faster than thermal analysis, and requires only a small quantity of material. There are, however, some weaknesses. Phase changes are detected visually only, and only the heating mode is used. Under these circumstances the eutectic temperature is usually more accurately determined than the liquidus temperature. This is because the first appearance of the liquid phase is readily detected from a completely solidified melt. Once the eutectic temperature has been passed, there is greater uncertainty in detecting the disappearance of the solid, for a number of reasons. The two-phase mixture may become cloudy, due perhaps to the presence of impurities; since there is no stirring, residual solid sinks to the bottom of the narrow column of liquid and there may no longer be equilibrium between solid and liquid.³⁵ This uncertainty is magnified when the composition being studied is situated on a steep portion of the liquidus (thermal analysis is also less dependable in this case).

The method used by Bergman and Arestenko³⁷ was called by them *visual-polythermal*. Few details were given,³⁷ but it evidently was similar to the thaw-melt method, except that only the liquidus temperature was noted. For systems containing phenols and naphthols, the mixtures were stirred and seeds were introduced.

2.3. Microthermal Method

This may be considered as a variation of the thaw-melt procedure. The small quantity of sample is placed between microscope slides, slowly heated and observed through a microscope. The technique was developed and used extensively by Kofler,³⁸ who called it a *microthermal* method. It was used here by Stancic *et al.*³⁹

3. Computer-coupled Thermodynamic/ Phase Diagram Analysis

This technique is based upon well-known principles of calculation of phase diagrams from the thermodynamic properties of the phases. Such an analysis provides a set of selfconsistent thermodynamic equations, which simultaneously reproduce the thermodynamic properties and the phase diagram of the system. It also yields a thermodynamically correct smoothing of experimental data and thereby a more reliable estimate of error limits.

The principles and general procedure of this type of analysis are the same as those detailed previously,² where they were applied to binary molten salt systems. The method was equally successful for the binary organic system benzene-cyclohexane.³ In the present article the same approach is used, with minor differences occasioned by the nature of the systems studied. These are discussed further in this section.

3.1. Thermodynamics

The pertinent thermodynamic relationships were outlined previously.² In the present work, the excess Gibbs energy of the liquid phase was represented by a simple polynomial in mole fractions

$$G^{\rm E} = x_{\rm A} x_{\rm B} (g_0 + g_1 x_{\rm B} + g_2 x_{\rm B}^2 + \dots) \tag{1}$$

for the binary system A + B. The parameters g_0 , g_1 , etc. are empirical coefficients. Various other representations for G^E could have been used such as the Redlich-Kister expansion, Legendre polynomials, the Quasi-chemical model, etc. It was found that the simple expression, Eq. (1), was entirely adequate, with at most three coefficients. It is implicitly assumed, therefore, that the liquid phase is not highly structured and that there are no liquid miscibility gaps.

In all systems studied, G^{E} was taken to be independent of temperature. This assumption was justified in the present work, for two reasons: (a) the temperature range represented by the liquidus was small, and data scatter was often severe; (b) there have been no independent measurements of the heat of mixing in these systems (e.g., by calorimetry) which would enable a separation of the H^{E} and S^{E} terms in the relation $G^{E} = H^{E} - TS^{E}$.

3.2. Limiting Slopes of Liquidus Lines and Solid Solubility

This consideration proved to be of some importance in the critical evaluation of the experimental phase diagram data, and so is treated in some detail here. From purely thermodynamic principles, a relation can be derived between the slopes of the liquidus at the composition extremes $(x_B = 0, x_B = 1)$ and the extent of solid solution at these compositions. For example, in the limiting case $x_B \rightarrow 1$ (pure B), both liquid and solid phases become Henrian and the excess Gibbs energies approach zero. The Gibbs energy of fusion of *B* at temperature *T* is well approximated by the expression $\Delta_{fus}H_B^{\circ}(1 - T/T_{fus})$, where $\Delta_{fus}H_B^{\circ}$ is the heat of fusion at the melting point T_{fus} . In this case it can be derived thermodynamically² that

$$(\mathrm{d}x_{\mathrm{B}}/\mathrm{d}T)_{\ell} - (\mathrm{d}x_{\mathrm{B}}/\mathrm{d}T)_{\mathrm{s}} = \Delta_{\mathrm{fus}}H_{\mathrm{B}}^{\circ}4/RT_{\mathrm{fus}}^{2}$$
(2)

where dx_B/dT is the slope of the liquidus or solidus at $x_B = 1$. The expression on the RHS of Eq. (2) is simply the reciprocal of the well-known freezing point depression constant and depends only on properties of the solvent (B in this case). A similar equation may be written for component A.

In none of the systems dealt with in the present evaluations was solid solubility reported or measured; it was assumed, tacitly or not, that it was zero. (Similarly, intermediate compounds were assumed to be stoichiometric.) In those phase diagram measurements where eutectic data were reported, the eutectic temperature remained constant as far as the compositions studied approached the pure substances (usually up to within 0 - 10 mol %). In phase diagrams of organic substances, the crystallographic structures of the components are usually quite incompatible, and the assumption of zero solid solubility is justified (for example, in the case of benzene-cyclohexane³, it was about 3 mol %). Thus, if the solidus term in Eq. (2) is set to zero,

$$(\mathrm{d}x_{\mathrm{B}}/\mathrm{d}T)_{\ell} = \Delta_{\mathrm{fus}} H_{\mathrm{B}}^{\mathrm{o}}/RT_{\mathrm{fus}}^{2} \tag{3}$$

In the present evaluations, Eq. (3) was used extensively in weighting experimental liquidus data near the composition extremes. In all the calculated phase diagrams (Figs. 1 - 47) the limiting liquidus slopes conform to this requirement.

3.3. Optimization Procedure

The actual steps followed in an optimization of phase diagram data varied somewhat from system to system, but some generalizations can be made². Data for the A- and B-side liquidi yielded, through a least-squares optimization, an expression for the excess Gibbs energy of the liquid. This calculation was supplemented — if the system contained intermediate compound(s) — by a similar optimization using liquidus data of the compound(s). This resulted in the deduction of the Gibbs energies of fusion and formation (from the pure liquids) of the compound(s). The derived thermodynamic data were then used to generate the calculated phase diagram. Weighting of the phase diagram data and *fine tuning* of the optimized thermodynamic expressions are described in Sec. 4.2.

In this kind of optimization, measured heats of fusion of intermediate compounds can be used as *given* data, in the same way as pure component data. Heats of fusion of intermediate compounds in a number of cases were reported, measured by DSC or DTA. In the ideal situation — accurately determined heat of fusion data — these could be used in the present applications; it was found, however, that in many cases experimental heat of fusion data were more or less inconsistent with the rest of the reported phase diagram. Thus, as a general rule, the heat of fusion of compounds was calculated by optimization and simply compared with experimental values.

In one or two cases, thermodynamic expressions were simply assigned, rather than derived from optimization, for reasons peculiar to the cases involved. Pertinent details of optimization and evaluation for each system are mentioned in Sec. 6.

4. Principles of the Evaluation Procedure 4.1. General Phase Diagram Considerations

In the original publications not all phase diagram data were tabulated; any untabulated data were read off the published phase diagrams. All experimental points — eutectic and liquidus — appear in the calculated phase diagrams.

Disagreement concerning the number of intermediate compounds for a system was often found when the system was studied by more than one investigator. In addition, simple thermodynamic consistency considerations often dictated, in the present evaluations, the positing of a change in the stoichiometry or number of compounds present in the system. In particular, the excess Gibbs energy, Eq. (1), was found to be relatively small with little composition asymmetry. Consequently the liquidi on either side of a intermediate compound are closely symmetric. The reported phase diagrams sometimes violated this elementary requirement. Such cases are discussed individually in Sec. 6.

4.2. Weighting of Phase Diagram Data

As a consequence of strengths and weaknesses among experimental method (Sec. 2) as well as limiting liquidus slope considerations (Sec. 3.2), reported phase diagram data both within and among investigators were weighted differently in the optimization step (Sec. 3.3). Thus for data derived from the thaw-melt method (used by the majority of investigators), the following classification was generally used: a) Data given greater weight: eutectic temperatures and compositions; melting points of congruently-melting intermediate compounds.

b) Data given less weight: other liquidus data.

In a few cases where this weighting was overridden, reasons are given in the evaluations. In some cases, the liquidus was better defined in one report than in another, e.g., by a greater number of compositions. Despite their age, the data of Kremann *et al.*^{4.5}, from thermal analysis, were found to be of good quality and were given more weight than more recent data from the thaw-melt method in a number of cases.

4.3. Status of the Calculated Results

The final calculated phase diagrams, shown in Figs. 1–47, as well as the calculated excess Gibbs energies of the liquid (Table A1) and Gibbs energies of fusion and formation of compounds (Table A2), represent the *best* results for the systems under consideration, based upon available experimental data and evaluative criteria discussed in Secs. 2, 3 and 4. Where calculated and experimental heats of fusion of compounds differ noticeably, this does not mean that the experimental value is necessarily in error. Such cases are discussed individually in Sec. 6. For each system a *probable maximum inaccuracy* of the evaluated phase diagram is offered; this simply reflects experimental data scatter, as well as possible bias in experimental method.

Information in parentheses in Tables A1 and A2 indicates data of possibly considerable uncertainty, but which were used in calculating the recommended phase diagrams. Such data are consistent with all other evaluated data in each system.

In the evaluations and in Tables 1, A1 and A2 the large number of significant figures given for thermodynamic properties does not indicate high precision; they are included for accurate reproduction of the calculated phase boundaries.

In those systems in which a diamino compound forms one component, it is placed uniformly on the right-hand side of the diagram. This facilitates comparison of phase diagram features among related systems.

5. Properties of the Pure Substances

For an evaluation of the present type, the quality of the recommended data depends upon the quality of the thermodynamic data of the pure components used in the calculations. A number of recent compilations of melting points and heats of fusion are useful^{40–45}. Of these, the collections of Domalski and co-workers^{40,41} are particularly valuable because an attempt was made to evaluate and rank data from different sources. Acree's two compilations^{42,43} are practically identical. The choice of data used in the calculations (Table 1) is discussed briefly here. All heats of fusion mentioned were determined by DTA or DSC. All temperatures are quoted to the nearest 0.1°, irrespective of source, since the precision of experimental phase diagram data does not warrant citation of hundredths of a degree.

5.1. The Diamino Compounds

The melting points of 1,2-, 1,3- and 1,4-diaminobenzene lie in the ranges 100.7–103.0 °C, 62.3–65.9 °C and 139.1– 145.0 °C, respectively^{13,15,31,41,42,46}. The chosen values are from Dhillon¹³. There is only one value available for the heat of fusion of the 1,2-isomer⁴⁶. For the 1,3- and 1,4-compounds, the data are 15400, 15570 and 21700, 24860 J/mol, respectively^{41,42,46}. The chosen data are from Domalski *et al.*⁴¹ and Acree⁴². For benzidine, the reported^{24,37} melting points are 127.0 and 128.0 °C; the more recent value was chosen²⁴. There is only one datum available for the heat of fusion²⁴.

5.2. Phenol and Substituted Phenols

The melting point of phenol⁴⁰⁻⁴² lies in the range 39.5 – 40.9 °C; the highest temperature is recommended⁴⁰. The heat of fusion⁴⁰⁻⁴² was reported as 10581, 11514 and 11289 J/mol and the recommended⁴⁰ value was chosen. For the 2-, 3- and 4-nitrophenols, the melting points are 44.8, 46.0 and 96.8, 97.0 and 112.0–114.0 °C, respectively^{37,41,42,47}; the recommended data⁴¹ were used. For 2,4-dinitrophenol, there is only one source⁴¹. For 3-aminophenol, there is an appreciable reported^{43,46,47} melting point range, 123.0–127.0 °C. The value chosen, 125.4 °C, was read off from the phase diagram²⁴ evaluated in the present work. The reported heats of fusion^{24,45} are 22980 and 24700 J/mol.

5.3. Di- and Trihydroxybenzenes

Melting points^{13,15,31,40,42,46,48} for 1,2-dihydroxybenzene (catechol) lie in the range 103.0-105.0 °C; the value chosen is from the most recent phase diagram article¹⁵. For the heat of fusion, values between 22000 and 22760 J/mol were reported^{18,40,42,46}. For the 1,3-isomer (resorcinol), the melting point^{40,41,42,46} lies between 109.4 and 110.0 °C, with the latter value being most frequently cited. Values for the heat of fusion^{18.40-42,46} vary between 18900 and 21676 J/mol. The true value is probably closer to the higher datum⁴¹. Resorcinol displays a solid-solid transition^{41,46} at 96.0 °C, which is not indicated in reported phase diagrams; this transition is included in evaluated phase diagrams in the present work whenever it lies above the eutectic temperature. For the 1,4isomer (hydroquinone), the melting point^{12,42,46,48,49} lies in the range 171.8-174.0 °C and there is no recommended value. The value chosen^{40,42} therefore carries some uncertainty. The heat of fusion^{40,46} is 27110 or 26500 J/mol. There is only one source²⁸ of data for 1,2,3-trihydroxybenzene (pyrogallol).

