$A_1 = \int_0^1 \ln \gamma_1 dx_1$

$A_2 = \int_0^1 \ln \gamma_2 dx_1$

$A_H = \int_{x=0}^{x=1} (\Delta H/RT^2) dT$

$\Delta A = A_1 - (A_2 + A_H)$

ΣA = area sum as defined in Table V

B_{11} = second virial coefficient for pure component 1

B_{22} = second virial coefficient for pure component 2

B_{12} = second virial cross coefficient

ΔH = molar enthalpy of mixing, J/g mol

P = total pressure

P_1^0, P_2^0 = vapor pressures of pure components 1, 2

R = gas constant

T = temperature, °K

v_1^L, v_2^L = pure component liquid molar volumes, cc/g mol

x_1, x_2 = mole fractions of components 1, 2 in liquid phase

y_1, y_2 = mole fractions of components 1, 2 in vapor phase

GREEK LETTERS

α^{12} = relative volatility

γ_1, γ_2 = liquid-phase activity coefficients of components 1, 2

$\delta_{12} = 2B_{12} - B_{11} - B_{22}$

SUBSCRIPTS

1 = component 1

2 = component 2

i = component 1 or component 2

LITERATURE CITED

(1) Brown, I., *Austr. J. Sci. Res., Ser. A; Phys. Sci.*, **5** (3), 530 (1952).

(2) Fowler, R. T., Morris, G. S., *J. Appl. Chem. (London)*, **5**, 266 (1955).

(3) Gillespie, D. T. C., *Ind. Eng. Chem., Anal. Ed.*, **18**, 575 (1946).

(4) Hala, E., Pick, J., Fried, V, Villim, O., "Vapor-Liquid Equilibrium," 2nd ed., p 280, Pergamon Press, New York, N.Y., 1967.

(5) "Handbook of Chemistry and Physics," 50th ed., p C321, Chemical Rubber, Cleveland, Ohio, 1969.

(6) "International Critical Tables," Vol. 3, pp 27, 29, McGraw-Hill, New York, N.Y., 1929.

(7) Jones, C. A., Schoenborn, E. M., Colburn, A. P., *Ind. Eng. Chem.*, **35**, 666 (1943).

(8) Jordan, T. E., "Vapor Pressure of Organic Compounds," pp 6, 65, Interscience, New York, N.Y., 1954.

(9) Katz, K., Newman, M., *Ind. Eng. Chem.*, **48**, 137 (1956).

(10) "Kirk Othmer Encyclopedia of Chemical Technology," 2nd ed., Vol. 8 p 42; Vol. 11, p 1; Vol. 13, p 370, Interscience, New York, N.Y., 1965.

(11) Knoebel, D. H., Edmister, W. C., *J. Chem. Eng. Data*, **13**, 312 (1968).

(12) McGlashan, M. L., Potter, D. J. B., *Proc. Roy. Soc.*, **267A**, 478 (1962).

(13) Otsuki, H., Williams, C. F., *Chem. Eng. Progr. Symp. Ser.*, **49** (6), 55 (1953).

(14) Pitzer, K. S., Curl, R. F., *J. Amer. Chem. Soc.*, **79**, 2369 (1957).

(15) Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibrium," pp 74, 157, 214, 471, Prentice-Hall, Englewood Cliffs, N.J., 1969.

(16) Prausnitz, J. M. Eckert, C. A., Orye, R. V., O'Connell, J. P., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria," p 20, Prentice-Hall, Englewood Cliffs, N.J., 1967.

(17) Savini, C. G., Winterhalter, D. R., Van Ness, H. C., *J. Chem. Eng. Data*, **10**, 168 (1965).

(18) Van Ness, H. C., Soczek, C. A., Kochar, N. K., *ibid.*, **12**, 346 (1967).

RECEIVED for review January 28, 1971. Accepted November 1, 1971. Paper presented at the Chicago meeting of the AIChE, 1970. This work was supported in part by grants from the National Research Council of Canada.

Emf Measurements in Additive Ternary Molten Salt Systems $PbCl_2$–KCl–NaCl and $PbCl_2$–CsCl–NaCl

KJELL HAGEMARK,[1] DENNIS HENGSTENBERG, and MILTON BLANDER[2]

North American Rockwell Science Center, Thousand Oaks, Calif. 91360

Emf measurements in the binary molten systems, $PbCl_2$–NaCl, $PbCl_2$–KCl, and $PbCl_2$–CsCl, and in the ternary systems, $PbCl_2$–NaCl–KCl and $PbCl_2$–NaCl–CsCl, were made at mole fractions of $PbCl_2$ of 0.5 and 0.3. Our data (as well as some previous data) on excess free energies of solution in the three binary systems are consistent with the equation first suggested by Førland (Equation 1) in terms of equivalent fractions, with the coefficients λ = −1800, −10,300, and −15,500 cal/mol for the mixtures with NaCl, KCl, and CsCl, respectively. Measurements of $\bar{G}_{PbCl_2}^E$ at constant mole fractions of $PbCl_2$ in the ternary systems exhibited small negative deviations from additivity.

