Heat Capacities of Liquids

Estimation of Heat Capacity at Constant Pressure and 25° C., Using Additivity Rules

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Existing methods for estimating the heat capacity of liquids at constant pressure and 25° C. have a precision of not better than ±4 cal. mole^{-1} deg.$^{-1}$. From previously measured data and the principle of group additivity, groups have been derived which enable heat capacities of liquids at constant pressure and 25° C. to be calculated to within ±1.5 cal. mole^{-1} deg.$^{-1}$ in all cases, and in most instances to better than ±1.0 cal. mole^{-1} deg.$^{-1}$.

THIS PAPER resulted from an investigation of how the heat capacity of a liquid is estimated at a constant pressure of 1 atm. and at 25° C.

In the case of ideal gases, thermodynamic properties such as heat capacities have a sound theoretical basis, and in addition, group additivity rules (2, 3) have been developed which allow accurate estimation—for heat capacities, better than 1 cal. mole^{-1} deg.$^{-1}$. Liquids are less well understood theoretically than gases, and the principle of group additivity has not been applied. In the course of surveying existing methods for estimating the heat capacities of liquids, a considerable amount of previously measured data was accumulated. It was then a relatively simple matter to derive the groups which allow estimation, using group additivity of the heat capacities of the original and chemically related liquids, to an accuracy of around 1 cal. mole^{-1} deg.$^{-1}$.

In this paper, the heat capacity of a liquid at constant pressure and 25° C. will be denoted $C_p(l)$, and the heat capacity of an ideal gas at constant pressure and 25° C. will be denoted $C_p(g)$.

EXISTING METHODS FOR ESTIMATING $C_p(l)$

There are several existing methods for estimating the $C_p(l)$. The simplest is Kopp's Rule (4, 7), which states that $C_p \sim 8m$, where m is the number of atoms, except that smaller values than 8 cal. mole^{-1} deg.$^{-1}$ should be used as follows: 2.8 for carbon, 4.3 for hydrogen—Lange (4) gives 4.8 for hydrogen—6.0 for oxygen, 7.0 for fluorine, 5.8 for silicon, and 7.4 for sulfur. For nitromethane, CH_3NO_2, the calculated $C_p(l)$ is 35.7, compared with the observed (5) value 25.4, a difference of 10.3 cal. mole^{-1} deg.$^{-1}$, or about 40%.

Benson (1) showed that the difference between $C_p(l)$ and $C_p(g)$, ΔC_p, is related to the change of the energy of vaporization

$$-\Delta C_p \sim \left[\frac{\partial \Delta E}{\partial T} \right] + R \tag{1}$$

where ΔE is the energy of vaporization and R is the gas constant. Taking nitromethane as an example, from the variation of the heat of vaporization with temperature (6), $\partial \Delta E/\partial T$ at 25° C. is −14, giving $-\Delta C_p = -12$. From $C_p(g)$ = 13.8 (6), $C_p(l)$ is 25.8, in excellent agreement with the observed value of 25.4 cal. mole^{-1} deg.$^{-1}$.

The variation of the energy of vaporization with temperature has not been measured for many liquids, so Benson introduced the approximation

$$\frac{\partial \Delta E}{\partial T} \sim n \Delta E \left(\frac{\partial \ln D_l}{\partial T} \right) \tag{2}$$

where D_l is the molar density of the liquid and n is an empirical constant, 1.67. Substitution gives

$$-\Delta C_p = n \Delta E (\partial \ln D_l/\partial T) + R \tag{3}$$

Now $\partial \ln D_l/\partial T \sim (1/\bar{d}_l)(\Delta d_l/\Delta T)$, where d_l is the density in grams per cubic centimeter. From the density data of Toops on nitromethane (11) and the heat of vaporization (5) at 25° C., $-\Delta C_p = -[1.67(8550)0.00122] + 2 = -15.4$, giving $C_p(l)$ = 29.2, compared with the observed 25.4, a difference of 3.8 cal. mole^{-1} deg.$^{-1}$, or 15%.