5.4. Naphthols

1-Naphthol melts^{31,40,42,44,48} in the range 94.0–96.0 °C, and the chosen value, 95.5 °C, was chosen as lying close to the values read off evaluated phase diagrams. The heat of fusion^{17,22,40,42,44,51} is 22802, 23470 or 23332 J/mol. For 2naphthol, melting points^{10,31,40,42,48} lie in the range 120.0– 123.9 °C; there is no recommended value and the chosen temperature is closest to data read off evaluated phase diagrams. The heat of fusion^{22,40,42} is 21940, 18790 or 17511

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Substance	Abbreviation	Temperature, °C	trs or fus	ΔΗ	ΔS
Diamino compounds		,			
1,2-Diaminobenzene	1,2-DAB	103.0	fus	23100	61.404
1,3-Diaminobenzene	1,3-DAB	63.8	fus	15570	46.202
1,4-Diaminobenzene	1,4-DAB	140.0	fus	24860	60.165
4,4'-Diaminobiphenyl	4,4'-DABP	127.0	fus	19100	47.732
Polyhydroxy benzenes					
1,2-Dihydroxybenzene	1,2-DHB	104.5	fus	22740	60.207
1,3-Dihydroxybenzene	1,3-DHB	96.0	trs	1370	3.711
		109.6	fus	21290	55.631
1,4-Dihydroxybenzene	1,4-DHB	172.3	fus	27110	60.853
1,2,3-Trihydroxybenzene	1,2,3-THB	134.0	fus	18550	45.561
Naphthols					
1-Naphthol	1-N	95.5	fus	23182	62.875
2-Naphthol	2-N	123.5	fus	18790	47.366
Phenols and substituted phenol	5				
Phenol	Р	40.9	fus	11514	36.657
2-Nitrophenol	2-NP	44.8	fus	17446	54.862
3-Nitrophenol	3-NP	96.8	fus	19196	51.881
4-Nitrophenol	4-NP	113.8	fus	18254	47.168
2,4-Dinitrophenol	2,4-DNP	114.8	fus	24174	62.304
3-Aminophenol	3-AP	125.4	fus	22980	57.659
Other compounds					
Benzamide	BENZ	130.0	fus	18490	45.858
Benzoic acid	BA	122.4	fus	17580	44.439
3-Nitrobenzoic acid	3-NBA	141.1	fus	21730	52.445

TABLE 1. Gibbs energies of fusion or transition of pure compounds $\Delta G = \Delta H - T \Delta S \text{ J/mol}$

J/mol, and since there is no recommended datum, the middle value was chosen.

5.5. Remaining Compounds

The melting point of benzoic acid 40,42,50 is 122.0 or 122.4 °C and the heat of fusion 19,40,42,50,51 lies in the range 16230–18062 J/mol. The better data⁴⁰ for the heat of fusion lie closer to the upper value. 3-Nitrobenzoic acid melts 40,42 at 141.1 °C, and the heat of fusion 23,27,40,42 lies in the range 19292–21730 J/mol. The chosen heat of fusion is the most recent value²⁷. Benzamide^{11,42} melts at 129.1 or 130.0 °C and there is one value for the heat of fusion⁴².

5.6. Experimental Melting Points and Purity of Substances

The quality of the starting materials used in the phase diagram measurements quoted in the present article was not uniform. In the earliest work^{4,5} and also in that of Stancic *et al.*³⁹, there was no statement about purity or purification. Bergman and Arestenko³⁷ *thoroughly purified* their materials. It was the general practice of Rastogi *et al.* Dhillon *et al.*^{8 14} and Rai *et al.*^{15 30} to purify the components by sublimation,

fractional crystallization or distillation under reduced pressure. In the summary that follows, the term *accurate* melting point signifies a temperature within 1° of the accepted value (Table 1); a plus (+) or a minus (-) signifies a melting point higher or lower than the accepted value.

For 1,2-, and 1,3-DAB, all reported data are accurate except for Kremann *et al.*^{4,5} (-2°). For 1,4-DAB, Stancic *et al.*³⁹, Dhillon *et al.*⁸⁻¹⁴ and Kremann⁴ are accurate; the remainder were high¹⁵⁻³⁰ (+3°) or low⁵ (-1.5°). All benzidine data are accurate.

For 1,2-, 1,3-DHB and 1,2,3-THB all data are accurate. For 1,4-DHB, the experimental datum¹² is high $(+1.5^{\circ})$.

For the naphthols, all data are accurate except Bergman and Arestenko³⁷ for $2-N(-2^{\circ})$.

For phenol, only Dhillon¹² was faulty (+2.1°). For 2-NP, both Dhillon⁸ and Bergman and Arestenko³⁷ are high (+1.7°, +1.2°). For 3-NP, 4-NP and 2,4-DNP Kremann⁴ is low $(-1.3^{\circ}, -2.3^{\circ}, -3.8^{\circ})$.

The observed melting points for benzamide¹¹, benzoic acid^{19,39} and 3-nitrobenzoic acid²³ are all accurate.

In the evaluation of the phase diagram data, Sec. 6 below, it was found that a perceived inaccuracy in melting point of the end components was not necessarily associated with a corresponding inaccuracy in the melting behaviour of mixtures.

6. The Evaluations

The same convention is used throughout this paper for identifying the left- and right-hand components of binary systems. For example, in the case of 1,2-DHB (A) + 1,2-DAB (B) the left-hand component is always component A and the right-hand component, B. This corresponds to the layout in all phase diagrams and also identifies A and B components in the expression for the excess Gibbs energy of the liquid, Eq. (1). In the same manner it identifies the stoichiometry of intermediate compounds, e.g., in the above-mentioned binary system the designation 2:1 refers to the compound of mole ratio A_2B .

In the evaluations, where there are more than one eutectic in the system studied, these are identified as E_1 , E_2 , etc. In all cases, the temperatures and compositions indicated in Figs. 1-47 are the calculated (evaluated) data.

6.1 Systems with 1,2-Diaminobenzene

6.1.1. Dihydroxybenzenes as Second Component

1,2-DHB(A) + 1,2-DAB(B)

Data were obtained by the thaw-melt method, checked by thermal analysis⁹. The reported⁹ eutectics are $E_1 = 71.1$ °C, $x_B = 0.32$ and $E_2 = 69.5$ °C, $x_B = 0.67$. The 1:1 compound melts congruently⁹ at 88.1 °C and its measured heat of fusion⁹ is 7840 J/mol. In the optimization, greater weight was given to reproducing the eutectic and 1:1 compound melting temperatures. The evaluated phase diagram (Fig. 1) was calculated with the use of Eq. (4)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-8300 - 600 x_{\rm B}) \,\text{J/mol}$$
 (4)

and the calculated thermodynamic properties of the 1:1 compound are, for (AB)/2

$$\Delta_{\rm fus}G^{\circ} = 9107 - 25.2143T \,\text{J/mol}$$
(5)

$$\Delta_{\rm f}G^{\circ} = -11257 + 19.4531T \,\text{J/mol} \tag{6}$$

Other calculated data are: $E_1 = 71.1$ °C, $x_B = 0.329$ and $E_2 = 69.5$ °C, $x_B = 0.677$; the calculated melting point of the compound is 88.0 °C.

Probable maximum inaccuracy in calculated liquidus: $\pm 2^{\circ}$.

1,3-DHB (A) + 1,2-DAB (B)

Data were obtained by the thaw melt method^{13,31} and checked by thermal analysis¹³. Eutectic data reported by the two investigators are not in good agreement:

	XB	°C	Ref.	
E	0.39	48.5	13	
	0.39	52.0	31	
E_2	0.62	47.1	13	
	0.61	53.5	31	

The reported melting points^{13,31} of the 1:1 compound are 51.8 and 57.2 °C, respectively. Photographic microstructure of this compound was presented³¹. The heat of fusion of the compound³¹ is 16500 J/mol. In this case, there is good agreement^{13,31} about the eutectic compositions, but not about temperatures, although both investigators^{13,31} individually find that E_1 and E_2 temperatures are close to each other. Since there is much uncertainty about the melting point of the compound and eutectic temperatures, the experimental³¹ heat of fusion was used in the optimization, and eutectic compositions could best be reproduced by eutectic temperatures intermediate between reported values. The calculated diagram, Fig. 2, was generated with the use of Eq. (7)



FIG. 1. The system 1,2-DHB (A) + 1,2-DAB (B).

$$G^{\rm E}(\ell) = -13495 x_{\rm A} x_{\rm B} \, {\rm J/mol}$$
 (7)

The transition for resorcinol at 96.0 °C appears on the calculated liquidus at $x_B = 0.144$. The thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus} G^{\circ} = 16500 - 50.3509T \,\text{J/mol} \tag{8}$$

$$\Delta_{\rm f}G^{\circ} = -19874 + 44.5881T \,\rm J/mol \tag{9}$$

where, in Eq. (8), the heat of fusion is the experimental value³¹. Other calculated data are: $E_1 = 50.4$ °C, $x_B = 0.395$ and $E_2 = 49.5$ °C, $x_B = 0.616$; the compound melts congruently at 54.5 °C.

Probable maximum inaccuracy in calculated diagram: \pm 5°.

1,4-DHB (A) + 1,2-DAB (B)

Data were obtained by the thaw-melt method and checked by thermal analysis¹². The reported eutectics¹² are $E_1 = 104.3$ °C, $x_B = 0.59$ and $E_2 = 92.3$ °C, $x_B = 0.90$. The 1:2 compound melts congruently¹² at 108.0 °C. The experimental limiting liquidus slope¹² at $x_B = 0$ is noticeably steeper than the theoretical value, and the hydroquinone liquidus has a point of inflection — this is rarely found in simple systems such as this, and may be spurious. The eutectic and compound melting temperatures were given more weight in the optimization, and the calculated phase diagram, Fig. 3, was generated with the use of Eq. (10)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-6000 - 2500 x_{\rm B}) \,\text{J/mol}$$
 (10)

The calculated properties of the compound are, for $(AB_2)/3$,

$$\Delta_{\rm fus}G^{\circ} = 19390 - 50.8677T \,\text{J/mol} \tag{11}$$

$$\Delta_{\rm f}G^\circ = -21094 + 45.5758T \,\text{J/mol} \tag{12}$$

Other calculated data are: $E_1 = 103.3$ °C, $x_B = 0.537$ and $E_2 = 92.9$ °C, $x_B = 0.866$; the compound melts congruently at 108.0 °C.

Probable maximum inaccuracy in calculated liquidus: $\pm 5^{\circ}$.

6.1.2. Naphthols as Second Component

1-N(A) + 1,2-DAB(B)

Data were obtained by the thaw-melt method^{10,31} and checked by thermal analysis¹⁰. The observed eutectics are

	x _B	°C	Ref.	
E_1	0.30	58.4	10	
	0.36	57.9	31	
E_2	0.63	59.5	10	
	0.62	60.8	31	

The 1:1 compound melts congruently^{10,31} at 62.0 or 63.4 °C, respectively; its heat of fusion³¹ is 20600 J/mol. The phase diagram, Fig. 4, was calculated with the use of Eq. (13)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-10299 + 1565 x_{\rm B}) \, {\rm J/mol}$$
 (13)

and the calculated thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus}G^{\circ} = 24151 - 71.8114T \,\text{J/mol} \tag{14}$$

$$\Delta_{\rm f}G^\circ = -26530 + 66.0502T \,\,{\rm J/mol} \tag{15}$$



FIG. 2. The system 1,3-DHB (A) + 1,2-DAB (B).







FIG. 4. The system 1-N(A) + 1,2-DAB(B).

Other calculated data are: $E_1 = 57.5$ °C, $x_B = 0.340$ and $E_2 = 60.5$ °C, $x_B = 0.613$. The compound melts congruently at 63.2 °C.

Probable maximum inaccuracy in calculated diagram: $\pm 2^{\circ}$.

2-N(A) + 1, 2-DAB(B)

Data were obtained by the thaw-melt method^{10,31} and checked by thermal analysis¹⁰. The reported eutectics are

	x _B	്	Ref.
E1	0.35	81.3	10
	0.38	84.4	31
2	0.71	80.1	10
	0.69	81.5	31

There is thus substantial disagreement about the LHS eutectic temperature (E_1) and much scatter toward the extremes of composition. The congruent melting point of the 1:1 compound^{10,31} is 87.3 or 88.1 °C. The heat of fusion of the compound³¹ is 19200 J/mol. In the optimization, more weight was given to the melting point and liquidus data of the compound, since there is less disagreement in the central part of the phase diagram. The diagram, Fig. 5, was calculated with the use of Eq. (16)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-4240 + 1302 x_{\rm B}) \, \text{J/mol}$$
 (16)

and the calculated thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus}G^{\circ} = 18489 - 51.2342T \,\rm J/mol \tag{17}$$

$$\Delta_{\rm f}G^{\circ} = -19386 + 45.4714 \,{\rm J/mol} \tag{18}$$

Other calculated data are: $E_1 = 83.6$ °C, $x_B = 0.356$ and $E_2 = 81.2$ °C, $x_B = 0.688$; the compound melts congruently at 87.7 °C.

Probable maximum inaccuracy in calculated diagram: \pm 3°.

6.1.3. Phenol and Substituted Phenols as Second Component

P(A) + 1,2-DAB(B)

Data were obtained by thermal analysis⁴ and also by the thaw-melt method (checked by thermal analysis)¹². There is marked disagreement concerning the liquidus over most of the composition range. There is also disagreement concerning the number and identity of intermediate compounds. Dhillon and Dhillon¹² show a 1:1 compound melting congruently at 54.8 °C and eutectics at 29.5 °C, $x_{\rm B} = 0.21$ and 40.0 °C, $x_{\rm B} =$ 0.62. Kremann and Petritschek⁴ postulated two incongruently melting compounds (1:1 and 2:1) and perhaps a congruently melting 4:1 compound. In preliminary calculations, it was ascertained that a congruently melting 1:1 compound was thermodynamically quite incompatible with liquidus data near it, whereas an incongruently melting compound fitted much better. Since the thermal analysis data⁴ are much more plentiful in the critical region of the phase diagram, these data were given more weight. The postulated⁴ 2:1 compound proved to be unnecessary, whereas the shape of the liquidus around $x_{\rm B} = 0.2$ suggested that indeed there might be a 4:1 compound. Such a stoichiometry, though rarely seen in systems such as these, enabled the calculated liquidus to follow experimental data^{4,12} closely. The phase diagram, Fig. 6, was calculated with the use of Eq. (19)

$$G^{\mathsf{E}}(\ell) = -4176x_{\mathsf{A}}x_{\mathsf{B}} \text{ J/mol}$$
(19)



FIG. 5. The system 2-N (A) + 1,2-DAB (B).

and the thermodynamic properties used for the compounds are, for (AB)/2

$$\Delta_{\rm fus}G^{\,\circ} = 14764 - 46.5937T \,\,\text{J/mol} \tag{20}$$

$$\Delta_{\rm f}G^\circ = -15808 + 40.8326T \,\text{J/mol} \tag{21}$$

and for $(A_4B)/5$

 $\Delta_{\rm fus}G^{\circ} = 9112 - 30.0000T \,\rm J/mol \tag{22}$

$$\Delta_{\rm f}G^{\circ} = -9780 + 25.8400T \,\text{J/mol} \tag{23}$$

The heat and entropy of fusion of the 4:1 compound seem rather low; both the existence of this compound and its thermodynamic properties require experimental confirmation. Other calculated data are: $E_1 = 28.8 \,^{\circ}$ C, $x_B = 0.137$ and $E_2 = 29.8 \,^{\circ}$ C, $x_B = 0.246$; the 4:1 compound melts congruently at 30.6 $^{\circ}$ C and the peritectic is 42.2 $^{\circ}$ C, $x_B = 0.415$.