In this paper we present electromotive force measurements and partial molar quantities for $PbCl_2$ in the three binary systems $PbCl_2$–NaCl, $PbCl_2$–KCl, and $PbCl_2$–CsCl, and in the two ternary systems, $PbCl_2$–NaCl–KCl and $PbCl_2$–NaCl–CsCl, at mole fractions of $PbCl_2$ of 0.5 and 0.3. A critique of previous work on the binary systems is given, and we show that the simplest representation of the data on the activity coefficients, γ, and the partial molar excess free energy, $\bar{G}^E$, of $PbCl_2$ has a form first suggested for the binaries by Førland (*2*, *6*):

$$\bar{G}_{PbCl_2}^E = RT \ln \gamma_{PbCl_2} = \lambda(1 - N_{PbCl_2}')^2 \qquad (1)$$

[1] Present address, 3M Central Research Laboratory, St. Paul, Minn. 55119

[2] Present address, Chemical Engineering Division, Argonne National Laboratory, Argonne, Ill. 60439. To whom correspondence should be addressed.

where N_{PbCl_2}' is the equivalent fraction of $PbCl_2$ defined by the relationship

$$N_{PbCl_2}' = \frac{2\,N_{PbCl_2}}{2\,N_{PbCl_2} + N_{ACl}} = \frac{2\,n_{PbCl_2}}{2\,n_{PbCl_2} + n_{ACl}}$$

where N designates mole fraction, n the number of moles, and ACl alkali chloride. Values of $G_{PbCl_2}^{E}$ in the ternary systems at constant mole fraction of $PbCl_2$ exhibit negative deviations from additive behavior. These data will be analyzed in terms of the thermodynamic treatment we have utilized previously (*7, 8*).

Previous work on $PbCl_2$-containing systems include emf measurements of the activities of $PbCl_2$ in the binary systems $PbCl_2$–NaCl and $PbCl_2$–KCl (*11, 13, 14*) vapor pressure and transpiration measurements in the $PbCl_2$–KCl and $PbCl_2$–CsCl systems (*1, 3*) and calorimetric measurements of enthalpies of mixing of $PbCl_2$ with all the alkali halides (*15*). The only prior measurements in the ternary systems are for a 48–36–16 mol % $PbCl_2$–KCl–NaCl mixture (*4*) and a dilute solution of $PbCl_2$ in equimolar NaCl–KCl (*5*).

Systematic emf studies of ternary molten salt mixtures have been seldom reported. Partial molar excess properties of $NiCl_2$ in 1:1 molar NaCl–KCl have been reported (*10*) and the ternary systems AgCl–NaCl–KCl and AgCl–NaCl–CsCl have been studied.

EXPERIMENTAL

The measurements were carried out in the reversible formation cell graphite, $Pb|PbCl_2 + ACl|Cl_2$, graphite, (A = Na, K, Cs, Na–K, Na–Cs) which has provided reliable emf data for the free energy of formation of $PbCl_2$. The construction of the cell is identical to the one previously described (*9*). Except for CsCl (Penn Rare Metals, 99.9% pure), the chemicals were Baker "Analyzed" reagents and were used without any further purification. The Cl_2 gas was 99.5% pure from Matheson Co. and was bubbled through H_2SO_4 prior to being passed into the chlorine electrode.

The composition of the salt mixture was calculated from the weighed-out portions of the salts, and in some cases they were checked by wet chemical analysis after the experiments. (Lead was done by back titration with Ca^{2+} after addition of excess EDTA. Na, K, and Cs were done by flame emission spectroscopy.) Although vaporization was observed, the concentration did not change significantly during an experiment (less than ±1 mol %). To check the electrodes, emf measurements were frequently checked in pure $PbCl_2$. The contamination of these electrodes by their handling and exposure to oxygen upon opening and closing of the cell compartment led to emf values for pure $PbCl_2$ which differed by 1.0–2.6 mV from measurements made by using lead carefully purified by acid washing.

The absolute values of the emf given here have been corrected for this measured difference, which is due to impurities in the lead and should be the same for all cells for a given impurity level. The solution properties calculated from differences of emf values are, of course, unaffected by this shift. The emf measurements were calibrated with a standard Eppley cell and the platinum–platinum-10% rhodium thermocouple was calibrated vs. a standard thermocouple to ±0.2°C. Measurements were made to ±1°C.