Tsien (12) has also developed a method for estimating ΔC_p. From the Lennard-Jones and Devonshire theory of normal liquids, and assuming that the internal degrees of freedom must be the same in the liquid and gaseous states, he derived

$$\Delta C_p = R \left\{ 0.5 - 0.4 \frac{T}{T_b} + \frac{(\alpha T_b)^2}{\left(\beta \frac{RT_b}{V_l} \right)} \frac{T}{T_b} \right\} \tag{4}$$

where T_b is the boiling point (° K.), α is the coefficient of thermal expansion, β is the compressibility, and V_l is the molar volume. Evaluating α and β by empirical methods, he found ΔC_p = 10 cal. mole^{-1} deg.$^{-1}$. Tsien pointed out (12) that, as the theory was developed for normal liquids, molecules containing hydroxyl or amino group and molecules that are excessively elongated, so that the rotational degree of freedom is reduced, should be excluded.

In Table I are values of $C_p(l)$ and $C_p(g)$ for some organic liquids. Although Tsien's suggested value of 10 for ΔC_p is a good approximation, the data show that for most molecules, except linear hydrocarbons containing more than 8 carbon atoms, ΔC_p = 12 ± 4 cal. mole^{-1} deg.$^{-1}$, a small but significant increase. Values of $C_p(g)$ are often available, so a simple method of estimating $C_p(l)$ is $C_p(l)$ = 12 + $C_p(g)$ cal. mole^{-1} deg.$^{-1}$. If $C_p(g)$ has not been measured, it may be estimated from the additivity rules for ideal gases. If the necessary groups are available so that group additivity can be used, then the precision in estimating $C_p(g)$ is ± 1 cal. mole^{-1} deg.$^{-1}$. If the groups are not

Table I. Comparison of Observed and Estimated Constant-Pressure Heat

	$C_p(l)$,[a] Obs.	$C_p(g)$,[b] Obs.	ΔC_p, l - g	$C_p(l)$,[a] Est.	$\Delta C_p(l)$,[c] Obs. - Est.
			Alkanes		
2-Methyl butane	39.4	28.5	10.9	38.6	0.8
n-Hexane	46.6	34.2	12.4	46.6	0.0
2-Methyl pentane	46.2	34.5	11.7	45.9	0.3
3-Methyl pentane	45.6	34.2	11.4	45.9	−0.3
2,3-Dimethyl butane	45.0	33.6	11.4	45.2	−0.2
2,2-Dimethyl butane	45.0	33.9	11.1	44.2	0.8
n-Heptane	53.7	39.7	14.0	53.9	−0.2
2-Methyl hexane	53.1			53.2	−0.1
3-Ethyl pentane	52.5			53.2	−0.7
2,2-Dimethyl pentane	52.8			51.5	1.3
2,3-Dimethyl pentane	51.8			52.4	−0.6
2,4-Dimethyl pentane	53.5			52.4	1.1
3,3-Dimethyl pentane	51.4			51.5	−0.1
2,2,3-Trimethyl butane	51.0	39.3	10.7	50.7	0.3
n-Octane	60.7	45.1	15.6	61.1	−0.4
2,2,4-Trimethyl pentane	56.5			58.0	−1.5
2,2,3,3-Trimethyl butane	55.9	46.0	9.9	56.3	−0.4
n-Nonane	68.0	50.6	17.4	68.4	−0.4
n-Decane	75.2	56.1	19.1	75.6	−0.4
2-Methyl nonane	75.6			74.9	−0.7
n-Undecane	82.5	61.5	21.0	82.9	−0.4
n-Dodecane	89.7	67.0	22.7	90.2	−0.5
n-Tridecane	97.2	72.5	24.7	97.4	−0.2
n-Tetradecane	104.8	77.9	26.9	104.7	0.1
n-Pentadecane	112.2	83.4	28.8	111.9	0.3
n-Hexadecane	119.9	88.9	31.0	119.2	0.7
			Olefins		
Pentene-1	37.1	26.2	10.9	36.2	0.9
cis-Pentene-2	36.3	24.3	12.0	36.3	[0.0]
trans-Pentene-2	37.6	25.9	11.7	37.6	[0.0]
2-Methyl butene-1	37.5	26.7	10.8	36.4	1.1
3-Methyl butene-1	37.3	28.4	8.9	37.3	0.0
2-Methyl butene-2	36.4	25.1	11.3	35.3	1.1
Hexene-1	43.8	31.6	12.2	43.4	0.4
2,3-Dimethyl butene-2	41.7	30.5	11.2	42.8	−1.1
Heptene-1	50.5	37.1	13.4	50.7	−0.2
Octene-1	57.7	42.6	15.1	57.9	−0.2
Decene-1	71.8	53.5	18.3	72.5	−0.7
Undecene-1	78.9	59.0	19.9	79.7	−0.8
Dodecene-1	86.2	64.4	21.8	87.0	−0.8
Hexadecene-1	115.9	86.3	29.6	116.0	−0.1
Butadiene-1,3	29.5	19.0	10.5	29.6	[−0.1][f]
Pentadiene-1,4	34.8	25.1	9.7	34.9	[−0.1]
2-Methyl butadiene-1,3	36.7	25.0	11.7	36.7	[0.0]
Butyne-2	29.4	18.6	10.8	29.4	[0.0]

