721. *Thermodynamics of Hydrocarbon Mixtures. Part III.* The Heats of Mixing of Ternary, Quaternary, and Quinary Mixtures formed by Benzene, cyclo*Hexane, Heptane, Toluene, and Hexane.

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The heats of mixing of ternary, quaternary, and quinary systems formed by benzene, toluene, *cyclo*hexane, hexane, and heptane have been measured at 20° c in order to examine various equations which enable the heats of mixing of multicomponent mixtures to be predicted from a knowledge of the heats of mixing of the constituent binary mixtures. It has been found that values agreeing to within the limit of experimental error with those measured may be predicted by some of these equations. An empirical equation has also been suggested.

By using the method described in Part I,[1] the heats of mixing of multicomponent hydrocarbon mixtures have been measured. For quaternary and quinary mixtures a known amount of a binary mixture, which was contained in the sealed glass ampoule, was mixed with a known amount of a second binary (or ternary) mixture, and the heat of mixing was measured. Since the heats of mixing for both of the mixtures were known at the concentrations used, the total heat of mixing for the multicomponent mixture could be determined.

* Part II, preceding paper.

[1] Part I, *J.*, 1955, 4141.

Since this technique involved two sets of concentration determinations, together with errors in the measurement of temperature and in extrapolation, the estimated experimental error is larger than the error involved in work on binary mixtures, and the percentage errors are estimated as ±3% for ternary systems, ±5% for quaternary systems, and about ±6% for quinary systems.

Results

Properties of the Materials.—These were the same as for the liquids described in Parts I and II.[1,2]

Heats of Mixing at 20° c.—In Tables 1—9 the subscript numerals given to x correspond to the order of citation of compounds in the Table heading. ΔH_m is expressed in J/mole throughout.

Discussion

Tables 1—9 show the results for the heats of mixing at 20° c of six of the ternary mixtures, two of the quaternary mixtures, and the quinary mixture formed by benzene, toluene, *cyclo*hexane, hexane, and heptane. The results for the ternary mixture, benzene–*cyclo*hexane–heptane have already been reported.[1]

Several equations have been suggested to enable the heats of mixing of multicomponent systems to be predicted from the heats of mixing of the constituent binary mixtures.

That suggested by Redlich and Kister [3] can be expressed for a ternary mixture as:

$$\begin{aligned}\Delta H_{123} = {} & x_1^1 x_2^1[H_{12}^\circ + H_{12}^1(x_1^1 - x_2^1) + H_{12}^{11}(x_1^1 - x_2^1)^2 \ldots] \\ & + x_2^1 x_3^1[H_{23}^\circ + H_{23}^1(x_2^1 - x_3^1) + H_{23}^{11}(x_2^1 - x_3^1)^2 \ldots] \\ & + x_1^1 x_3^1[H_{13}^\circ + H_{13}^1(x_1^1 - x_3^1) + H_{13}^{11}(x_1^1 - x_3^1)^2 \ldots] \quad . \quad (1)\end{aligned}$$

where $H_{12} = x_1 x_2[H_{12}^\circ + H_{12}^1(x_1 - x_2) + H_{12}^{11}(x_1 - x_2)^2 \ldots]$ etc. and x_1^1, x_2^1, and x_3^1 are the ternary mole fractions and x_1, x_2 the binary.

For a quaternary mixture, eqn. 1 will consist of six terms involving the binary equations, and for the quinary mixture there will be ten such terms.

Eqn. 1 has been modified [4] by replacing all difference terms involving x_1, *e.g.* $(x_1 - x_2)$, by $(2x_1 - 1)$. Thus, when the modified form of eqn. 1 is applied to ternary mixtures only two terms, namely $(x_1^1 - x_2^1)$ and $(x_1^1 - x_3^1)$, will need to be replaced by $(2x_1^1 - 1)$. For the quaternary mixture three terms will be replaced, and for quinary mixtures the four terms involving x_1^1 will be replaced by $(2x_1^1 - 1)$. This modification (which will be referred to as eqn. 2) was originally intended for mixtures containing one polar component, or for mixtures where one of the components was appreciably different in some manner from the others.