RESULTS

Ternary mixtures of $PbCl_2$–NaCl–KCl and $PbCl_2$–NaCl–CsCl were examined at compositions N_{PbCl_2} equals 0.5 and 0.3. The ratio $x = n_{NaCl}/(n_{NaCl} + n_{ACl})$ was chosen equal to 0, 0.25, 0.5, 0.75, and 1.0. Data for the emf as a function of temperature are shown in Figures 1–4, where it is noted that at least two separate sets of measurements were made for each composition. The temperature range of the measurements was chosen well above the liquidus temperature to ensure that the salt mixture was completely molten; this explains the higher temperatures for the mixtures high in NaCl, or low in $PbCl_2$. The data are also given in Table I. A least-squares

Table I. Measured Values of Emf in Systems $PbCl_2$–NaCl–KCl and $PbCl_2$–NaCl–CsCl

T, °C	Emf, V
50 $PbCl_2$–50 KCl	
594.5	1.2733
606.2	1.2682
599.8	1.2728
589.2	1.2784
577.0	1.2863
567.5	1.2909
558.4	1.2953
557.4	1.2968
562.0	1.2933
569.9	1.2884
582.2	1.2813
590.2	1.2764
601.8	1.2699
597.7	1.2723
. . . . .	
564.3	1.2922
551.0	1.2999
567.1	1.2912
583.5	1.2805
593.6	1.2741
580.9	1.2825
571.8	1.2871
555.7	1.2965
578.0	1.2836
600.1	1.2712
50 $PbCl_2$–37.5 KCl–12.5 NaCl	
597.7	1.2678
590.0	1.2729
581.1	1.2776
567.7	1.2848
553.3	1.2932
568.5	1.2847
584.1	1.2755
593.6	1.2701
598.6	1.2668
573.5	1.2816
. . . . .	
604.7	1.2635
592.5	1.2708
582.0	1.2770
572.3	1.2824
50 $PbCl_2$–25 KCl–25 NaCl	
595.0	1.2640
603.8	1.2589
586.9	1.2679
579.2	1.2723
574.8	1.2746
566.2	1.2792
558.3	1.2843
553.0	1.2874
561.8	1.2825
570.1	1.2777
579.0	1.2725
588.8	1.2664
. . . . .	
657.7	1.2286
644.9	1.2357
627.3	1.2459
615.5	1.2524
666.9	1.2239
636.1	1.2405
653.1	1.2302
585.8	1.2683
50 $PbCl_2$–12.5 KCl–37.5 NaCl	
650.5	1.2251
643.1	1.2290
671.1	1.2142
643.3	1.2309
668.3	1.2168
629.1	1.2379
659.8	1.2208
633.9	1.2346
. . . . .	
637.4	1.2341
620.1	1.2428
645.8	1.2298
663.5	1.2205
669.6	1.2171
657.5	1.2233
628.0	1.2400
652.1	1.2264
50 $PbCl_2$–50 NaCl	
672.3	1.2092
652.9	1.2194
640.2	1.2262
622.3	1.2355
672.8	1.2100
639.6	1.2269
620.9	1.2365
. . . . .	
670.5	1.2103
652.2	1.2199
620.8	1.2333
636.2	1.2283
661.6	1.2150
645.8	1.2227
30 $PbCl_2$–70 KCl	
686.6	1.2782
689.0	1.2771
699.6	1.2721
679.0	1.2827
672.6	1.2856
664.4	1.2898
658.2	1.2926
652.8	1.2955
650.7	1.2966
656.1	1.2942
663.6	1.2906
. . . . .	
683.4	1.2821
679.0	1.2842
669.7	1.2895
660.4	1.2943
653.9	1.2982
663.3	1.2926
667.6	1.2900
675.5	1.2855
681.2	1.2839
689.3	1.2798
696.7	1.2763
684.6	1.2813
684.7	1.2821
30 $PbCl_2$–52.5 KCl–17.5 NaCl	
689.5	1.2704
693.4	1.2683
695.8	1.2670

(*Continued on next page*)

fit of the data to an equation of the form

$$E(\mathrm{V}) = a + b(t - t_0) \qquad (2)$$

led to the coefficients in Table II. The standard deviations were generally less than 1 mV and always less than 2 mV. In each case t_0 (in °C) is chosen close to the average temperature of the series of measurements. To make an isothermal comparison of the data, values for the emf were obtained by a linear extrapolation (or interpolation) to an intermediate temperature, 625°C. The emf value of the formation cell for pure $PbCl_2$, $E°$ at 625°C was obtained by a short extrapola-

Table I. (Continued)

30 $PbCl_2$–52.5 KCl–1.75 NaCl (*Contd.*)

T, °C	Emf, V
692.9	1.2685
687.2	1.2722
682.3	1.2738
680.8	1.2748
676.6	1.2770
667.1	1.2817
650.5	1.2895
654.5	1.2875
661.1	1.2851
. . . . .	
678.4	1.2759
663.9	1.2841
659.5	1.2856
650.2	1.2902
657.2	1.2856
670.0	1.2795
678.4	1.2756
688.1	1.2712
699.8	1.2651
688.5	1.2717