C_p Liquid extrapolated from 11° C.

			Aromatics		
Benzene	32.4	19.5	12.9	31.8	0.6
Toluene	37.3	24.8	12.5	38.2	−0.9
Ethyl benzene	44.5	30.7	13.8	44.5	[0.0]
p-Xylene	43.6	30.3	13.3	44.6	−1.0
1,2,3-Trimethyl benzene	51.8	36.9	14.9	51.0	0.8
1,2,4-Trimethyl benzene	51.6	37.1	14.5	51.0	0.6
1,3,5-Trimethyl benzene	50.1	35.9	14.2	51.0	−0.9

			Oxygen-Containing		
Methanol	19.5	10.5	9.0	19.5	[0.0]
Ethanol	27.0	15.7	11.3	27.0	0.0
Propanol-1	34.3	20.9	13.4	34.3	0.0
Propanol-2	37.1	21.3	15.8	37.1	[0.0]
2-Methyl propanol-2	53.2	27.2	26.0	53.2	[0.0]
estimated alternative	42.2		15.0	42.2	[0.0]
Diethyl ether	41.1	25.8[e]	15.3	41.1	[0.0]
Acetone	30.2	18.0	12.2	30.2	[0.0]
Formic acid	23.6	10.8	12.8	23.6	[0.0]
Acetic acid	29.4	16.0	13.4	29.4	[0.0]
Ethyl acetate	40.6			40.6	[0.0]
Benzyl alcohol	52.1			52.1	[0.0]
Diphenyl ether	64.2			64.2	[0.0]
Furan	27.4			too many unknown groups	

[a] The values of C_p liquid are from (10). [b] The values of C_p gas are from (8) for hydrocarbons and from (3) for the remainder. [c] Square brackets in the ΔC_p liquid column indicate that the compound was the sole source of that group, so that there is necessarily a fit between observed and estimated data. [d] Compounds which are too small to be broken down into groups and are in a sense "unique" groups in themselves. [e] Calculated from group additivity (3). [f] Estimated value of ΔC_p (liquid − gas) = 10, ∴ C_p liquid = 22.2 cal. mole^{-1}deg.$^{-1}$.