Probable maximum inaccuracy in calculated diagram: $\pm 6^{\circ}$.

2-NP(A) + 1, 2-DAB(B)

Data were obtained by thermal analysis⁴ and the thaw-melt method⁸. The system is a simple eutectic and the reported eutectic⁸ is 40.4 °C, $x_B = 0.14$. There is scatter in the liquidus data at high temperature^{4,8} and the limiting liquidus slope⁸ at the LHS is faulty. The true eutectic temperature therefore is defined by the thermal analysis results⁴ on the LHS of the diagram. The phase diagram, Fig. 7, was calculated with the use of Eq. (24)

$$G^{\rm E}(\ell) = 1688 x_{\rm A} x_{\rm B} \, \text{J/mol}$$
 (24)

and the calculated eutectic is 38.6 °C, $x_{\rm B} = 0.133$.

Probable maximum inaccuracy in calculated diagram: $\pm 2^{\circ}$.

3-NP (A) + 1,2-DAB (B)

Data were obtained by thermal analysis⁴ and the thaw-melt method⁸. The observed eutectics are $E_1 = 72.1$ °C, $x_B = 0.29$ and $E_2 = 63.0$ °C, $x_B = 0.55$. Dhillon⁸ shows a 2:1 compound melting congruently at 76.8 °C. The thermal analysis data⁴ are more plentiful in the central part of the diagram and these authors⁴ postulated, in addition to the 2:1 compound, a 1:1 and/or 1:2 compound(s). The liquidus data⁴ near $x_B = 0.6$ definitely indicate a break in the liquidus curve, suggesting a peritectic. The stoichiometry of the compound is undefined by the available data; it was nominally set at 1:2. A 1:1 compound proved unnecessary. In the optimization, greater weight was given to the more plentiful thermal analysis results⁴ in the central region. Since the 1:2 compound is in equilibrium with the liquid over a very small temperature range, its thermodynamic properties could not be obtained from the optimization and hence were set at nominal values of reasonable magnitude. Due to the ambiguity of the data in the interval 0.5 < $x_{\rm B}$ < 0.7, the calculated phase diagram is somewhat conjectural in this region.

The phase diagram, Fig. 8, was calculated with the use of Eq. (25)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-6903 + 1460 x_{\rm B}) \,\text{J/mol}$$
 (25)

and the optimized data for the compound $(A_2B)/3$ are

$$\Delta_{\rm fus}G^\circ = 12278 - 35.1890T \,\rm J/mol \tag{26}$$

$$\Delta_{\rm f}G^{\circ} = -13689 + 29.8987T \,\text{J/mol} \tag{27}$$

The nominal values for $(AB_2)/3$ are



FIG. 6. The system P(A) + 1,2-DAB(B).

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$$\Delta_{\rm fus}G^{\circ} = 18614 - 55.0000T \,\rm J/mol \tag{28}$$

$$\Delta_{\rm f}G^{\circ} = -19932 + 49.7080T \,\rm J/mol \tag{29}$$

Other calculated data are: $E_1 = 72.3$ °C, $x_B = 0.246$ and $E_2 = 61.6$ °C, $x_B = 0.534$. The 2:1 compound melts congruently at 75.3 °C and the peritectic is 63.8 °C, $x_B = 0.584$.

Probable maximum inaccuracy in calculated diagram: $\pm 4^{\circ}$.

4-NP (A) + 1,2-DAB (B)

Data were obtained by thermal analysis⁴, the thaw-melt method (checked by thermal analysis)⁹ and by the microthermal method³⁹. Data for the two eutectics are summarized:

	ХB	°C	Ref.	
<i>E</i> ₁	0.24	84.4	9	
	0.26	85.0	39	
E ₂	0.64	70.4	9	
	0.60	68.5	39	

All investigators^{4,9,39} report the existence of a congruently melting 2:1 compound, of melting point^{9,39} 92.8 or 87.5 °C. The LHS limiting liquidus slope⁹ is faulty. There is substantial data scatter over the whole composition range, particularly around the 2:1 composition. Data from thermal analysis⁴ and the microthermal method³⁹ agree well in this region and hence in the optimization these data^{4,39} were given more weight than the other⁹. This weighting thermodynamically entailed the lower E_2 eutectic temperature^{4,39}. The phase diagram, Fig. 9, was calculated with the use of Eq. (30)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-9438 + 4000 x_{\rm B}) \,\text{J/mol}$$
 (30)

and the calculated thermodynamic properties of the compound $(A_2B)/3$ are

$$\Delta_{\rm fus}G^{\circ} = 16999 - 47.0170T \,\rm J/mol \tag{31}$$

$$\Delta_{\rm f}G^{\circ} = -18800 + 41.7197T \,\text{J/mol} \tag{32}$$

Other calculated data are: $E_1 = 84.4$ °C, $x_B = 0.230$ and $E_2 = 68.1$ °C, $x_B - 0.604$; the compound melts congruently at 88.4 °C.

Probable maximum inaccuracy in calculated diagram: $\pm 4^{\circ}$.

2,4-DNP (A) + 1,2-DAB (B)

Data were obtained by thermal analysis⁵. Since the experimental melting points of the pure substances⁵ are more or less inaccurate, the liquidus data near the pure components were given less weight than the eutectic and 1:2 compound data. The reported eutectics⁵ are $E_1 = 85.3$ °C, $x_B = 0.37$ and $E_2 = 72.0$ °C, $x_B = 0.69$. The 1:1 compound was reported⁵ to melt congruently at 85.0 °C. The liquidus arms of the compound are not symmetrical, and moreover the RHS of the phase diagram is better defined experimentally than the LHS. The phase diagram, Fig. 10, was calculated with the use of Eq. (33)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-4691 - 2926 x_{\rm B}) \, \text{J/mol}$$
 (33)

and the calculated thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus} G^{\circ} = 12702 - 35.3677T \, \text{J/mol} \tag{34}$$

$$\Delta_{\rm f}G^{\circ} = -14240 + 29.6065T \,\rm J/mol \tag{35}$$



FIG. 7. The system 2-NP (A) + 1,2-DAB (B).

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FIG. 8. The system 3-NP (A) + 1,2-DAB (B).



FIG. 9. The system 4-NP (A) + 1,2-DAB (B).

Other calculated data are: $E_1 = 81.9$ °C, $x_B = 0.388$ and $E_2 = 72.1$ °C, $x_B = 0.691$. The compound melts congruently at 86.0 °C.

Probable maximum inaccuracy in calculated diagram: $\pm 4^{\circ}$.

6.1.4. Other Substances as Second Components

BA(A) + 1,2-DAB(B)

Data were obtained by the microthermal method³⁹. Three eutectics were reported³⁹:

	x _B	°C	
 E_1	0.27	103.0	
$\dot{E_2}$	0.47	90.0	
E_3	0.73	85.0	

together with two congruently melting compounds: 2:1 at 106.0 °C and 1:1 at 95.0 °C. The presence of a congruently melting 1:1 compound and the experimental liquidus around $x_{\rm D} = 0.5$, as shown on the phase diagram³⁹, are thermodynamically incompatible. In order to fit in with the rest of the phase diagram, the 1:1 compound must melt incongruently. The liquidus data for the two end components were optimized, giving an excess Gibbs energy of the liquid

$$G^{\rm E}(\ell) = -2432x_{\rm A}x_{\rm B} \, {\rm J/mol}$$
 (36)

and the calculated thermodynamic properties of the compound $(A_2B)/3$, derived principally from a melting point of 106.0 °C, are

$$\Delta_{\rm fus}G^{\circ} = 15000 - 39.5570T \,\text{J/mol} \tag{37}$$

$$\Delta_{\rm f}G^{\circ} = -15540 + 34.2651T \,\rm{J/mol} \tag{38}$$

The 1:1 compound was set to melt incongruently near the experimental datum³⁹ of 95.0 °C; the thermodynamic properties were calculated upon the basis of the reported phase diagram for compositions $x_B > 0.6$. For (AB)/2, therefore,

$$\Delta_{\rm fus}G^{\circ} = 15915 - 43.2230T \,\rm J/mol \tag{39}$$

$$\Delta_{\rm f}G^{\circ} = -16523 + 37.4619T \,\rm J/mol \tag{40}$$

The phase diagram, Fig. 11, was calculated with the use of Eqs. (36), (38) and (40). The central part of the diagram necessarily remains uncertain, but the construction shown in Fig. 11 represents a reasonable compromise between experimental data and thermodynamic constraints. Other calculated data are: $E_1 = 102.5$ °C, $x_B = 0.219$ and $E_2 = 84.5$ °C, $x_B = 0.725$; the calculated peritectic is 94.1 °C, $x_B = 0.567$ and the 2:1 compound melts congruently at 106.0 °C.

Probable maxim inaccuracy in calculated diagram: \pm 4°.

BENZ(A) + 1,2-DAB(B).

Data were obtained by the thaw-melt method and checked by thermal analysis¹¹. The data were tabulated but not plotted. This is a simple eutectic system. When the data are plotted, it is seen that both arms of the liquidus exhibit inflection points; such behavior may be spurious. The stated eutectic temperature¹¹ is 70.2 °C; the eutectic composition (not stated) is $x_B \sim 0.36$. The benzamide liquidus drops off rather precipitously, but the other liquidus is close to ideal. This behavior, though thermodynamically innocuous, is unusual in a system where there is probably little interaction between the two liquid components¹¹. For calculating the phase diagram, the eutectic temperature (70.2 °C) was taken as the most accurate information in this system. In order to avoid inflection points on



FIG. 10. The system 2,4-DNP (A) + 1,2-DAB (B).

the liquidus, the benzamide liquidus data were given very little weight in the optimization; instead an approximation to the RHS of the diagram was attempted. The final phase diagram, Fig. 12, was calculated with the use of the expression above, the calculated RHS liquidus is probably closer to true behavior. The excess Gibbs energy at $x_B = 0.5$, from Eq. (41), is about -400 J/mol; the same quantity for the other binary systems with benzamide (Secs. 6.2 and 6.3) lie in the range -300 to -500 J/mol. All three are simple eutectic systems in which interactions between A and B components are expected to be similar.

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-3795 + 4405 x_{\rm B}) \,\mathrm{J/mol}$$
 (41)

and the calculated eutectic is 70.2 °C, $x_B = 0.475$. Neither liquidus is reproduced accurately, but for reasons given

Probable maximum inaccuracy in calculated liquidus: $\pm 10^{\circ}$.



FIG. 11. The system BA (A) + 1,2-DAB (B).





6.2. Systems with 1,3-Diaminobenzene

6.2.1. Dihydroxybenzenes as Second Component

1,2-DHB (A) + 1,3-DAB (B)

Data were obtained by the thaw-melt method and checked by thermal analysis¹³. The two reported eutectics¹³ are $E_1 = 58.5$ °C, $x_B = 0.38$ and $E_2 = 41.4$ °C, $x_B = 0.79$. The 1:1 compound melts congruently¹³ at 66.7 °C. The experimental limiting liquidus slope¹³ at $x_B = 1$ is grossly inaccurate; the LHS liquidus is, however, much better situated. For this system, therefore, the eutectic temperatures, the LHS liquidus and the observed melting point of the compound were given more weight than liquidus data on the RHS. The liquidus data between $x_B = 0.55$ and $x_B = 0.82$ are not compatible with the rest of the phase diagram, for either a 1:1 or 1:2 compound. These data were therefore ignored. The phase diagram, Fig. 13, was calculated with the use of Eq. (42)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} \ (-10000 + 3000 x_{\rm B}) \ {\rm J/mol}$$
 (42)

and the thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus}G^{\circ} = 12225 - 35.7612T \,\rm J/mol \tag{43}$$

$$\Delta_{\rm f}G^{\circ} = -14220 + 30.0000T \,\rm{J/mol} \tag{44}$$

The RHS of the phase diagram remains poorly defined and hence the quantities in Eqs. (42) – (44) are somewhat uncertain. Other calculated data are: E_1 =58.3° C, x_B = 0.373 and E_2 = 41.1 °C, x_B = 0.757; the compound melts congruently at 65.0 °C.

Probable maximum inaccuracy in calculated LHS liquidus: $\pm 4^{\circ}$.

RHS liquidus: $\pm 10^{\circ}$

1,3-DHB (A) + 1,3-DAB (B) .

Data were obtained by the thaw-melt method and checked by thermal analysis¹³. The reported¹³ eutectics are $E_1 = 52.1$ °C, $x_B = 0.29$ and $E_2 = 31.5$ °C, $x_B = 0.79$. The 1:1 compound melts congruently at¹³ 79.1 °C. The limiting liquidus slopes¹³ at both LHS and RHS correspond to thermodynamic values. The phase diagram, Fig. 14, was calculated with the use of Eq. (45)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-23950 + 4194 x_{\rm B}) \,\mathrm{J/mol}$$
 (45)

and the calculated thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus}G^{\circ} = 14402 - 40.7700T \,\rm J/mol \tag{46}$$

$$\Delta_{\rm f}G^\circ = -19865 + 35.0000T \,\rm J/mol \tag{47}$$

The resorcinol transition at 96.0 °C, not shown in the experimental¹³ phase diagram, appears on the calculated liquidus at $x_B = 0.117$. Other calculated data are: $E_1 = 52.4$ °C, $x_B = 0.304$ and $E_2 = 31.5$ °C, $x_B = 0.778$; the compound melts congruently at 80.1 °C.