30 $PbCl_2$–35 KCl–35 NaCl

691.1	1.2526
687.5	1.2549
683.3	1.2572
679.2	1.2592
673.6	1.2622
669.4	1.2644
662.7	1.2677
656.7	1.2710
649.3	1.2747
644.7	1.2770
647.9	1.2754
654.3	1.2722
660.3	1.2693
667.1	1.2662
677.6	1.2609
. . . . .	
684.6	1.2558
673.8	1.2612
652.1	1.2722
640.5	1.2779
644.7	1.2753
657.1	1.2695
673.1	1.2610
684.1	1.2562
688.4	1.2536
699.1	1.2477
694.1	1.2499
690.9	1.2517
687.6	1.2537
683.2	1.2557
679.2	1.2579
670.0	1.2625
662.9	1.2666
658.0	1.2681
676.5	1.2589
686.5	1.2537
695.3	1.2496

30 $PbCl_2$–17.5 KCl–52.5 NaCl

687.9	1.2407
692.0	1.2381
694.3	1.2371
663.6	1.2527

30 $PbCl_2$–17.5 KCl–52.5 NaCl (*Contd.*)

T, °C	Emf, V
659.5	1.2561
664.4	1.2525
672.3	1.2485
678.1	1.2458
685.3	1.2423
690.9	1.2396
681.8	1.2445
676.4	1.2472
. . . . .	
685.9	1.2425
667.8	1.2515
660.0	1.2556
664.2	1.2526
671.9	1.2484
682.5	1.2436
695.8	1.2351
690.0	1.2392
678.0	1.2459
650.5	1.2597

30 $PbCl_2$–70 NaCl

692.7	1.2222
697.7	1.2201
684.6	1.2270
676.6	1.2314
671.4	1.2341
667.8	1.2362
664.8	1.2379
655.4	1.2427
. . . . .	
692.3	1.2224
689.2	1.2242
675.3	1.2321
663.0	1.2388
657.6	1.2417
651.9	1.2448
655.1	1.2433
667.6	1.2360
682.0	1.2286
687.5	1.2257
695.5	1.2213

50 $PbCl_2$–50 CsCl

678.4	1.2395
661.0	1.2487
642.7	1.2584
. . . . .	
625.7	1.2669
644.8	1.2565
662.4	1.2474
679.9	1.2387
667.6	1.2454
656.9	1.2505
650.1	1.2539
635.2	1.2611
613.2	1.2732
631.4	1.2639

50 $PbCl_2$–37.5 CsCl–12.5 NaCl

650.2	1.2493
672.7	1.2387
655.3	1.2477
632.5	1.2591
614.0	1.2678
643.8	1.2517
667.1	1.2417

50 $PbCl_2$–37.5 CsCl–12.5 NaCl (*Contd.*)

T, °C	Emf, V
679.0	1.2365
630.1	1.2596
. . . . .	
654.4	1.2466
668.2	1.2395
644.1	1.2511
638.4	1.2549
625.5	1.2605
659.8	1.2433

50 $PbCl_2$–25 CsCl–25 NaCl

662.9	1.2355
674.2	1.2297
648.6	1.2430
663.2	1.2350
679.7	1.2273
655.2	1.2396
630.2	1.2509
622.3	1.2545
. . . . .	
646.1	1.2428
677.4	1.2267
668.6	1.2313
633.7	1.2488
656.6	1.2370

50 $PbCl_2$–12.5 CsCl–37.5 NaCl

625.7	1.2506
656.8	1.2338
680.0	1.2209
669.6	1.2260
649.6	1.2361
630.0	1.2469
617.5	1.2540
641.0	1.2414
660.6	1.2306
. . . . .	
630.5	1.2474
665.5	1.2289
678.9	1.2209
671.8	1.2254
651.1	1.2356
640.1	1.2418
653.7	1.2355
646.0	1.2387

30 $PbCl_2$–70 CsCl

676.7	1.3207
688.6	1.3152
673.5	1.3229
663.0	1.3286
672.2	1.3234
. . . . .	
669.6	1.3257
700.0	1.3099
692.0	1.3139
680.5	1.3195
663.8	1.3276
654.8	1.3317
648.5	1.3358
689.0	1.3162
700.5	1.3100
640.7	1.3393

30 $PbCl_2$–52.5 CsCl–17.5 NaCl

650.9	1.3142

30 $PbCl_2$–52.5 CsCl–17.5 NaCl (*Contd.*)

T, °C	Emf, V
658.4	1.3096
664.1	1.3068
683.6	1.2978
701.0	1.2890
688.5	1.2960
676.7	1.2921
656.8	1.3109
670.9	1.3035
693.7	1.2929
668.5	1.3048
. . . . .	
673.0	1.3034
648.5	1.3143
662.7	1.3081
691.5	1.2942
680.5	1.2996
655.7	1.3112