Capacity of Liquids and Gases at 25° C. and 1 Atm., Cal./Mole^{-1} Deg.$^{-1}$

	$C_p(l)$,^{c} Obs.	$C_p(g)$,^{c} Obs.	ΔC_p, 1 – g	$C_p(l)$,^{a} Est.	$\Delta C_p(l)$,^{c} Obs. – Est.
			Nitrogen-Containing		
Hydrogen cyanide^d	16.9	8.6	8.3	...	
Hydrazine	22.2^f	12.2	10.0^f	22.2	[0.0]
Unsym. dimethyl hydrazine	39.2			39.2	[0.0]
Trimethyl hydrazine	44.5			44.5	[0.0]
Aniline	46.2	26.1	20.1	46.2	[0.0]
Quinoline	47.6			too many unknown groups	
Acrylonitrile	26.5	14.9	11.6	26.5	[0.0]
Perfluoro piperidene	71.0			too many unknown groups	
Methyl nitrate	37.5			37.5	[0.0]
Tetrahydropyrole	37.4			too many unknown groups	
Nitromethane	25.4	13.8	11.6	...	
			Ring Compounds		
Cyclopentane	30.4	19.8	10.6	31.5	−1.1
Methyl cyclopentane	38.0	26.2	11.8	38.0	0.0
Ethyl cyclopentane	44.5	31.5	13.0	45.3	−0.8
1,1-Dimethyl cyclopentane	44.6	31.9	12.7	43.6	1.0
cis-1,2-Dimethyl cyclopentane	45.1	32.1	13.0	44.6	0.5
trans-1,2-Dimethyl cyclopentane	45.1	32.1	13.0	44.6	0.5
trans-1,3-Dimethyl cyclopentane	45.1	32.1	13.0	44.6	0.5
Cyclopentane	29.4	18.0	10.6	29.4	[0.0]
Cyclohexane	36.4	25.4	11.0	37.1	−0.7
Methyl cyclohexane	44.2	32.3	11.9	43.6	0.6
Ethyl cyclohexane	50.0	38.0	12.0	50.9	−0.9
1,2-Dimethyl cyclohexane	50.4	37.4	13.0	50.1	0.3
cis-1,3-Dimethyl cyclohexane	50.0	37.6	12.4	50.1	−0.1
trans-1,3-Dimethyl cyclohexane	50.8	37.6	13.2	50.1	0.7
cis-1,4-Dimethyl cyclohexane	50.5	37.6	12.9	50.1	0.4
trans-1,4-Dimethyl cyclohexane	50.3	37.7	12.6	50.1	0.2
Cyclohexane	35.6	25.1	10.5	35.6	[0.0]
Cyclooctatetraene	44			44	[0.0]
Tetralin $\overline{C_6H_4(CH_2)_4}$	52			52	[0.0]
cis-Decalin	55.4			55.0	0.4
trans-Decalin	54.5			55.0	−0.5
			Halogen-Containing		
Chloroform^d	27.6	15.7	11.9	...	
Carbon tetrachloride^d	31.7	19.9	11.4	...	
1,2-Dibromoethane	32.2	18.2^e	14	32.2	[0.0]
1,1,1-Trichloro ethane	34.4	22.4	12.0	34.4	[0.0]
1,1-Dichloro ethylene	26.6	16.1	10.5	26.6	[0.0]
Fluoro benzene	35.1	22.7	12.4	35.1	[0.0]
Chloro benzene	34.9	23.6	11.3	34.9	[0.0]
Bromo benzene	37.1	24.2	12.9	37.1	[0.0]
			Sulfur-Containing		
Carbon disulfide^d	18.2	10.9	7.3		
Dimethyl sulfide	28.3	17.8	10.5	28.3	0.0
Methylethyl sulfide	34.6	22.8	11.8	34.1	0.5
Methyl n-propyl sulfide	41.0	28.2	12.8	41.4	−0.4
Methyl n-butyl sulfide	48.0	33.8	14.2	48.6	−0.6
Diethyl sulfide	40.9	28.1	12.8	39.9	1.0
Ethyl n-propyl sulfide	47.4	33.4	14.0	47.2	0.2
Di-n-propyl sulfide	54.0	38.7	15.3	54.4	−0.4
Di-n-butyl sulfide	68.0	49.7	18.3	68.9	−0.9
Methyl isopropyl sulfide	41.2	28.8	12.4	40.8	0.4
Ethyl mercaptan	28.2	17.4	10.8	27.1	1.1
N-butyl mercaptan	41.3	28.4	12.9	41.6	−0.3
Iso-butyl mercaptan	41.1	28.4	12.7	40.9	0.2
Amyl mercaptan	48.2	33.9	14.3	48.8	−0.6
Iso-propyl mercaptan	34.7	23.1	11.6	33.8	0.9
Sec-butyl mercaptan	40.9	28.6	11.3	41.1	−0.2
Cyclo-pentyl mercaptan	39.5	25.9	13.6	40.4	−0.9
Tert-butyl mercaptan	41.8	29.0	12.8	41.8	[0.0]
Dimethyl disulfide	34.9	22.6	12.3	36.0	−1.1
Diethyl disulfide	48.7	33.9	14.8	47.6	1.1
$\overline{(CH_2)_3S}$	27.1	16.7	10.4	27.1	[0.0]
$\overline{(CH_2)_4S}$	33.5	21.9	12.6	33.5	[0.0]
$\overline{(CH_2)_5S}$	39.0	26.0	13.0	39.0	[0.0]
Phenyl mercaptan	39.1	25.2	13.9	39.1	[0.0]
			Silicon-Containing		
Tetramethylsilane	49.8	33.5	16.3	49.8	[0.0]
Hexamethyldisiloxane	74.4			74.4	[0.0]

available, then atom additivity may be used, and the precision in estimating $C_p(g)$ is now ± 3 cal. mole^{-1} deg.$^{-1}$. Depending on whether $C_p(g)$ has been measured or has been estimated by group or atom additivity, the overall precision in $C_p(l)$ is between ±4 and ±7 cal. mole^{-1} deg.$^{-1}$ for most organic liquids.