Probable maximum inaccuracy in calculated liquidus: $\pm 3^{\circ}$

1,4-DHB(A) + 1,3-DAB(B)

Data were obtained by the thaw-melt method and checked by thermal analysis¹³. The reported eutectics¹² are $E_1 =$ 122.2 °C, $x_B = 0.41$ and $E_2 = 62.0$ °C, $x_B = 0.93$. The 1:1 compound melts congruently at¹² 128.0 °C. Upon optimization, the data¹² appeared to be of uniformly good quality and so all were weighted equally. The phase diagram, Fig. 15, was calculated with the use of Eq. (48)



FIG 13. The system 1,2-DHB (A) + 1,3-DAB (B).



FIG. 14. The system 1,3-DHB (A) + 1,3-DAB (B).



FIG. 15. The system 1,4-DHB (A) + 1,3-DAB (B).

$$G^{1}(\ell) = -9000 x_{\rm A} x_{\rm B} \, \text{J/mol}$$
 (48)

Since the liquidus data for the compound are of good quality and cover a wide temperature range, more complete expressions for the thermodynamic properties of the compound (AB)/2 were calculated:

$$\Delta_{fus}G^{\circ} = 100917 - 1443.010T + 198.72462T \ln T \text{ J/mol} (49)$$

$$\Delta_{f}G^{\circ} = -103167 + 1437.2485T - 198.72462T \ln T \text{ J/mol} (50)$$

For uniformity of presentation, these properties are given in Table A2 in shorter form, viz., Eqs. (49) and (50) evaluated at the melting point of the compound (126.3 °C). The calculated eutectics are $E_1 = 122.9$ °C, $x_B = 0.391$ and $E_2 = 61.3$ °C, $x_B = 0.963$.

Probable maximum inaccuracy in calculated diagram: $\pm 2^{\circ}$

6.2.2. Naphthols as Second Components

1-N(A) + 1,3-DAB(B)

Data were obtained by the thaw-melt method and checked by thermal analysis¹⁰. The reported¹⁰ eutectics are $E_1 = 33.0$ °C, $x_B = 0.37$ and $E_2 = 32.0$ °C, $x_B = 0.75$. The 1:1 compound melts congruently at¹⁰ 36.5 °C. The experimental RHS liquidus¹⁰ limiting slope differs noticeably from the thermodynamic value. In the optimization, the eutectic temperatures and the LHS liquidus data were given greater weight. The phase diagram, Fig. 16, was calculated with the use of Eq. (51)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-22470 + 9840 x_{\rm B}) \, \text{J/mol}$$
 (51)

and the calculated thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus}G^{\circ} = 61722 - 199.2891T \,\text{J/mol} \tag{52}$$

$$\Delta_{\rm f}G^{\circ} = -66110 + 193.5271T \,\rm J/mol \tag{53}$$

The calculated heat and entropy of fusion of the compound, Eq. (52), are considerably greater than those of either pure components (Table 1). The excess Gibbs energy of the liquid, Eq. (51), is highly negative to an unusual degree. The temperature range covered by the compound liquidi is small (4.5°), and consequently the uncertainty in calculated thermodynamic properties is high. For this reason, these data appear in Table A2 in parentheses, indicating a need for confirmation. Other calculated data are: $E_1 = 33.0$ °C, $x_B = 0.335$ and $E_2 =$ 32.0 °C, $x_B = 0.721$ and the compound melts congruently at 36.5 °C.

Probable maximum inaccuracy in calculated liquidus: $\pm 4^{\circ}$

2-N(A) + 1,3-DAB(B).

Data were obtained by the thaw-melt method^{10.21} and checked by thermal analysis¹⁰. The observed eutectics are

	x _B	°C	Ref.
 1	0.09	103.2	10
	0.15	111.0	21
2	0.97	59.0	10
	0.96	60.5	21

and the 2:1 compound melts congruently^{10,21} at 115.5 or 119.0 °C. This compound was characterized by its IR spectrum²¹. The LHS limiting liquidus slope of the later work²¹ is theoretically correct, while the other¹⁰ is grossly inaccurate. In the optimization, it was found that the lower melting point¹⁰ of the 2:1 compound was more consistent with the rest of the



FIG. 16. The system 1-N (A) + 1,3-DAB (B).

phase diagram. The phase diagram, Fig. 17, was calculated with the use of Eq. (54). The excess Gibbs energy of the liquid, calculated principally from the preferred LHS liquidus²¹, is

$$G^{\rm E}(\ell) = -3602x_{\rm A}x_{\rm B} \,\mathrm{J/mol}$$
 (54)

Since the liquidus of the 2:1 compound covers a wide temperature range, more complete expressions for the thermodynamic properties of the compound $(A_2B)/3$ could be calculated:

$$\Delta_{\rm fus}G^{\circ} = 242194 - 3985.7635T + 563.94108T \ln T \,\text{J/mol} (55)$$

$$\Delta_{\rm f}G^{\rm T} = -242995 + 3980.4731 - 563.940921 \,\ln l \,\rm{J/mol} \,\,(56)$$

For uniformity of presentation, these values are given in Table A2 in shorter form, viz., Eqs. (55) and (56) evaluated at the melting point of the compound (115.5 °C). The calculated eutectics are $E_1 = 109.6$ °C, $x_B = 0.163$ and $E_2 = 61.0$ °C, $x_B = 0.957$.

Probable maximum inaccuracy in calculated diagram: $\pm 10^{\circ}$ (LHS) $\pm 3^{\circ}$ (RHS).

6.2.3. Phenois and Substituted Phenois as Second Components

P (A) + 1,3-DAB (B)

Data were obtained by thermal analysis⁴ and the thaw-melt method, checked by thermal analysis¹². The observed eutectics¹² are $E_1 = 29.4$ °C, $x_B = 0.18$ and $E_2 = 40.0$ °C, $x_B = 0.81$. According to the later work¹², there is one congruently melting compound (1:1, at 52.8 °C). The earlier work⁴ postulated a compound of undetermined stoichiometry (2:1, 3:2 or 1:1). The central part of the phase diagram is poorly defined, as is the phenol liquidus. Preliminary calculations showed that the assumption of two compounds was not thermodynamically compatible with the general shape of the liquidus. Instead, the 1:1 compound and the RHS eutectic temperature were taken as defining features of the calculated phase diagram. The final diagram, Fig. 18, was calculated with the use of Eq. (57)

$$G^{\rm E}(\ell) = -5673 x_{\rm A} x_{\rm B} \, {\rm J/mol}$$
 (57)

and the calculated thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus}G^{\circ} = 17283 - 52.8499T \,\rm J/mol \tag{58}$$

$$\Delta_{\rm f}G^{\,\circ} = -18701 + 47.0887T \,\,{\rm J/mol} \,\,. \tag{59}$$

Although most of the phase diagram remains somewhat uncertain, the calculated thermodynamic properties, Eqs. (57) and (58) are of reasonable magnitude. Other calculated data are: $E_1 = 25.8$ °C, $x_B = 0.155$ and $E_2 = 40.0$ °C, $x_B = 0.750$ and the compound melts congruently at 53.9 °C.

Probable maximum inaccuracy in calculated diagram: $\pm 2^{\circ}$.

2-NP(A) + 1,3-DAB(B)

Data were obtained by thermal analysis⁴ and by the thawmelt method⁸. This is a simple eutectic system. The observed eutectic is⁴ 33.5 °C, $x_B = 0.33$ or⁸ 34.3 °C, $x_B = 0.35$. The data of Dhillon⁸ lie everywhere somewhat higher than the other⁴. In the optimization, all data were weighted equally. The calculated phase diagram, Fig. 19, was generated with the use of Eq. (60)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (3687 - 1008 x_{\rm B}) \,\mathrm{J/mol}$$
 (60)

and the calculated eutectic is 33.6 °C, $x_B = 0.357$. Probable inaccuracy in calculated diagram: $\pm 2^\circ$.



FIG. 17. The system 2-N(A) + 1,3-DAB(B).



FIG. 18. The system P(A) + 1,3-DAB (B).



FIG. 19. The system 2-NP (A) + 1,3-DAB (B).

3-NP(A) + 1, 3-DAB(B).

Data were obtained by thermal analysis⁴ and by the thawmelt method⁸. The reported eutectics⁸ are $E_1 = 70.9$ °C, $x_B = 0.25$ and $E_2 = 50.2$ °C, $x_B = 0.83$. Both investigations report the existence of a 1:1 compound melting congruently at⁴ 80.2 °C or⁸ 81.6 °C. In addition, a congruently melting 2:1 compound was postulated⁴. The data from thermal analysis⁴ are more plentiful than the other⁸ in the region of the 2:1 composition, and indicate a break in the liquidus. The phase diagram as a whole proved to be reproduced best by the assumption of two congruently melting compounds, 1:1 and 2:1. The calculated phase diagram, Fig. 20, was generated with the use of Eq. (61)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-9309 + 4491 x_{\rm B}) \, \text{J/mol}$$
 (61)

and the calculated thermodynamic properties of the compounds are, for $(A_2B)/3$

$$\Delta_{\rm fus}G^{\circ} = 14774 - 42.4601T \,\rm{J/mol} \tag{62}$$

 $\Delta_{\rm r}G^{\circ} - -16510 + 37.1689T \,\rm J/mol \tag{63}$

and for (AB)/2

$$\Delta_{\rm fus}G^{\circ} = 12402 - 35.0686T \,\rm J/mol \tag{64}$$

$$A_{G}^{\circ} = -14168 + 29.3078T \,\text{J/mol} \,, \tag{65}$$

Other calculated data are: $E_1 = 70.4$ °C, $x_B = 0.231$; $E_2 = 74.2$ °C, $x_B = 0.375$; $E_3 = 50.1$ °C, $x_B = 0.811$; the 2:1 and 1:1 compounds melt congruently at 74.8 °C and 80.5 °C, respectively.

Probable maximum inaccuracy in calculated diagram: $\pm 2^{\circ}$.

4-NP(A) + 1,3-DAB(B).

Data were obtained by thermal analysis⁴ and the thaw-melt method⁸. The reported eutectics⁸ are $E_1 = 102.0$ °C, $x_B = 0.12$ and $E_2 = 53.3$ °C, $x_B = 0.84$. The congruent melting point of the 1:2 compound is⁴ 119.9 °C or⁸ 121.8 °C. In the optimization, the excess Gibbs energy of the liquid

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-3900 + 1700 x_{\rm B}) \, \text{J/mol}$$
 (66)

was obtained by weighting the eutectic temperatures preferentially. The calculated phase diagram, Fig. 21, was generated with the use of Eq. (66). Since the compound liquidi cover an extended range of temperature, more complete expressions for the thermodynamic properties could be calculated. Thus, for $(A_2B)/3$,

$$\Delta_{\rm fus}G^{\circ} = 35809 - 465.074T + 62.6131T \ln T \,\text{J/mol} \quad (67)$$

$$\Delta_{\rm f}G^{\circ} = -36550 + 459.782T - 62.6131T \ln T \,\text{J/mol} \,. \tag{68}$$

For uniformity of presentation, these data appear in Table A2 in shorter form, viz., Eqs. (67) and (68) evaluated at the melting point (121.0 °C). Other calculated data are: $E_1 - 102.1$ °C, $x_B = 0.137$ and $E_2 = 53.1$ °C, $x_B = 0.840$.

Probable maximum inaccuracy in calculated liquidus: $\pm 2^{\circ}$

2,4-DNP(A) + 1,3-DAB(B).

Data were obtained by thermal analysis⁵. The reported eutectics⁵ are $E_1 = 91.5$ °C, $x_B = 0.36$ and $E_2 = 53.0$ °C, $x_B = 0.88$. The 1:1 compound metts congruently at⁵ 100.0 °C. The reported melting points of the pure components are low⁵, so in the optimization more weight was given to the compound liquidus data. The phase diagram, Fig. 22, was calculated with the use of Eq. (69)

$$G^{\rm E}(\ell) = -1357 x_{\rm A} x_{\rm B} \, {\rm J/mol}$$
 (69)



FIG. 20. The system 3-NP (A) + 1,3-DAB (B).



FIG. 21. The system 4-NP (A) + 1,3-DAB (B).



FIG. 22. The system 2,4-DNP (A) + 1,3-DAB (B).

and the calculated thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus}G^{\circ} = 10481 - 28.0128T \,\rm J/mol \tag{70}$$

$$\Delta_{\rm f}G^\circ = -10820 + 22.2488T \,\text{J/mol} \,. \tag{71}$$

Considerable experimental scatter remains, which increases the uncertainty of the calculations. Other calculated data are: $E_1 = 92.9$ °C, $x_B = 0.330$ and $E_2 = 55.2$ °C, $x_B = 0.871$; the compound melts congruently at 101.0 °C.

Probable maximum inaccuracy in calculated diagram: $\pm 4^{\circ}$.

6.2.4. Other Compounds as Second Component

BENZ(A) + 1,3-DAB(B)

Data were obtained by the thaw-melt method and checked by thermal analysis¹¹. This is a simple eutectic system. The data were tabulated but not plotted in this report¹¹; the eutectic temperature is 39.5 °C, and when the data are plotted, the eutectic composition is $x_B \sim 0.54$. The experimental¹¹ limiting liquidus slopes at both ends of the diagram both differ noticeably from thermodynamic expectation. The eutectic temperature was taken as the most accurate datum in this system. Based upon this assumption, optimization showed that most of the liquidus data lie too high; in particular, the sudden curvature in the benzamide liquidus is suspect. The phase diagram, Fig. 23, was calculated with the use of Eq. (72)

$$G^{\rm E}(\ell) = -2125 x_{\rm A} x_{\rm B} \, {\rm J/mol}$$
 (72)

and the liquidus remains poorly defined. The calculated eutectic is 39.5 °C, $x_B = 0.698$.