30 $PbCl_2$–35 CsCl–35 NaCl

650.2	1.2914
656.7	1.2882
665.8	1.2837
681.7	1.2765
691.6	1.2715
699.0	1.2686
686.4	1.2752
673.8	1.2816
681.9	1.2763
698.0	1.2686
685.6	1.2749
671.7	1.2819
657.6	1.2886
610.5	1.2817
. . . . .	
671.9	1.2809
660.0	1.2866
648.5	1.2923
682.0	1.2763
697.0	1.2691
688.4	1.2733

30 $PbCl_2$–17.5 CsCl–52.5 NaCl

686.6	1.2567
698.2	1.2508
685.9	1.2559
671.2	1.2627
663.5	1.2672
656.5	1.2706
668.7	1.2645
682.9	1.2575
691.9	1.2522
679.8	1.2580
. . . . .	
677.6	1.2582
663.6	1.2654
649.0	1.2733
671.7	1.2612
688.1	1.2531
700.5	1.2467
686.5	1.2542
673.1	1.2610
656.8	1.2693
680.3	1.2570
698.0	1.2486
689.1	1.2526

tion of the values for E° in the range 500–620°C from a previous paper (9).

The activity of a component, i, in solution (here, $i = PbCl_2$), a_i, may be defined through the relationship

$$RT \ln a_i = \bar{G}_i - \bar{G}_i^\circ = -2F(E - E^\circ) \quad (3)$$

where R is the gas constant in cal/mol-degree, T is the temperature in degrees Kelvin, $\bar{G}_i - G_i^\circ$ is the partial molar free energy of solution of $PbCl_2$; the Faraday constant, $F = 23{,}062$ cal/V, and $E - E^\circ$ is the difference in emf between a cell containing i in solution and a cell containing pure i, respectively. The activity coefficient, γ_i, is related to the activity by Equation 4:

$$\gamma_i = a_i/N_i \quad (4)$$

where N_i is the mole fraction of $PbCl_2$ in the system. The partial molar excess free energy,

$$\bar{G}_i^E \equiv RT \ln \gamma_i = \bar{G}_i - G_i^\circ - RT \ln N_i \quad (5)$$