A combination of eqns. 1 and 2 enables the following equation to be obtained for ternary mixtures:

$$\begin{aligned}\Delta H_{123} = {} & x_1^1 x_2^1[H_{12}^\circ + H_{12}^1(x_1^1 - x_2^1 - x_3^1/2) + H_{12}^{11}(x_1^1 - x_2^1 - x_3^1/2)^2 + \ldots] \\ & + x_1^1 x_3^1[H_{13}^\circ + H_{13}^1(x_1^1 - x_3^1 - x_2^1/2) + H_{13}^{11}(x_1^1 - x_3^1 - x_2^1/2)^2 + \ldots] \\ & + x_2^1 x_3^1[H_{23}^\circ + H_{23}^1(x_2^1 - x_3^1) + H_{23}^{11}(x_2^1 - x_3^1)^2 + \ldots] \quad . \quad (4)\end{aligned}$$

i.e. difference terms involving x_1^1, *e.g.* $(x_1^1 - x_2^1)$, are replaced by $(x_1^1 - x_2^1 - x_3^1/2)$. For quaternary and quinary mixtures the replacement terms for $(x_1^1 - x_2^1)$ will be:

$[x_1^1 - x_2^1 - (x_3^1 + x_4^1)/2]$ and $[x_1^1 - x_2^1 - (x_3^1 + x_4^1 + x_5^1)/2]$, respectively.

This equation will be referred to as eqn. 4.

[2] Part II, Mathieson and Thynne, preceding paper.
[3] Redlich and Kister, *Ind. Eng. Chem.*, 1948, **40**, 31.
[4] Scatchard, Goates, Ticknor, and Macastney, *J. Amer. Chem. Soc.*, 1952, **74**, 3724.

Tsao and Smith [5] proposed an equation for the prediction of the heats of mixing of ternary systems which may be stated :

$$\Delta H_{123} = H_{12}[x_2^1/(x_2^1 + x_3^1)] + H_{13}[x_3^1/(x_2^1 + x_3^1)] + H_{23}(1 - x_1^1) \quad . \quad (3)$$

where, as before :

$$H_{12} = x_1x_2[H_{12}^\circ + H_{12}^1(x_1 - x_2) + H_{12}^{11}(x_1 - x_2)^2 + \ldots] \text{ etc.}$$

The values of the heats of mixing calculated from eqns. 1—4 are shown together with the experimental values in Tables 1—9. When eqn. 1 was applied to the 73 results obtained for the ternary systems (*i.e.* including 31 results given in Part I) then an average deviation

TABLE 1. *Benzene–cyclohexane–hexane.*

			ΔH_m				
x_1	x_2	x_3	Exptl.	Eqn. 1	Eqn. 2	Eqn. 3	Eqn. 4
0·266	0·398	0·335	745	761	699	950	695
0·383	0·335	0·282	874	895	841	996	866
0·307	0·376	0·317	803	820	757	983	787
0·344	0·356	0·300	841	854	799	996	828
0·424	0·282	0·294	866	920	870	979	895
0·455	0·230	0·315	870	912	870	937	895
0·578	0·250	0·172	883	912	887	799	895
0·359	0·479	0·162	816	841	795	912	812
0·309	0·517	0·174	757	782	732	887	749
0·295	0·527	0·178	741	761	711	874	732
0·300	0·578	0·122	749	741	695	803	711

TABLE 2. *Benzene–toluene–heptane.*

0·166	0·733	0·101	293	268	284	406	280
0·161	0·741	0·098	284	255	272	397	268
0·144	0·768	0·088	255	234	243	351	247
0·308	0·400	0·292	640	640	682	766	644
0·437	0·298	0·265	695	678	715	833	686
0·673	0·232	0·095	393	377	393	540	368
0·320	0·458	0·222	552	548	586	506	573

TABLE 3. *Benzene–toluene–hexane.*

0·073	0·716	0·211	222	192	205	351	201
0·073	0·715	0·212	222	192	205	351	201
0·084	0·675	0·241	238	217	234	414	230
0·079	0·693	0·228	238	209	222	385	217
0·078	0·698	0·224	251	209	222	385	217
0·182	0·294	0·524	519	494	523	686	498
0·204	0·209	0·587	602	565	590	711	556

TABLE 4. *Toluene–cyclohexane–heptane.*

0·157	0·767	0·076	402	364	364	435	368
0·183	0·401	0·416	510	527	531	628	527
0·404	0·398	0·198	623	653	657	858	657
0·480	0·271	0·249	703	661	669	849	669
0·647	0·235	0·118	531	577	577	711	577
0·649	0·198	0·153	548	573	577	707	573

TABLE 5. *Toluene–cyclohexane–hexane.*

0·360	0·450	0·190	615	586	590	753	586
0·384	0·434	0·182	602	594	598	753	598
0·722	0·195	0·083	481	464	469	577	469
0·749	0·177	0·074	435	435	439	536	439
0·785	0·150	0·065	393	389	389	473	389

TABLE 6. *Benzene–toluene–cyclohexane.*

0·174	0·255	0·571	602	640	678	527	661
0·261	0·239	0·500	669	707	741	636	749
0·338	0·245	0·417	741	728	749	736	741
0·386	0·296	0·318	678	661	669	782	669
0·462	0·284	0·254	602	611	611	761	615
0·562	0·239	0·198	536	519	510	686	515

[5] Tsao and Smith, " Applied Thermodynamics," *Chem. Eng. Progr. Symp. Series* No. 7, 1953, **49**, 107.