Probable maximum inaccuracy in calculated liquidus: $\pm 10^{\circ}$.

6.3. Systems with 1,4-Diaminobenzene

6.3.1. Dihydroxybenzenes as Second Component

1,2-DHB(A) + 1,4-DAB(B)

The data were obtained by the thaw-melt method^{13,15,18} and checked by thermal analysis¹³. Identical data appear in two reports^{15,18}. A eutectic summary is as follows:

	x _B	°C	Ref.
	0.14	89.5	13
-	0.13	92.5	15,18
2	0.62	100.3	13
-	0.68	100.5	15,18

The earlier work¹³ reported the existence of a 2:1 compound melting congruently at 109.3°, while the later work^{15,18} showed a 1:1 compound melting congruently at 110.0 °C. This compound was characterized by its IR spectrum^{15,18}. Xray analysis¹⁸ showed that the compound has monoclinic crystal structure, with cell parameters a = 1.026 nm, b = 0.610 nm, c = 0.486 nm and $\beta = 72.0^{\circ}$. The heat of fusion of the 1:1 compound is¹⁸ 18680 J/mol. There is disagreement about the E_1 temperature, and the limiting liquidus slope at the RHS¹³ is faulty. In order to construct a thermodynamically consistent phase diagram, it is necessary to include both 2:1 and 1:1 compounds. In the optimization, the E_2 temperature and the melting point of the 1:1 compound were given greater weight than other data. The phase diagram, Fig. 24, was calculated with the use of Eq. (73)

$$G^{\rm E}(\ell) - x_{\rm A} x_{\rm B} (-20200 + 8833 x_{\rm B}) \, \rm J/mol$$
 (73)



FIG. 23. The system BENZ (A) + 1,3-DAB (B).

and the thermodynamic properties of the compounds are, for $(A_2B)/3$

$$\Delta_{\rm fus} G^{\circ} = 31695 - 83.2873T \,\rm J/mol \tag{74}$$

$$\Delta_{\rm f}G^\circ = -35530 + 77.9870T \,\,{\rm J/mol} \tag{75}$$

and for (AB)/2

$$\Delta_{\rm fus}G^{\circ} = 17652 - 46.0707T \,\rm J/mol \tag{76}$$

$$\Delta_{\rm f} G^{\circ} = -21598 + 40.3075T \,\,{\rm J/mol} \tag{77}$$

The calculated E_1 temperature falls between the two reported values, and there is uncertainty concerning the central part of the diagram. Other calculated data are: $E_1 = 90.4$ °C, $x_B = 0.128$; $E_2 = 105.7$ °C, $x_B = 0.409$; $E_3 = 100.3$ °C, $x_B = 0.651$ and the 2:1 and 1:1 compounds melt congruently at 107.4 and 110.0 °C, respectively.

Probable maximum inaccuracy in calculated diagram: $\pm 4^{\circ}$.

1,3-DHB (A) + 1,4-DAB (B).

Data were obtained by the thaw-melt method^{13,15,16} and checked by thermal analysis¹³. The reported eutectics are

<u>,</u> ,	x _B	°C	Ref.	
E1	0.14	94.7	13	
-1	0.16	93.5	15,16	
E ₂	0.68	102.3	13	
	0.66	102.5	15,16	

Data are identical in two reports^{15,16}. The 1:1 compound melts congruently at¹³ 118.5 °C or^{15,16} 119.0 °C. It was characterized by its IR^{15,16} as well as by its unindexed X-ray¹⁶ spectra; the crystal structure is¹⁶ probably monoclinic. The heat of fusion of the 1:2 compound¹⁶ is 21783 J/mol. In order to construct a thermodynamically consistent phase diagram, another compound – of assigned stoichiometry 2:1 – must be included. All liquidus data were optimized, and greater weight was given to the E_2 temperature and the melting point of the 1:2 compound. The phase diagram, Fig. 25, was calculated with the use of Eq. (78)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-12098 - 2575 x_{\rm B}) \, \text{J/mol}$$
 (78)

and the calculated thermodynamic properties of the compounds are, for $(A_2B)/3$

$$\Delta_{\rm fus}G^{\circ} = 15305 - 39.9413T \,\rm J/mol \tag{79}$$

$$\Delta_{\rm f}G^{\circ} = -17803 + 34.6510T \,\rm{J/mol} \tag{80}$$

and for (AB)/2

$$\Delta_{\rm fus}G^{\circ} = 10335 - 26.3636T \,\rm J/mol \tag{81}$$

$$\Delta_{\rm f}G^{\circ} = -13038 + 20.6024T \,\text{J/mol} \,. \tag{82}$$

The calculated heat of fusion of the 1:1 compound thus differs considerably from the experimental value¹⁶. A separate calculation showed, however, that a heat of fusion of 20 kJ/mol would be incompatible with the well-defined E_2 eutectic.

Other calculated data are: $E_1 = 93.5$ °C, $x_B = 0.161$; $E_2 = 109.0$ °C, $x_B = 0.380$; $E_3 = 102.3$ °C, $x_B = 0.663$. The 2:1 and



FIG 24. The system 1,2-DHB (A) + 1,4-DAB (B).

1:1 compounds melt congruently at 110.0 and 118.9 °C, respectively, and the resorcinol transition appears on the calculated liquidus at 96.0 °C, $x_B = 0.142$.

Probable maximum inaccuracy in calculated diagram: $\pm 4^{\circ}$

1,4-DHB(A) + 1,4-DAB(B).

Data were obtained by the thaw-melt method and checked by thermal analysis¹². The reported¹² eutectics are $E_1 =$ 152.3 °C, $x_B = 0.22$ and $E_2 = 135.0$ °C, $x_B = 0.92$. The 1:1 compound melts congruently at¹² 193.8 °C. In the experimental phase diagram¹², the two liquidi of the compound are asymmetric about the 1:1 composition (the data could be fitted as they are with a slightly off-center stoichiometry). For the optimization, the E_1 and E_2 temperatures and the melting point of the compound were given more weight than other data. The phase diagram, Fig. 26, was calculated with the use of Eq. (83)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-2206 + 4770 x_{\rm B}) \, \text{J/mol}$$
 (83)

and the calculated thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus}G^{\circ} = 8277 - 17.7257T \,\,\text{J/mol} \tag{84}$$

$$\Delta_{\rm f}G^{\circ} = -8232 + 11.9612T \,\,{\rm J/mol} \,\,. \tag{85}$$

The calculated heat of fusion of the compound is only about one-third of that of either pure component; this is unusual, but is a result of the thermodynamic constraints posed by the eutectic temperatures. Other calculated data are: $E_1 = 152.3 \,^{\circ}$ C, $x_B = 0.237$; $E_2 = 135.0 \,^{\circ}$ C, $x_B = 0.895$ and the compound melts congruently at 193.8 $^{\circ}$ C.

Probable maximum inaccuracy in calculated liquidus: $\pm 5^{\circ}$.

6.3.2. Naphols as Second Component

1-N(A) + 1,4-DAB(B)

Data were obtained by the thaw-melt method^{10,20,22} and checked by thermal analysis¹⁰. The data in two reports^{20,22} are identical. A eutectic summary is as follows:

	ХB	°C	Ref.
E	0.07	85.0	10
	0.07	89.0	20,22
E_2	0.56	96.2	10
-	0.62	98.5	20,22

The congruent melting point of the 2:1 compound is 10,20,22 111.5 °C. This compound was characterized by its IR^{20,22} and X-ray²² (unindexed) spectra, as well as by microphotography²². The experimental limiting liquidus slope¹⁰ for 1-naphthol is grossly in error, and so the lower E_1 eutectic temperature¹⁰ is faulty. There is disagreement concerning both eutectic temperatures, especially E_1 . The heat of fusion of the compound²² is 18980 J/mol. In view of disagreement in experimental data, the RHS liquidus data and the liquidus data of the compound were given greater weight in the optimization, and the experimental heat of fusion of the compound²² was used. The phase diagram, Fig. 27, was calculated with the use of Eq. (86)

$$G^{\rm E}(\ell) = -6172 x_{\rm A} x_{\rm B} \, {\rm J/mol}$$
 (86)

and the thermodynamic properties of the compound $(A_2B)/3$ are

$$\Delta_{\rm fus}G^{\circ} = 18980 - 49.3436T \,\rm J/mol \tag{87}$$

$$\Delta_{\rm f}G^{\circ} = -20355 + 44.0572T \,\,{\rm J/mol} \tag{88}$$



FIG 25. The system 1,3-DHB (A) + 1,4-DAB (B).







FIG. 27. The system 1-N (A) + 1,4-DAB (B).

In Eq. (87), the heat of fusion is the experimental value²². Considerable uncertainty remains about the eutectic temperatures. Other calculated data are: $E_1 = 90.2$ °C, $x_B = 0.090$; $E_2 = 95.4$ °C, $x_B = 0.587$ and the compound melts congruently at 111.5 °C.

Probable maximum inaccuracy in calculated diagram: \pm 5°.

2-N(A) + 1,4-DAB(B)

Data were obtained by the thaw-melt method^{10,20,22} and checked by thermal analysis¹⁰. The data in two reports^{20,22} are identical. The reported eutectics are

	X _B	°C	Ref.	
<i>E</i> ₁	0.05	116.2	10	
	0.07	118.0	20,22	
E_2	0.75	118.1	10	
	0.75	121.5	20,22	

The 2:1 compound melts congruently at¹⁰ 151.7 °C or^{20.22} 154.5 °C. This compound was characterized by its $IR^{20.22}$ and X-ray²² (unindexed) spectra, as well as by microphotography²². The heat of fusion of the compound²² is 19540 J/mol. There is data scatter over the whole composition range, especially pronounced in the central region. In order to construct a thermodynamically consistent phase diagram, a second compound must be included; its stoichiometry was set at 1:1 as a most probable value. All liquidus data were weighted equally in the optimization. The phase diagram, Fig. 28, was calculated with the use of Eq. (89)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} \left(-9600 + 3829 x_{\rm B}\right) \,\mathrm{J/mol}$$
 (89)

and the calculated thermodynamic properties of the compounds are, for $(A_2B)/3$

$$\Delta_{\rm fus}G^{\circ} = 22509 - 52.6342T \,\rm J/mol \tag{90}$$

$$\Delta_{\rm f}G^{\circ} = -24359 + 47.3383T \,\text{J/mol} \tag{91}$$

and for (AB)/2

$$\Delta_{\rm fus}G^{\circ} = 9040 - 21.1588T \,\text{J/mol} \tag{92}$$

$$\Delta_{\rm f}G^{\circ} = -10961 + 15.3924T \,\rm J/mol \tag{93}$$

The calculated heat of fusion of the 1:1 compound is rather small compared to that of the 2:1 compound and those of the individual components. In an alternative construction, the 1:1 compound could be made to melt incongruently at a lower temperature, and its liquidus would fall closer to the data of Dhillon and Singh¹⁰. The existing liquidus data, however, are too ambiguous to support a definitive choice. Other calculated data are: $E_1 = 118.0$ °C, $x_B = 0.063$; $E_2 = 151.3$ °C, $x_B = 0.437$; $E_3 = 119.0$ °C, $x_B = 737$; and 2:1 and 1:1 compounds melt congruently at 154.5 and 154.1 °C, respectively.

Probable maximum inaccuracy in calculated diagram: $\pm 7^{\circ}$

6.3.3. Phenol and Substituted Phenols as Second Component

P(A) + 1,4-DAB(B)

Data were obtained by thermal analysis⁴ and by the thawmelt method (checked by thermal analysis).¹² The reported eutectics¹² are $E_1 = 40.3$ °C, $x_B = 0.03$ and $E_2 = 82.8$ °C, $x_B =$ 0.59. The 2:1 compound melts congruently at⁴ 104.8 °C or¹² 105.6 °C. Although there are no eutectic halts from thermal analysis⁴ for E_2 , it is evident that the E_2 temperature defined by the liquidus data of Kremann and Petritschek⁴ is about 12°



FIG. 28. The system 2-N (A) + 1,4-DAB (B).

higher than the one from the thaw-melt method. This is a serious discrepancy. In preliminary calculations, it was found that, in order to reproduce the lower E_2 temperature¹², the RHS liquidus must lie below the liquidus data of both investigators^{4,12}. The liquidus of the compound is well defined by thermal analysis⁴, so it was decided to weight all liquidus data equally in the optimization. The phase diagram, Fig. 29, was calculated with the use of Eq. (94)

$$G^{\rm E}(\ell) = -5334 x_{\rm A} x_{\rm B} \, \text{J/mol}$$
 (94)

and the calculated thermodynamic properties of the compound $(A_2B)/3$ are

$$\Delta_{\rm fus}G^{\circ} = 12566 - 33.1103T \,\,{\rm J/mol} \tag{95}$$

$$\Delta_{\rm f}G^\circ = -13752 + 27.8201T \,\rm J/mol \tag{96}$$

Other calculated data are: $E_1 = 39.3$ °C, $x_B = 0.022$ and $E_2 = 91.0$ °C, $x_B = 0.544$; the compound melts congruently at 106.4 °C.

Probable maximum inaccuracy in calculated diagram: $\pm 3^{\circ}$ (LHS) $\pm 8^{\circ}$ (RHS).

2-NP (A) + 1,4-DAB (B)

Data were obtained by the thaw-melt method⁸ and by thermal analysis⁴. The reported eutectic is⁴ 42.5 °C, $x_B = 0.06$ or⁸ 39.6 °C, $x_B = 0.05$; this is a simple eutectic system. The liquidus is well defined by both investigators^{4.8}. All liquidus data^{4.8} were weighted equally in the optimization and the phase diagram, Fig. 30, was calculated with the use of Eq. (97)

$$G^{\rm E}(\ell) = 1595 x_{\rm A} x_{\rm B} \, \text{J/mol} \,.$$
 (97)

All liquidus data^{4,8} lie close to the calculated liquidus, but the calculated eutectic temperature lies above all the eutectic data^{4,8}. The experimental limiting liquidus slopes^{4,8} at both composition extremes are thermodynamically correct. In a case such as this, the experimental liquidus, well defined over the whole composition range, was taken as definitive and thermodynamically entails a eutectic temperature higher than that indicated by experiment. The calculated eutectic is 41.9 °C, $x_B = 0.061$.