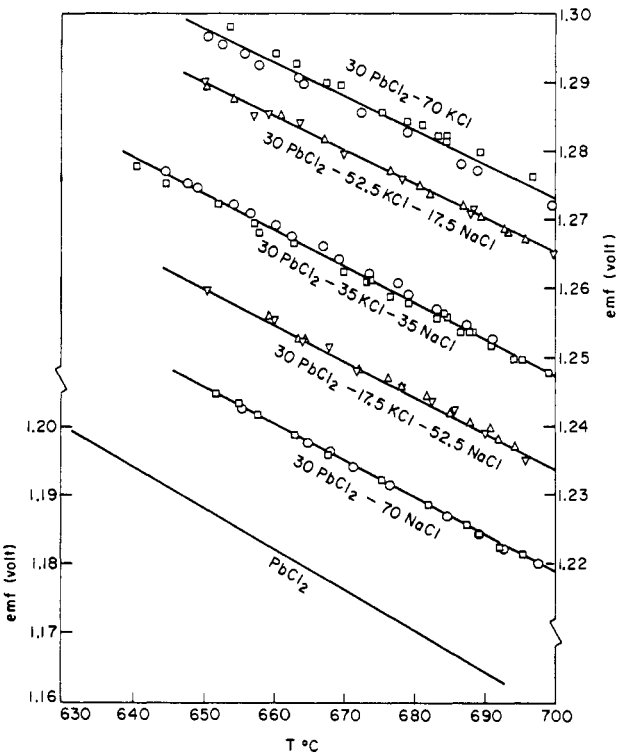

Figure 1. Emf vs. temperature in $PbCl_2$–NaCl–KCl system

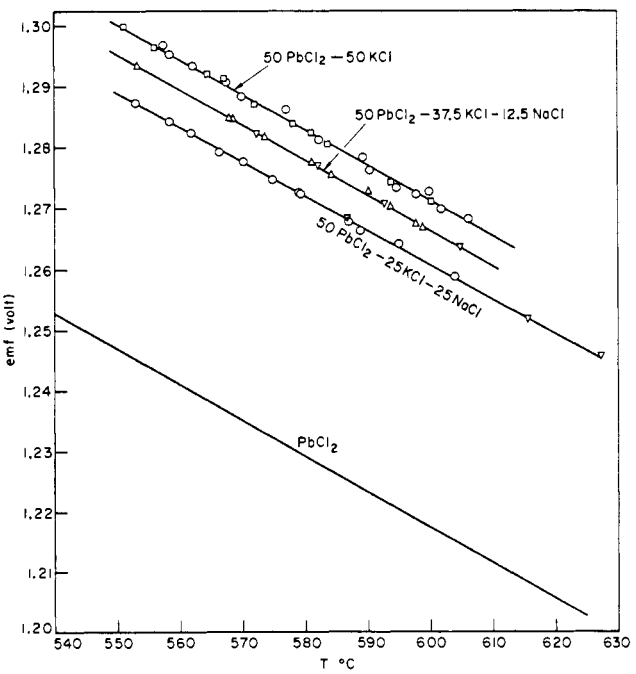

Figure 2. Emf vs. temperature in $PbCl_2$–NaCl–KCl system

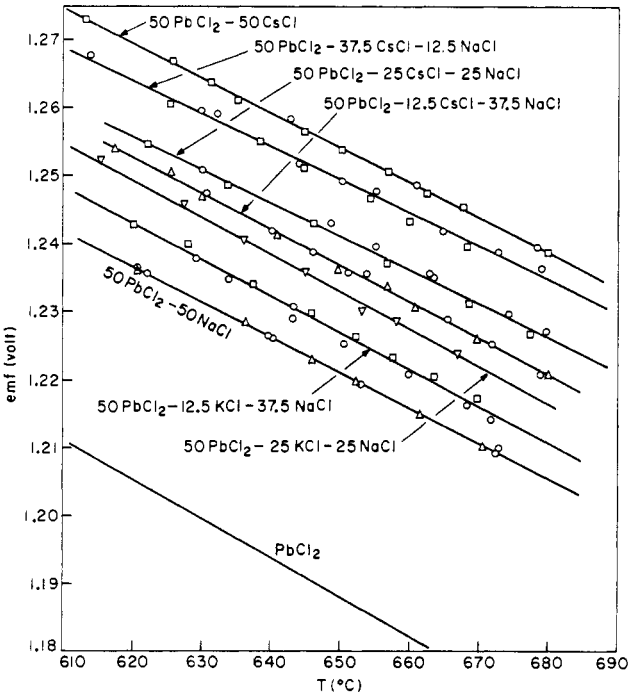

Figure 3. EMF vs. temperature in $PbCl_2$–NaCl–CsCl system

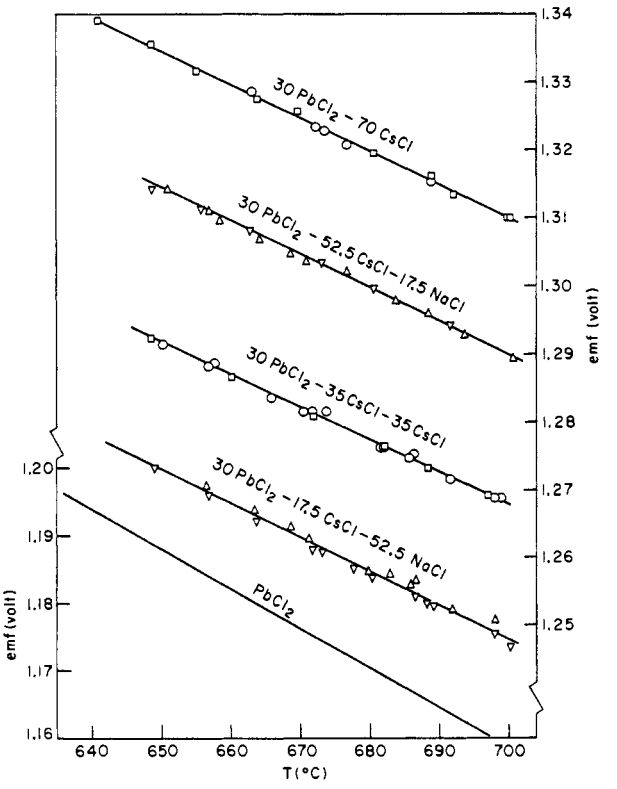

Figure 4. EMF vs. temperature in $PbCl_2$–NaCl–CsCl system

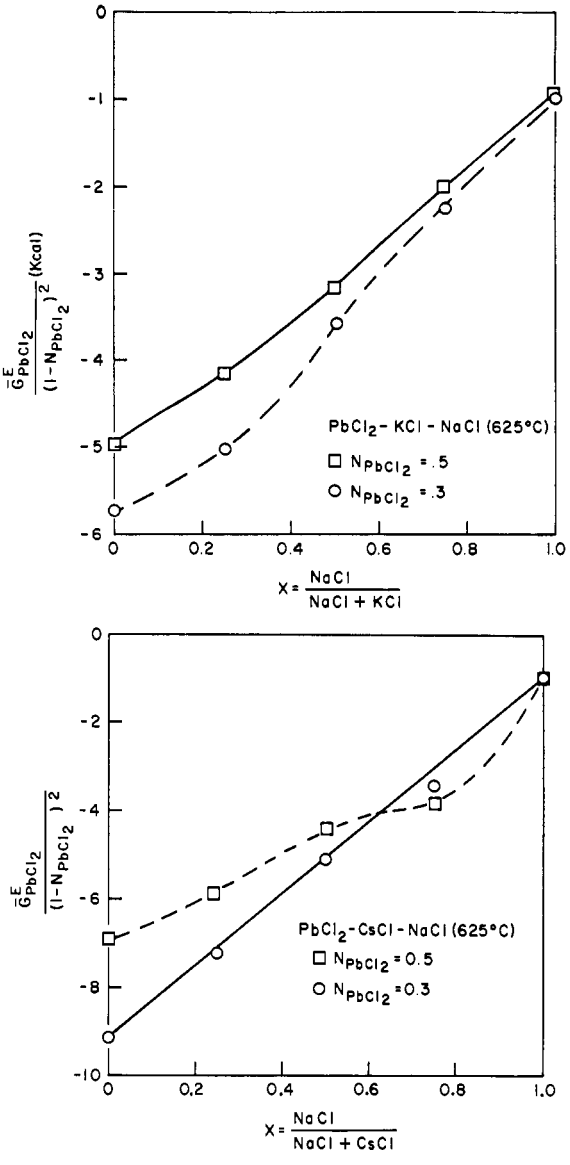

Figure 5. Top, free energy function at constant N_{PbCl_2} in $PbCl_2$–NaCl–KCl system at 625°C. Bottom, free energy function at constant N_{PbCl_2} in the $PbCl_2$–NaCl–CsCl system at 625°C

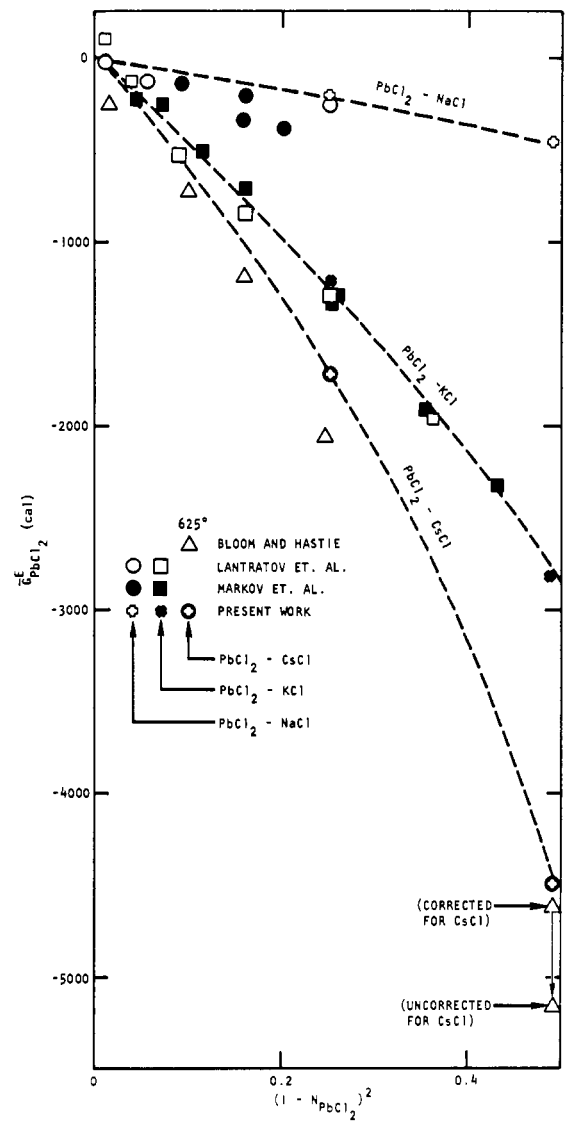

Figure 6. Plot of $\bar{G}_{PbCl_2}^E$ vs. $(1 - N_{PbCl_2})^2$ at 625°C

Values of $\bar{G}_{PbCl_2}^E$ at 625°C are given in the last column of Table II.