If the principle of group additivity were applied directly to the $C_p(l)$ data and the groups derived, the estimation of $C_p(l)$ would be facilitated, the precision should be improved to better than ±2 cal. mole^{-1} deg.$^{-1}$, and linear molecules such as hydrocarbons longer than C_8 would be included.

RESULTS AND DISCUSSION

The success of additivity methods depends on the quality and extent of the measured data. Except for nitromethane (5), all the data were taken from Timmermans' critical reviews (10). In most cases, it was necessary to make a small interpolation, usually over a temperature range of less than 5° C., to get the value at 25° C. In one or two cases where the molecule was particularly interesting, a slightly larger extrapolation was made. These few cases are noted. The measured $C_p(l)$ for t-butyl alcohol (2 methyl

propanol-2) looks high, and an alternative value is estimated, using ΔC_p (liquid − gas) = 15. The $C_p(l)$ for hydrazine, required for the calculation of some interesting groups, was estimated as $C_p(g)$ + 10.

One of the indirect benefits of the present compilation is that it highlights the distribution of the measured data and indicates areas where more measurements are needed. The alkanes, mercaptans, and thioethers contain more than enough data to generate group values. The alkanes, ring compounds, aromatics, and alcohols have few gaps. There are important omissions in the other areas, for example, alkynes, halogen compounds (only two fluorine-containing molecules), oxygen compounds (e.g., acetaldehyde, hydrogen peroxide), and nitrogen compounds (e.g., hydrazine, amines).

The group values are given in Table II.

The principle of group additivity is explained in detail elsewhere (2, 3), so only a brief outline will be given here. A useful way to look at it is to consider an example. The n-hexane molecule is made up of two methyls bonded to carbon atoms, indicated by $2[C—(C)(H)_3]$, and four methylenes bonded to two carbon atoms, indicated by $4[C—(C)_2H_2]$. Similarly, n-heptane is composed of $2[C—(C)(H)_3]$ + $5[C—(C)_2H_2]$; i.e.,

Table II. Group Values Used to Calculate Constant-Pressure Heat Capacity of Liquids at 25° C. and 1 Atm., Cal. Mole^{-1} Deg.$^{-1}$

Group	Value	Group	Value
Alkane		**Oxygen**	
C—(C)(H)₃	8.80	O—(C)(H)	10.7
C—(C)₂(H)₂	7.26	O—(C)₂	8.5
C—(C)₃(H)	5.00	O—(CO)(H)	13.6
C—(C)₄	1.76	O—(CO)(C)	8.5
		O—(C_B)₂	11.2
Olefin		CO—(O)(H)	10.0 (assigned)
		CO—(O)(C)	7.0
C_d—(H)₂	5.2	CO—(C)₂	12.6
C_d—(C)(H)	5.1	C—(O)(C)(H)₂	7.5
C_d—(C)₂	3.8	C—(O)(C)₂(H)	8.8
C_d—(C_d)(H)	9.6	C—(O)(C)₃	16.1 or 5.1
C_d—(C_d)(C)	7.9	C—(O)(C_B)(H)₂	12.0
C—(C_d)₂(H)₂	14.3	C_B—O	0.0 (assigned)
C—(C_d)(C)(H)₂	9.8		
C—(C_d)(C)₂(H)	9.4	**Nitrogen**	
C_t—(C)	5.9	N—(N)(H)₂	11.1
cis-Corr	−1.3	N—(N)(C)₂	10.5
		N—(N)(C)(H)	7.6
Aromatics		N—(C_B)(H)₂	19.7
		C_B—N	0.0 (assigned)
C_B—(H)	5.3	C_d—(CN)(H)	21.3
C_B—(C)	2.9	O—(C)(NO₂)	28.7
C—(C_B)(C)(H)₂	6.3		
		Sulfur	
Rings		S—(C)(H)	12.5
Cyclopentane	−4.8	S—(C)₂	10.7
Cyclopentene	−7.7	S—(C_B)(H)	12.6
Cyclohexane	−6.5	S—(S)(C)	9.2
Cyclohexene	−8.7	C—(S)(C)(H)₂	5.8
Cyclooctatetraene	−32.8	C—(S)(C)₂(H)	3.7
Decalin	−13.1	C—(S)(C)₃	2.9
Tetralin	−2.5	C_B—(S)	0.0 (assigned)
		(CH₂)₃S	−2.5
Halogen		(CH₂)₄S	−3.3
C—(Br)(C)(H)₂	16.1	(CH₂)₅S	−5.1
C—(Cl)₃(C)	25.6		
C_d—(Cl)₂	21.4	**Silicon**	
C_B—F	8.6	Si—(O)(C)₃	0.0 (assigned)
C_B—Cl	8.4	O—(Si)₂	21.6
C_B—Br	10.6		