Probable maximum inaccuracy in calculated liquidus: $\pm 2^{\circ}$.

3-NP (A) + 1,4-DAB (B)

Data were obtained by thermal analysis⁴ and by the thawmelt method⁸. The reported eutectics⁸ are $E_1 = 92.9$ °C, $x_B = 0.03$ and $E_2 = 110.0$ °C, $x_B = 0.65$. The 2:1 compound melts congruently at⁸ 139.0 °C. In addition to the 2:1 compound, the earlier work⁴ postulated the existence of a congruently melting 1:2 compound and possibly another (incongruent, 1:3 or 1:4). The data from thermal analysis⁴ are plentiful in the composition interval $0.6 < x_B < 0.8$, and definitely indicate a break in the liquidus. The liquidus in this region could then be represented best by a eutectic and peritectic very close to each other (the existence of a 1:2 congruently melting compound would be excluded by thermodynamic constraints). The stoichiometry of the incongruently melting compound was assigned arbitrarily as 1:4.

The liquidus of the 2:1 compound is well defined by both investigators^{4,8}. The LHS experimental^{4,8} limiting liquidus slope is much steeper than thermodynamic expectation. The excess Gibbs energy of the liquid was obtained by optimization of the RHS liquidus data^{4,8}:

$$G^{\rm E}(\ell) = -5000 x_{\rm A} x_{\rm B} \, \text{J/mol} \,.$$
 (98)



FIG. 29. The system P(A) + 1,4-DAB(B).

The calculated thermodynamic properties of the 2:1 compound $(A_2B)/3$ are

$$\Delta_{\rm fus}G^{\circ} = 18273 - 44.4328T \,\rm J/mol \tag{99}$$

$$\Delta_{\rm f}G^\circ = -19384 + 39.1446T \, \text{J/mol} \,. \tag{100}$$

Since the temperature range in which the suggested AB_4 compound is in equilibrium with the liquid is extremely narrow, no thermodynamic properties for this compound could be obtained by optimization; instead, quantities of reasonable magnitude were assigned, which reproduced the observed eutectic⁸ and peritectic⁴ temperatures. The assigned quantities for the compound (AB₄)/5, of nominal stoichiometry, are

$$\Delta_{\rm fus}G^\circ = 29032 - 75.0000T \,\text{J/mol} \tag{101}$$

$$\Delta_{\rm f} G^{\circ} = -29800 + 70.8397T \, \text{J/mol} \,. \tag{102}$$

The phase diagram, Fig. 31, was calculated with the use of Eqs. (98), (100) and (102). The existence of the 1:4 compound remains conjectural, and the calculated E_1 temperature, lying above experimental data^{4,8}, is retained as being necessarily entailed by the better defined liquidus of the 2:1 compound. Other calculated data are: $E_1 = 94.5$ °C, $x_B = 0.037$; $E_2 = 110.2$ °C, $x_B = 0.660$ and the peritectic is 111.0 °C, $x_B = 0.680$.

Probable maximum inaccuracy in calculated liquidus: \pm 3°.

4-NP (A) + 1,4-DAB (B)

Data were obtained by thermal analysis⁴, the thaw-melt method⁸ and the microthermal method³⁹. There is disagreement among investigators concerning the number and stoichiometry of intermediate compounds in this system. The existence of a 4:1 compound is indicated in all reports, melt-

ing congruently at⁴ 134.2 °C or⁸ 135.7 °C or³⁹ 133.0 °C. The earliest work⁴ suggested the existence also of 1:1 and/or 2:1 compounds, while Stancic *et al.*³⁹ show a 1:1 compound melting congruently at 120.0 °C. A eutectic summary is as follows:

	x _B	°C	Ref.
E1	0.02	109.6	8
	0.02	108.0	39
E ₂	0.45	118.0	39
E_3	0.65	109.6	8
-	0.64	109.0	39

If all liquidus data are taken into consideration, it is seen that, in addition to the 4:1 compound, there is another, most probably 2:1 melting incongruently. To obtain the excess Gibbs energy of the liquid, the RHS liquidus data^{4.8.39} were optimized to give

$$G^{\rm E}(\ell) = -3656 x_{\rm A} x_{\rm B} \, {\rm J/mol} \,.$$
 (103)

Liquidus data^{4,8,39} for the 4:1 and 2:1 compounds were optimized together, the main constraint being the E_3 eutectic temperature and composition. The calculated thermodynamic properties of the (A_4 B)/5 compound are

$$\Delta_{\rm fus}G^{\circ} = 14525 - 35.7092T \,\rm J/mol \tag{104}$$

$$\Delta_{\rm f}G^{\,\circ} = -15110 + 31.5500T \,\,{\rm J/mol} \tag{105}$$

and for $(A_2B)/3$

$$\Delta_{\rm fus}G^{\circ} = 28174 - 71.0275T \,\text{J/mol} \tag{106}$$



FIG. 30. The system 2-NP (A) + 1,4-DAB (B).

$$\Delta_{\rm f}G^{\,\circ} = -28987 + 65.7372T \,\,{\rm J/mol} \tag{107}$$

The calculated phase diagram, Fig. 32, was generated with the use of Eqs. (103), (105) and (107). There is considerable data scatter in the diagram. The calculated E_1 eutectic temperature lies above experimental data^{4,8,39} because of the low experimental melting point of 4-nitrophenol⁴ or limiting liquidus data which deviate^{8,39} from thermodynamic expectation. Other calculated data are: $E_1 = 111.6$ °C. $x_B = 0.032$: $E_2 = 109.4$ °C, $x_B = 0.647$; the 4:1 compound melts congruently at 133.6 °C and the peritectic is 123.2 °C, $x_B = 0.382$.

Probable maximum inaccuracy in calculated diagram: $\pm 4^{\circ}$.

2,4-DNP(A) + 1,4-DAB(B)

Data were obtained from thermal analysis⁵. The experimental⁵ melting point of 2,4-dinitrophenol is 5° lower than the accepted value and data are lacking in the central part of the phase diagram. The LHS eutectic temperature⁵ is 107.0 °C and on the RHS, 88.5 °C (no compositions were mentioned⁵). The authors⁵ claim the existence of two congruently melting compounds, 3:1 (118.0 °C) and 2:1 (109.3 °C). In order for there to be a RHS eutectic at 88.5 °C and $x_B \sim 0.75$, there must be a compound in the central part of the phase diagram; a congruently melting 1:1 compound was assigned as a reasonable conjecture. As a guide to the calculations, the three eutectics were taken to be at or near the three eutectic halts indicated experimentally⁵. All liquidus data were included in the optimization. The phase diagram, Fig. 33, was calculated with the use of Eq. (108)

$$G^{\rm E}(\ell) = -27114 x_{\rm A} x_{\rm B} \, \text{J/mol}$$
 (108)

and the calculated thermodynamic properties of the compounds are, for $(A_3B)/4$

$$\Delta_{\rm fus}G^\circ = 39336 - 100.5178T \,\rm J/mol \tag{109}$$

$$\Delta_{\rm f}G^{\circ} = -44419 + 95.8440T \,\,{\rm J/mol} \tag{110}$$

and for (AB)/2

$$\Delta_{\rm fus}G^{\circ} = 25992 - 67.0226T \,\rm J/mol \tag{111}$$

$$\Delta_t G^\circ = -32771 + 61.2614T \,\text{J/mol} \tag{112}$$

Other calculated data are: $E_1 = 107.1$ °C, $X_B = 0.086$; $E_2 = 110.1$ °C, $x_B = 0.404$; $E_3 = 89.4$ °C, $x_B = 0.724$; the 3:1 and 1:1 compounds melt congruently at 118.2 and 114.7 °C, respectively.

Probable maximum inaccuracy in calculated diagram: \pm 5°.

6.3.4. Other Compounds as Second Components

BENZ (A) + 1,4-DAB (B)

Data were obtained by the thaw-melt method and checked by thermal analysis¹¹. The data were tabulated but not plotted. This is a simple eutectic system. The eutectic temperature¹¹ us 87.2 °C; if the data are plotted, the eutectic composition is seen to be $x_B \sim 0.4$. All the liquidus data were weighted equally in the optimization, with the following result:

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} \left(-3695 + 7691 x_{\rm B} - 7457 x_{\rm B}^2\right) \,\mathrm{J/mol}$$
(113)

and the phase diagram, Fig. 34, was calculated with the use of Eq. (113). The calculated eutectic is 87.2 °C, $x_B = 0.396$.

Probable maximum inaccuracy in calculated diagram: $\pm 2^{\circ}$.



FIG. 31. The system 3-NP (A) + 1,4-DAB (B).



Fig. 32. The system 4-NP (A) + 1,4-DAB (B).



FIG. 33. The system 2,4-DNP (A) + 1,4-DAB (B).

BA (A) + 1,4-DAB (B)

Data were obtained by the thaw-melt method¹⁹ and by the microthermal method³⁹. A eutectic summary is as follows:

	х _в	°C	Ref.	
<i>E</i> ₁	0.19	107.0	19	
	0.15	107.3	39	
E_2	0.77	124.5	19	
	0.79	128.1	39	

The 1:1 compound melts congruently at¹⁹ 145.0 °C or³⁹ 144.0 °C and its heat of fusion¹⁹ is 19460 J/mol. It was characterized by its IR and unindexed X-ray spectra¹⁹; its crystalline structure is¹⁹ probably monoclinic. The data are scattered in most parts of the diagram. The experimental limiting liquidus slopes^{19,39} at the RHS are faulty. For construction of the phase diagram, the E_1 eutectic temperature and 1:1 compound melting point were given most weight. Since the liquidus of the compound is poorly defined, the experimental¹⁹ heat of fusion was used in the calculations. The calculated phase diagram, Fig. 35, was generated with the use of Eq. (114)

$$G^{E}(\ell) = x_{A}x_{B}(-5400 + 2000x_{B}) \text{ J/mol}$$
 (114)

and the thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus}G^{\circ} = 19460 - 46.5940T \,\rm J/mol \tag{115}$$

$$\Delta_{\rm f}G^\circ = -20537 + 40.7755T \,\,\text{J/mol} \tag{116}$$

In Eq. (115), the heat of fusion is the experimental value¹⁹. The calculated liquidus and eutectic temperatures are a com-

promise between the data of the two investigators^{19,39} and much uncertainty remains. Other calculated data are: $E_1 = 107.1 \,^{\circ}\text{C}$, $x_B = 0.153$; $E_2 = 124.9 \,^{\circ}\text{C}$, $x_B = 0.784$ and the compound melts congruently at 144.5 $^{\circ}\text{C}$.

Probable maximum inaccuracy in calculated diagram: $\pm 10^{\circ}$.

3-NBA(A) + 1,4-DAB(B)

Data were obtained by the thaw-melt method²³. The observed²³ eutectics are $E_1 = 130.0$ °C, $x_B = 0.12$ and $E_2 = 124.0$ °C, $x_B = 0.82$. The 2:1 compound melts congruently at²³ 163.0 °C and its heat of fusion ²³ is 18900 J/mol. It was characterized by its unindexed X-ray spectra, as well as by microphotography²³. Thermodynamic constraints require that there be another compound to the right of the 2:1 composition; the stoichiometry 1:1 was assigned as a most probable value. For the calculation of the phase diagram, the two eutectics, the melting points of the 2:1 compound and of the 1:1 compound (that is, the liquidus datum at $x_B = 0.5$) were taken as principal guides. The calculated phase diagram, Fig. 36, was generated with the use of Eq. (117)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-9510 - 200 x_{\rm B}) \, \text{J/mol}$$
 (117)

and the thermodynamic properties of the compounds are, for $(A_2B)/3$

$$\Delta_{\rm fus}G^{\circ} = 11946 - 27.3897T \,\text{J/mol} \tag{118}$$

$$\Delta_{\rm f}G^{\circ} = -14074 + 22.0951T \,\rm J/mol \tag{119}$$

and for (AB)/2

$$\Delta_{\rm fus}G^{\circ} = 22947 - 53.0505T \,\rm J/mol \tag{120}$$

$$\Delta_t G^\circ = -25350 + 47.2934T \, \text{J/mol} \tag{121}$$



FIG. 34. The system BENZ (A) + 1,4-DAB (B).



FIG. 35. The system BA (A) + 1,4-DAB (B).



Fig. 36. The system 3-NBA (A) + 1,4-DAB (B).

Other calculated data are: $E_1 = 130.0$ °C, $x_B = 0.124$; $E_2 = 157.6$ °C, $x_B = 0.426$; $E_3 = 124.0$ °C, $x_B = 0.821$; the 2:1 and 1:1 compounds melt congruently at 163.0 and 159.4 °C, respectively.

Probable maximum inaccuracy in calculated liquidus: $\pm 5^{\circ}$.