In Figures 5a and 5b, $\bar{G}_{PbCl_2}^E/(1 - N_{PbCl_2})^2$ is shown as a function of x at constant N_{PbCl_2}. With an uncertainty of ±1 mV in $E - E°$, the error in $\bar{G}_{PbCl_2}^E/(1 - N_{PbCl_2})^2$ is ±200 cal at $N = 0.5$ and ±100 cal at $N_{PbCl_2} = 0.3$. Within the limits of experimental error, $\bar{G}_{PbCl_2}^E/(1 - N_{PbCl_2})^2$ is not a linear function of x at constant N_{PbCl_2}. In the systems $PbCl_2$–NaCl–KCl, the negative deviation from linearity seems to be greater at smaller values of x, whereas the opposite is observed to be the case in the system $PbCl_2$–NaCl–CsCl where the negative deviation is at x close to 1. A short extrapolation of the emf measurements of Delimarskii and Roms (*4*) for the 48 mol % $PbCl_2$–36% KCl–16% NaCl systems gives $\bar{G}_{PbCl_2}^E/(1 - N_{PbCl_2})^2 = -4800$ cal for $x = 0.31$ and $N = 0.5$ at 625°C. This is 900 cal more negative than is calculated in the present work, although it supports the negative deviation from linearity observed in Figure 5a.