TABLE 7. *Toluene*–cyclo*hexane*–*heptane*–*hexane*.

x_1	x_2	x_3	x_4	ΔH_m Exptl.	Eqn. 1	Eqn. 2	Eqn. 4
0·170	0·383	0·124	0·323	473	464	464	464
0·456	0·166	0·266	0·112	565	611	607	611
0·188	0·423	0·137	0·243	510	498	494	494
0·166	0·347	0·121	0·366	427	448	448	448
0·180	0·178	0·300	0·342	389	423	427	423
0·225	0·147	0·255	0·373	435	444	452	448
0·207	0·136	0·200	0·458	410	418	423	418
0·216	0·142	0·300	0·342	410	440	448	444

TABLE 8. *Benzene*–cyclo*hexane*–*heptane*–*hexane*.

0·360	0·148	0·220	0·272	833	912	849	883
0·275	0·302	0·167	0·256	782	829	766	782
0·342	0·211	0·208	0·239	874	912	829	874
0·194	0·319	0·235	0·252	636	699	619	657
0·375	0·231	0·171	0·223	920	946	879	904
0·289	0·269	0·199	0·243	816	854	766	808
0·312	0·226	0·189	0·273	879	912	858	879
0·193	0·318	0·221	0·268	657	695	615	657
0·500	0·137	0·247	0·116	987	1000	941	979
0·364	0·225	0·222	0·189	891	946	862	904
0·185	0·153	0·309	0·353	602	623	556	598
0·157	0·129	0·430	0·284	531	548	490	535
0·492	0·190	0·239	0·080	954	1017	962	996
0·198	0·421	0·311	0·069	686	720	640	678
0·212	0·479	0·236	0·073	715	724	644	678

TABLE 9. *Benzene*–*toluene*–cyclo*hexane*–*hexane*–*heptane*.

x_1	x_2	x_3	x_4	x_5	ΔH_m Exptl.	Eqn. 1	Eqn. 2	Eqn. 4
0·290	0·198	0·238	0·099	0·175	812	845	836	849
0·192	0·172	0·216	0·086	0·234	766	791	795	799
0·235	0·174	0·290	0·087	0·214	766	828	828	828
0·335	0·204	0·207	0·101	0·153	816	845	833	841
0·156	0·152	0·449	0·101	0·142	674	711	732	728
0·255	0·154	0·370	0·104	0·116	766	816	828	828
0·267	0·278	0·175	0·118	0·162	732	787	770	787
0·208	0·208	0·284	0·240	0·060	745	766	766	770
0·293	0·158	0·337	0·105	0·107	782	841	849	849
0·299	0·165	0·246	0·109	0·181	833	862	849	862
0·291	0·207	0·240	0·202	0·060	812	812	804	812
0·183	0·151	0·302	0·254	0·110	724	745	741	749
0·230	0·143	0·284	0·239	0·104	791	791	778	791
0·258	0·287	0·178	0·120	0·157	766	782	766	782
0·347	0·145	0·198	0·100	0·210	820	891	874	883
0·293	0·245	0·189	0·095	0·178	770	820	803	816
0·330	0·184	0·170	0·115	0·201	791	858	836	836
0·308	0·193	0·207	0·105	0·187	782	853	836	849

of the predicted heat of mixing from the measured heat of +0·9% was observed. The average deviation given by eqn. 2 was −0·8%, and by eqn. 4 less than +0·1%. These deviations lie well within the range of experimental error. Eqn. 3 gives a much poorer representation of the results, the average deviation being +8·1%.

Application of eqns. 1, 2, and 4 to the quaternary mixtures resulted in average deviations of +4·5, −1·6, and +1·5%, respectively. Since the experimental error is about ±5% for such mixtures, these deviations are satisfactory.

The average deviations for the quinary mixture were, for equations 1, 2, and 4, +5·0, +4·2, and +5·1%, respectively. These values are rather high, but again in view of the possible experimental error, are reasonable.

From a consideration of these results, it seems that for hydrocarbon systems the heats of mixing of multicomponent systems may be predicted with considerable accuracy, when the heats of mixing of the constituent binary mixtures are known.

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