6.4. Systems with 4,4'-Diaminobiphenyl (Benzidine)

6.4.1. Di- and Trihydroxybenzenes as Second Components

1,2-DHB (A) + 4,4'-DABP (B)

Data were obtained by the thaw-melt²⁵ and visual-polythermal³⁷ methods. There is disagreement concerning the number and stoichiometry of intermediate compounds. The earlier work³⁷ indicated two compounds, 3:1 and 1:1, melting congruently at 145.0 and 140.0 °C, respectively. In the other report²⁵, only a congruently melting 2:1 compound (147.5 °C) is shown. The heat of fusion²⁵ of this 2:1 compound is 27000 J/mol. It was characterized by its IR and unindexed X-ray spectra, as well as by microphotography²⁵. The liquidus data of Bergman and Arestenko³⁷ are more numerous around the 1:1 composition, and definitely show a break in the liquidus. A eutectic summary follows:

	x _B	°C	Ref.
 <i>E</i> ₁	0.03	103.0	25
	0.02	101.0	37
E_2	0.62	138.4	37
E_3	0.85	110.0	25
	0.77	105.5	37

For the optimization, 2:1 and 1:1 stoichiometries were assumed, and the eutectic data and 2:1 compound melting point of the later work²⁵ were weighted preferentially. Preliminary calculations showed that an incongruently melting 1:1 compound fitted best. The phase diagram, Fig. 37, was calculated with the use of Eq. (122)

$$G^{\rm E}(\ell) = -3507 x_{\rm A} x_{\rm B} \, {\rm J/mol}$$
 (122)

and the calculated thermodynamic properties of the compounds are, for $(A_2B)/3$

$$\Delta_{\rm fus}G^{\circ} = 22126 - 52.5956T \,\rm J/mol \tag{123}$$

$$\Delta_{\rm f}G^{\circ} = -22905 + 47.3053T \,\rm J/mol \tag{124}$$

and for (AB)/2

$$\Delta_{\rm fus}G^{\circ} = 15678 - 38.0785T \,\rm J/mol \tag{125}$$

$$\Delta_{\rm f}G^{\circ} = -16555 + 32.3173T \,\text{J/mol} \tag{126}$$

Other calculated data are: $E_1 = 103.3$ °C, $x_B = 0.023$; $E_2 = 110.0$ °C, $x_B = 0.807$; the 2:1 compound melts congruently at 147.5 °C and the peritectic is 137.7 °C, $x_B = 0.556$.

Probable maximum inaccuracy in calculated liquidus: $\pm 7^{\circ}$.

1,3-DHB(A) + 4,4'-DABP(B)

Data were obtained by the thaw-melt²⁹ and visual-polythermal³⁷ methods. There is disagreement concerning the number of intermediate compounds in this system. Both reports^{29,37} indicate a 2:1 compound melting congruently at 140.5 °C. This compound was characterized by its IR and unindexed X-ray spectra, as well as by microphotography²⁹. In addition, the older work³⁷ shows a 1:1 compound melting peritectically at 132.0 °C. The eutectic data are



FIG. 37. The system 1,2-DHB (A) + 4,4'-DABP (B).

	x _B	°C	Ref.
 '1	0.05	106.0	29
	0.05	105.0	37
E2	0.85	112.0	29
-	0.81	110.0	37

IThe liquidus data of the earlier work³⁷ are more numerous in the region of the 1:1 composition, and definitely show a break in the liquidus. For the optimization, the eutectic data of the later work²⁹ and the melting point of the 2:1 compound were weighted preferentially; it was apparent that the 1:1 compound liquidus data of Bergman and Arestenko³⁷ were more accurate than the other²⁹. The phase diagram, Fig. 38, was calculated with the use of Eq. (127)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-2400 + 1300 x_{\rm B}) \, \text{J/mol}$$
 (127)

and the calculated thermodynamic properties of the compounds are, for $(A_2B)/3$

 $\Delta_{\rm fus} G^{\circ} = 16490 - 39.8648T \, \rm J/mol \tag{128}$

$$\Delta_{\rm f}G^\circ = -16927 + 34.5745T \,\text{J/mol} \tag{129}$$

and for (AB)/2

$$\Delta_{\rm fus}G^\circ = 15710 - 38.6615T \,\rm J/mol \tag{130}$$

$$\Delta_{\rm f}G^{\circ} = -16148 + 32.9003T \,\text{J/mol} \tag{131}$$

Other calculated data are: $E_1 = 106.0$ °C, $x_B = 0.056$; $E_2 = 112.0$ °C, $x_B = 0.803$; the 2:1 compound melts congruently at

140.5 °C and the peritectic is 133.1 °C, $x_B = 0.517$.

Probable maximum inaccuracy in calculated liquidus: $\pm\,10^\circ$

1,2,3-DHB (A) + 4,4'-DABP (B)

Data were obtained by the thaw-melt method²⁸. The observed eutectics²⁸ are $E_1 = 120.5$ °C, $x_B = 0.14$ and $E_2 = 118.0$ °C, $x_B = 0.90$. The 1:1 compound melts congruently²⁸ at 145.0 °C, and its heat of fusion is 21190 J/mol. It was characterized by its IR and unindexed X-ray spectra, as well as by microphotography²⁸. In the optimization, the eutectic temperatures were weighted preferentially. In a preliminary calculation, it was found that, if the thermodynamic properties of the compound were obtained by optimization, the calculated heat of fusion was ~ 40 kJ/mol; this was rejected as too unrealistic. The experimental²⁸ heat of fusion was therefore used in calculating the phase diagram, Fig. 39, together with the quantity

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-1220 + 1050 x_{\rm B}) \, \text{J/mol}$$
 (132)

The thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus}G^{\circ} = 21190 - 50.7970T \,\rm J/mol \tag{133}$$

$$\Delta_{\rm f}G^{\circ} = -21368 + 45.0432T \,\rm J/mol \tag{134}$$

where the heat of fusion in Eq. (133) is the experimental²⁸ value. Other calculated data are: $E_1 = 120.5 \text{ °C}$, $x_B = 0.159$; $E_2 = 118.0 \text{ °C}$, $x_B = 0.874$ and the compound melts congruently at 144.0 °C.

Probable maximum inaccuracy in calculated liquidus: $\pm 3^{\circ}$.



FIG. 38. The system 1,3-DHB (A) + 4,4'-DABP (B).

6.4.2. Naphthols as Second Component

1-N (A) + 4,4'-DABP (B)

Data were obtained by the thaw-melt³⁰ and the visual-polythermal³⁷ methods. The observed eutectics are

	ХB	°C	Ref.	
E ₁	0.13	85.0	30	
	0.14	87.0	37	
E_2	0.62	97.0	30	
	0.63	93.5	37	

The 1:1 compound melts congruently at³⁰ 100.5 °C or³⁷ 102.0 °C, and its heat of fusion³⁰ is 19380 J/mol. It was characterized by its IR and unindexed X-ray spectra, as well as by microphotography³⁰. The limiting liquidus slope on the RHS, shown in the older work³⁷, is faulty and the observed^{30,37} eutectic temperatures are not in good agreement. The liquidus arms of the compound^{30,37} are more or less asymmetric in both reports. The eutectic temperatures as reported by the later work³⁰ were taken to be more accurate than other phase diagram data. The phase diagram, Fig. 40, was calculated with the use of Eq. (137)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-2750 + 600 x_{\rm B}) \, \text{J/mol}$$
 (135)

and the calculated thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus}G^{\circ} = 27149 - 72.6383T \,\text{J/mol} \tag{136}$$

$$\Delta_{\rm f}G^\circ = -27760 + 66.8771T \,\,{\rm J/mol} \tag{137}$$

The calculated heat of fusion of the compound, Eq. (136), differs significantly from the experimental value³⁰. Separate calculations showed that a heat of fusion of 19.4 kJ/mol was not thermodynamically consistent with the observed³⁰ eutectic temperatures, and the LHS liquidus arm of the compound would remain below the experimental data ($0.2 < x_B < 0.4$). Other calculated data are: $E_1 = 85.0$ °C, $x_B = 0.174$; $E_2 = 97.0$ °C, $x_B = 0.672$ and the compound melts congruently at 100.6 °C.

Probable maximum inaccuracy in calculated liquidus: $\pm 6^{\circ}$.

2-N (A) + 4,4'-DABP (B)

Data were obtained by the thaw-melt²⁶ and visual-polythermal³⁷ methods. The observed eutectics are

	x _B	°C	Ref.	
E ₁	0.03	120.0	26	
	0.01	120.0	37	
E_2	0.91	118.0	26	
	0.92	121.0	37	

The congruent melting point of the 2:1 compound is^{26,37} 176.0 °C. This compound was characterized by its IR, unindexed X-ray and NMR spectra, as well as by microphotography²⁶. Its heat of fusion is²⁶ 30650 J/mol. The experimental limiting liquidus slopes^{26,37} on the LHS are both faulty, which suggests that the reported E_1 temperature^{26,37} is too low. The liquidus data of the two investigations are in poor agreement in the range $0.5 < x_B < 0.9$. In any case, thermodynamic constraints require that there be another compound, the most probable stoichiometry being 1:1. Preliminary calculations

FIG. 39. The system 1,2,3-THB (A) + 4,4'-DABP (B).

showed that, on the assumption that there is a 1:1 compound, the liquidus data of Bergman and Arestenko³⁷ in the range $0.5 < x_B < 0.9$ are more accurate than the other²⁶. In the optimization, therefore, the data weighted preferentially were: the E_2 eutectic temperature²⁶, the experimental melting point of the 2:1 compound^{26,37} and the preferred liquidus data³⁷ in the region of greatest discrepancy. The experimental heat of fusion²⁶ of the 2:1 compound proved to give a good fit for the steep LHS liquidus. The phase diagram, Fig. 41, was calculated with the use of Eq. (138)

$$G^{\rm E}(\ell) = -7661 x_{\rm A} x_{\rm B} \, \text{J/mol}$$
 (138)

The thermodynamic properties used for the compound $(A_2B)/3$ are

$$\Delta_{\rm fus}G^{\circ} = 30650 - 68.2400T \,\text{J/mol} \tag{139}$$

$$\Delta_{\rm f}G^\circ = -32352 + 62.9480T \,\text{J/mol}^{-} \tag{140}$$

where, in Eq. (139), the heat of fusion is the experimental²⁶ datum. The optimized thermodynamic properties of the compound (AB)/2 are

$$\Delta_{\rm fus}G^{\circ} = 23382 - 52.4792T \,\rm J/mol \tag{141}$$

$$\Delta_{\rm f}G^\circ = -25300 + 46.7180T \,\,{\rm J/mol} \tag{142}$$

Other calculated data are: $E_1 = 122.7$ °C, $x_B = 0.011$; $E_2 = 172.1$ °C, $x_B = 0.465$; $E_3 = 118.0$ °C, $x_B = 0.898$; the 2:1 and 1:1 compounds melt congruently at 176.0 and 172.4 °C, respectively.

Probable maximum inaccuracy in calculated diagram: $\pm 2^{\circ}$ (LHS) $\pm 20^{\circ}$ (RHS)

6.4.3. Phenol and Substituted Phenols as Second Components

P(A) + 4,4'-DABP(B)

Data were obtained by the visual-polythermal method³⁷. The observed eutectics³⁷ are $E_1 = 40.0$ °C, $x_B = 0.002$ and $E_2 = 113.5$ °C, $x_B = 0.78$ and the 2:1 compound melts congruently³⁷ at 141.0 °C. The experimental³⁷ RHS limiting liquidus slope is faulty, and thus the reported E_2 temperature is probably erroneous. Since there are hence no reliable liquidus data from which to derive the excess Gibbs energy of the liquid, this quantity was set arbitrarily as

$$G^{\rm E}(\ell) = -5000 x_{\rm A} x_{\rm B} \, \text{J/mol}$$
 (143)

This excess Gibbs energy is of the same order as those found by optimization in the system P + diaminobenzenes examined previously. Thermodynamic constraints require that there be another compound, the probable stoichiometry of which would be 1:1. In the optimization step for the compounds, all liquidus data were weighted equally. The calculated thermodynamic properties of the compound $(A_2B)/3$ are

$$\Delta_{\rm fus}G^{\circ} = 19289 - 46.5492T \,\rm J/mol \tag{144}$$

$$\Delta_{\rm f}G^{\circ} = -20400 + 41.2590T \,\rm{J/mol} \tag{145}$$

and for (AB)/2

$$\Delta_{\rm fus}G^{\circ} = 20646 - 50.9073T \,\text{J/mol} \tag{146}$$

$$\Delta_{\rm f}G^\circ = -21896 + 45.1461T \,\,{\rm J/mol} \tag{147}$$

The phase diagram, Fig. 42, was calculated with the use of Eqs. (143), (145) and (147). Other calculated data are: $E_1 =$

FIG. 40. The system 1-N(A) + 4,4'-DABP(B).

FIG. 41. The system 2-N (A) + 4,4'-DABP (B).

40.9 °C, $x_B = 0.001$; $E_2 = 108.7$ °C, $x_B = 0.806$; the 2:1 compound melts congruently at 141.2 °C and the peritectic is 132.3 °C, $x_B = 0.521$.

Probable maximum inaccuracy in calculated diagram: $\pm 8^{\circ}$.

2-NP(A) + 4,4'-DABP(B)

Data were obtained by the visual-polythermal method³⁷. The observed eutectic³⁷ is 37.0 °C, $x_B = 0.14$ and the 1:2 compound melts incongruently at^{37} 101.0 °C. In the optimization, all data were weighted equally. The phase diagram, Fig. 43, was calculated with the use of Eq. (148)

$$G^{\rm E}(\ell) = 406 x_{\rm A} x_{\rm B} \, {\rm J/mol}$$
 (148)

and the calculated thermodynamic properties of the compound $(AB_2)/3$ are

$$\Delta_{\rm fus}G^\circ = 9957 - 26.8113T \,\text{J/mol}$$
(149)

$$\Delta_{\rm f}G^\circ = -9867 + 21.5210T \,\,{\rm J/mol} \tag{150}$$

Other calculated data are: E = 37.3 °C, $x_B = 0.152$ and the peritectic is 97.8 °C, $x_B = 0.624$.

Probable maximum inaccuracy in calculated diagram: $\pm 5^{\circ}$.