$$2[C—(C)(H)_3] + 4[C—(C)_2(H)_2] = 46.6$$

$$2[C—(C)(H)_3] + 5[C—(C)_2(H)_2] = 53.7$$

Solving, $[C—(C)_2(H)_2] = 7.1$ and $[C—(C)(H)_3] = 9.1$.

The C_p of n-octane may then be estimated as $2[C—(C)(H)_3] + 6[C—(C)_2(H)_2] = 60.8$ (cf. 60.7 observed). The other groups were obtained similarly. In practice, when there is a large amount of measured data, the groups are derived by computer, using a least squares regression program (9). This was the case in the alkanes, alkenes, aromatics, and sulfur compounds. In some cases, it is not possible to determine a group independently of other groups. For example, methanol is $[C—(O)(H)_3] + [O—(C)(H)] = 19.5$. Continuing the practice adopted for gases (3), all $[C—(X)(H)_3]$ groups, where X is an atom other than C, were assigned the same value as $[C—(C)(H)_3] = 8.8$. It follows that $[O—(C)(H)] = 10.7$. This practice in no way affects the system; it only makes the computation simpler. In other cases, when pairs of groups are obtained and when one of them is not a $[C—(X)(H)_3]$, one group is arbitrarily assigned. In a number of cases, there were so many unknown groups that no assignments were made.

Group additivity does not take into account next to nearest neighbor interactions, such as gauche effects (3) or cis effects. The fit of the observed minus estimated for the alkenes improved only slightly using gauche corrections, so it was felt that the gain in precision was not worthwhile. The cis effect for olefins is significant and is included.

Table I shows that for all the data, the precision in estimating $C_p(l)$ is ± 1.5 cal. $mole^{-1}$ deg.$^{-1}$, and in most cases is better than ± 1 cal. $mole^{-1}$ deg.$^{-1}$.

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Phase Diagram of the System LiCl–KCl–CaCrO₄

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The phase diagram has been determined for the system LiCl–KCl–CaCrO₄. Binary eutectics have been located at 60 wt. % KCl–40 wt. % CaCrO₄ (m.p. 651°C.) and 62 wt. % LiCl–38 wt. % CaCrO₄ (m.p. 638°C.). A ternary eutectic was found at 41 wt. % LiCl–50 wt. % KCl–9 wt. % CaCrO₄ (m.p. 342°C.). It has been verified by x-ray diffraction that LiCl–KCl–CaCrO₄ is the stable diagonal section in the quaternary reciprocal system K, Li, Ca/ /CrO₄, Cl.

THE SALT mixture LiCl-KCl-CaCrO₄ is an electrolyte-depolarizer combination used in thermal cells (voltaic cells employing a molten salt electrolyte). The cell Ca/LiCl-KCl-CaCrO₄/Ni has been studied by Jennings (4). Recent investigations of this thermal cell system have demonstrated a need for a detailed phase diagram determination of the

mixture LiCl-KCl-CaCrO₄. This ternary system is actually a stable diagonal section of the K, Li, Ca/ /CrO₄, Cl quaternary reciprocal system.

The sides of the ternary diagram are the binary system LiCl-KCl and the stable diagonals of the ternary reciprocal systems K, Ca/ /Cl, CrO₄ and Li, Ca/ /Cl, CrO₄. That LiCl-CaCrO₄, KCl-CaCrO₄, and LiCl-KCl-CaCrO₄ are indeed stable systems has been confirmed by x-ray diffraction studies at Sandia Laboratories.