3-AP(A) + 4,4'-DABP(B)

Data were obtained by the thaw-melt method²⁴. The reported²⁴ eutectics are $E_1 = 116.0$ °C, $x_B = 0.05$ and $E_2 = 114.0$ °C, $x_B = 0.85$. The 2:1 compound melts congruently at²⁴ 136.0 °C. It was characterized by its IR and unindexed X-ray spectra, as well as by microphotography. The experimental²⁴ limiting liquidus slopes at both LHS and RHS are in error, and the thermodynamic constraints require that there be a second

compound; the 1:1 stoichiometry was chosen as most probable. Preliminary calculations showed that most of the experimental liquidus data²⁴ are apparently more or less erroneous. The following data were taken to be most accurate for purposes of optimization: the E_1 and E_2 temperatures and the experimental melting point of the 2:1 compound. The phase diagram, Fig. 44, was calculated with the use of Eq. (151)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-10000 + 5000 x_{\rm B}) \, \text{J/mol}$$
 (151)

and the calculated thermodynamic properties of the compounds are, for $(A_2B)/3$

$$\Delta_{\rm fus}G^{\circ} = 24651 - 60.2935T \,\rm J/mol \tag{152}$$

$$\Delta_{\rm f}G^{\circ} = -26503 + 55.0000T \,\,{\rm J/mol} \tag{153}$$

and for (AB)/2

$$\Delta_{\rm fus}G^{\circ} = 30691 - 75.8833T \,\rm J/mol \tag{154}$$

$$\Delta_{\rm f}G^{\circ} = -32566 + 70.1150T \,\,{\rm J/mol} \tag{155}$$

The calculated phase diagram remains tentative since the liquidus is not well defined. Other calculated data are: $E_1 =$ 116.0 °C, $x_B = 0.110$; $E_2 = 131.1$ °C, $x_B = 0.467$; $E_3 = 114.0$ °C, $x_B = 0.823$; the 2:1 and 1:1 compounds melt congruently at 135.7 and 131.3 °C, respectively.

Probable maximum inaccuracy in calculated diagram: \pm 7°

6.5. Systems Containing only the Diaminobenzenes

1,2-DAB (A) + 1,3-DAB (B)

Data were obtained by the thaw-melt method and checked by thermal analysis¹⁴. This is a simple eutectic system, and the

FIG 43. The system 2-NP (A) + 4,4'-DABP (B).

reported eutectic¹⁴ is 41.0 °C, $x_B = 0.74$. The experimental¹⁴ limiting liquidus slopes at both LHS and RHS are greater than thermodynamic expectation, and hence observed liquidus data are probably too low. The eutectic temperature was taken as the most accurate datum in this system and the phase diagram, Fig. 45, was calculated with the use of Eq. (156)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-2714 + 3881 x_{\rm B} - 2800 x_{\rm B}^2) \, \text{J/mol} \quad (156)$$

and the calculated eutectic is 41.0 °C, $x_B = 0.700$.

Probable maximum inaccuracy in calculated liquidus: $\pm 4^{\circ}$.

1,2-DAB (A) + 1,4-DAB (B)

Data were obtained by the thaw-melt method, checked by thermal analysis¹⁴ and also by the microthermal method³⁹. This is a simple eutectic system. The observed eutectic is¹⁴ 81.6 °C, $x_B = 0.30$ or³⁹ 84.0 °C, $x_B = 0.28$. The RHS limiting liquidus slope of Stancic *et al.*³⁹ is faulty, whereas that of Dhillon and Dhillon¹⁴ is thermodynamically correct. In the optimization, both the liquidus data and eutectic temperature in the later work¹⁴ were weighted preferentially. The phase diagram, Fig. 46, was calculated with the use of Eq. (157)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} \left(-2185 + 6112 x_{\rm B} - 5419 x_{\rm B}^2\right) \,\mathrm{J/mol} \qquad (157)$$

and the calculated eutectic is 81.6 °C, $x_B = 0.302$.

Probable maximum inaccuracy in calculated diagram: $\pm 10^{\circ}$.

1,4-DAB (A) + 1,3-DAB (B)

Data were obtained by the thaw-melt method, checked by thermal analysis¹⁴. This is a simple eutectic system, and the observed eutectic¹⁴ is 47.0 °C, $x_B = 0.59$. The limiting liquidus slopes¹⁴ at both the RHS and LHS do not correspond to thermodynamic expectation and the experimental liquidus data are probably too high. The steep descent of the LHS liquidus to the reported eutectic composition requires an excess Gibbs energy of the liquid which is incompatible with the RHS liquidus. The eutectic temperature was taken as the most accurate experimental datum in this system. The phase diagram, Fig. 47, was calculated with the use of Eq. (158)

$$G^{\rm E}(\ell) = x_{\rm A} x_{\rm B} (-8612 + 8255 x_{\rm B}) \, \text{J/mol}$$
 (158)

and the calculated eutectic is 47.0 °C, $x_B = 0.675$.

Probable maximum inaccuracy in calculated liquidus: $\pm 15^{\circ}$.

FIG. 44. The system 3-AP (A) + 4,4'-DABP (B).

FIG. 47. The system 1,4-DAB (A) + 1,3-DAB (B)

7. Acknowledgment

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9. Appendix

For ease of consultation, calculated thermodynamic properties for the 47 systems are presented here in two tables. Footnotes of these tables indicate any special status to be attached to particular data.

PHASE DIAGRAMS AND THERMODYNAMIC PROPERTIES OF BINARY ORGANIC SYSTEMS 337

A	В	go	81	82
Systems with 1,2-Diaminobenzene				
1,2-DHB	1,2-DAB	-8300	-600	0
1,3-DHB	1,2-DAB	- 13495	• 0	0
1,4-DHB	1,2-DAB	-6000	-2500	0
1-N	1,2 DAB	- 10299	1565	0
2-N	1,2-DAB	-4240	1302	0
Р	1.2-DAB	-4176	0	0
2-NP	1.2-DAB	1688	0	0
3-NP	1.2-DAB	-6903	1460	0
4-NP	1.2-DAB	-9438	4000	0
2.4-DNP	1.2-DAB	- 4691	-2926	ů 0
BA	1.2-DAB	-2432	0	0
BENZ	1,2-DAB	-3795	4405	0
Systems with 1,3-Diaminobenzene				
1,2-DHB	1,3-DAB	- 10000	3000	0
1,3-DHB	1,3-DAB	-23950	4194	0
1,4-DHB	1,3-DAB	-9000	0	0
1-N	1,3-DAB	-22470	9840	0
2-N	1.3-DAB	-3602	0	n n
Р	1,3 DAB	-5673	õ	0
2-NP	1.3-DAB	3687	1008	ñ
3-NP	1.3-DAB	-9309	4491	ů 0
4-NP	1 3-DAB	- 3900	1700	ů ů
2 4-DNP	13-DAB	- 1357	0	0
BENZ	1,3-DAB	-2125	0	0
Systems with 1,4-Diaminobenzene				
1,2-DHB	1.4-DAB	-20200	8833	0
1,3-DHB	1,4-DAB	- 12098	-2575	0
1,4-DHB	1.4-DAB	-2206	4770	0
1-N	1.4-DAB	-6172	0	ů 0
2-N	1,4-DAB	-9600	3829	ő
P	1,4-DAB	-5334	. 0	0
2-NP	1.4-DAB	1595	0	0
3-NP	1.4-DAB	-5000	0	Ő
4-NP	1,4-DAB	-3656	õ	ő
2,4-DNP	1,4-DAB	-27114	0	n
BENZ	1,4-DAB	-3695	7691	-7457
BA	1.4-DAB	-5400	2000	
3-NBA	1,4-DAB	-9510	-200	0
Systems with benzidine				
1,2-DHB	4,4'-DABP	-3507	0	0
1,3-DHB	4,4'-DABP	-2400	1300	ő
1,2,3-THB	4,4'-DABP	-1220	1050	ő
1-N	4,4'-DABP	-2750	600	ñ
2-N	4,4'-DABP	7661	. 0	ň
P	4,4'-DABP	$(-5000)^{a}$	0	0
2-NP	4,4'-DABP	406	õ	ů n
3-AP	4,4'-DABP	-10000	5000	0
Systems containing only diaminobenzenes				
1,2-DAB	- 1.3-DAB	-2714	3881	- 28(8)
1,2-DAB 1,2-DAB	I,3-DAB 1.4-DAB	-2714	3881	-2800

TABLE A1. Excess Gibbs energies of the liquid phase of the binary systems A + B $G^{E}(\Delta) = x_{A}x_{B}$ ($g_{0} + g_{1}x_{B} - g_{2}x_{B}^{2}$) J/mol

^a Nominal value only, not obtained from optimization.

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TABLE A2. Gibbs energies of fusion and formation (from the pure component liquids) of intermediate compounds^a $\Delta_{fus}G^{\circ} = a + bT(K) J/mol$ $\Delta_{f}G^{\circ} = a' + b'T(K) J/mol$

A	В	Stoichiometry	Fusion a	b	Formation	
					<i>a</i> ′	<i>b</i> '
Compounds wit	h 1.2-Diaminobenze	ne			· · · · · · · · · · · · · · · · · · ·	
1.2-DHB	1.2-DAB	(AB)/2	9107	-25 2143	-11257	19 4531
1.3-DHB	1.2-DAB	(AB)/2	16500*	50 3509	-19874	44 5881
1.4-DHB	1.2-DAB	(AB_)/3	10300	-50.8677	-21094	45 5758
1-N	1.2-DAB	(AB)/2	24151	-71 8114	-26530	66 0502
2-N	1.2-DAB	(AB)/2	18480	-51 2342	-19386	45 4714
P	1.2-DAB	(AB)/2	14764		-15909	40 8326
	1,2-070	(AD)/2 (AD)/5(9)	0112	- 20,0000		40.8320
2 ND	1 2 DAD	(A4D)/J(?)	9112	- 50,0000	-9780	23.0400
3-INP	1,2-DAD	$(A_2B)/3$	12278	-35.1890	-13089	29.8987
4 10		$(AB_2)/3(?)$	18614	-55.0000	-19932	49.7080
4-NP	1,2-DAB	$(A_2B)/3$	16999	-47.0170	-18800	41.7197
2,4-DNP	I,2-DAB	(AB)/2	12702	-35.3677	-14240	29,6065
ВА	1,2-DAB	(A ₂ B)/3	15000	-39.5570	-15540	34.2651
		(AB)/2	15915	-43.2230	-16523	37.4619
Compounds wit	h 1,3-Diaminobenze	ne				
1,2-DHB	1,3-DAB	(AB)/2	12225	-35.7612	-14220	30.0000
1,3-DHB	1,3-DAB	(AB)/2	14402	-40.7700	-19865	35.0000
1,4-DHB	1.3-DAB	(AB)/2	21536	-53.9153	-23786	48,1525
1-N	1.3-DAB	(AB)/2	(61722)	(-199.2891)	(-66110)	(193,5271)
2-N	1.3-DAB	$(A_2B)/3$	23018	-59 2255	-23819	53 9335
P	1.3-DAB	(AR)/2	17283	- 52 8499	-18701	47 0887
- 3-NP	13-DAR	$(A_{-}B)/3$	1/205	- 42 4601	-16510	37 1680
5-111	1,5-0110	(AR)/2	12402	-35.0686	-14168	29 3078
4.NP	1 3-DAR	$(A_B)/2$	11130	-28 2380	-11874	22,5070
2.4-DNP	1.3-DAB	(AR)/2	10481	-28.0128	- 10820	22.9400
2,4 2111	1,5-2715	(AD)/2	10401	20.0120	10820	22.2400
Compounds wit	h 1,4-Diaminobenze	ne				
1,2-DHB	1,4-DAB	(A ₂ B)/3	31695	-83.2873	-35530	77.9870
		(AB)/2	17652	- 46.0707	-21598	40.3075
1,3-DHB	1,4-DAB	(A ₂ B)/3(?)	15305	-39.9413	-17803	34.6510
		(AB)/2	10335	-26.3636	-13038	20.6024
1,4-DHB	1,4-DAB	(AB)/2	8277	- 17.7257	-8232	11.9612
1-N	I,4-DAB	(A ₂ B)/3	18980*	-49.3436	-20355	44.0572
2-N	1,4-DAB	$(A_2B)/3$	22509	-52.6342	-24359	47.3383
		(AB)/2(?)	9040	-21.1588	-10961	15.3924
Р	1,4-DAB	$(A_2B)/3$	12566	-33.1103	-13752	27.8201
3-NP	1,4-DAB	$(A_2B)/3$	18273	44.4328	-19384	39.1446
		(AB ₄)/5(?)	29032	-75,0000	-29800	70.8397
4-NP	1,4-DAB	(A₄B)/5	14525	-35.7092	-15110	31.5500
		$(A_2B)/3(?)$	28174	-71.0275	-28987	65.7372
2,4-DNP	1,4-DAB	(A ₃ B)/4	39336	-100.5178	- 44419	95.8440
		(AB)/2(?)	25992	-67.0226	-32771	61.2614
BA	1.4-DAB	(AB)/2	19460*	- 46,5940	-20537	40.7755
3-NBA	1.4-DAB	(A ₂ B)/3	11946	-27 3897	- 14074	22.0951
	.,	(AB)/2(?)	22947	-53.0505	-25350	47.2934
O	1. h					
compounds wit	n benzidine		2012			10 0070
1,2-DHB	4,4 ⁻ -DABP	(A ₂ B)/3	22126	-52.5956	-22905	47.3053
12 DUD		(AB)/2	15678	-38.0785	- 16555	32.3173
1,3-DHB	4,4'-DARP	$(A_2B)/3$	16490	- 39.8648	- 16927	34.5745
		(AB)/2	15710	-38.6615	-16148	32.9003
1,2,3-THB	4,4'-DABP	(AB)/2	21190*	-50.7970	-21368	45.0432
1-N	4,4'-DABP	(AB)/2	27149	-72.6383	-27760	66.8771
2-N	4,4'-DABP	$(A_2B)/3$	30650*	-68.2400	-32352	62.9480
		(AB)/2(?)	23382	-52.4792	-25300	46.7180
P	4,4'-DABP	(A ₂ B)/3	19289	-46.5492	-20400	41.2590
		(AB)/2(?)	20646	-50.9073	-21896	45.1461
2-NP	4,4'-DABP	(AB ₂)/3	9957	-26.8113	-9867	21.5210
3-AP	4,4'-DABP	$(A_2B)/3$	24651	-60.2935	-26503	55.0000
		· - ·				