DISCUSSION

Measured values of $\bar{G}_{PbCl_2}^E$ in the three binary systems are plotted in Figure 6 vs. $(1 - N_{PbCl_2})^2$. Our measurements on the $PbCl_2$–NaCl and $PbCl_2$–KCl systems are consistent with those of Lantratov and Alabyshev (*13*) and those of Markov et al. (*14*). The vapor pressure measurements in the $PbCl_2$–KCl system by Barton and Bloom (*1*) are inconsistent with the other results and were not plotted. The transpiration measurement of Bloom and Hastie (*3*) on the $PbCl_2$–CsCl system are plotted in Figure 6 and differ from ours. Re-examination of their data reveals two possible reasons for these discrepancies. First, the measurements at $N_{PbCl_2} = 0.299$ were uncorrected for a significant partial pressure of the species CsCl indicating a higher activity of $PbCl_2$ than they report. Second, they used a value for the pressure of pure $PbCl_2$ at 650°C of 9.860 mm which is higher than the value given in the JANAF Tables (*12*). If their points are thus corrected, they correspond closely to our emf measurements.

The curvature of the plots of $\bar{G}_{PbCl_2}^E$ in Figure 6 suggests the dependence upon concentration first suggested by Førland (*6*) and given in Equation 1. A replot of the data vs. $(1 - N_{PbCl_2}')^2$ in Figure 7 indicates no curvature within experimental precision and supports this form for these data with $\lambda = -1800$, $-10{,}300$, and $-15{,}500$ cal/mol for the $PbCl_2$–NaCl, $PbCl_2$–KCl, and $PbCl_2$–CsCl systems, respectively. Values of $\bar{H}_{PbCl_2}^E$ were calculated from the data of McCarty and Kleppa (*15*), and with values of $\bar{G}_{PbCl_2}^E$ at 665°C from our data, we calculated the small values of $\bar{S}_{PbCl_2}^E$ given in Table III, which are consistent with findings in many other systems.

Table II. Least Squares Fit to Emf Data and Partial Molar Excess Free Energy of $PbCl_2$ at 625°C

System	Emf, V $a + b\ (t - t_0)$	$\bar{G}_{PbCl_2}^E$ (625°C), cal/mol
50 $PbCl_2$–50 KCl–0 NaCl	$1.2858 - 585 \cdot 10^{-6}\ (t - 575)$	−1240
–37.5 KCl–12.5 NaCl	$1.2809 - 576 \cdot 10^{-6}\ (t - 575)$	−1040
–25 KCl–25 NaCl	$1.2748 - 562 \cdot 10^{-6}\ (t - 575)$	−790
–25 KCl–25 NaCl	$1.2329 - 556 \cdot 10^{-6}\ (t - 650)$	...
–12.5 KCl–37.5 NaCl	$1.2269 - 540 \cdot 10^{-6}\ (t - 650)$	−500
–0 KCl–50 NaCl	$1.2211 - 521 \cdot 10^{-6}\ (t - 650)$	−210
30 $PbCl_2$–70 KCl–0 NaCl	$1.2857 - 490 \cdot 10^{-6}\ (t - 675)$	−2810
–52.5 KCl–17.5 NaCl	$1.2777 - 497 \cdot 10^{-6}\ (t - 675)$	−2450
–35 KCl–35 NaCl	$1.2607 - 526 \cdot 10^{-6}\ (t - 675)$	−1740
–17.5 KCl–52.5 NaCl	$1.2468 - 523 \cdot 10^{-6}\ (t - 675)$	−1100
–0 KCl–70 NaCl	$1.2323 - 545 \cdot 10^{-6}\ (t - 675)$	−470
50 $PbCl_2$–50 CsCl–0 NaCl	$1.2541 - 516 \cdot 10^{-6}\ (t - 650)$	−1720
–37.5 CsCl–12.5 NaCl	$1.2494 - 488 \cdot 10^{-6}\ (t - 650)$	−1480
–50 CsCl–50 NaCl	$1.2412 - 488 \cdot 10^{-6}\ (t - 650)$	−1100
–12.5 CsCl–37.5 NaCl	$1.2368 - 535 \cdot 10^{-6}\ (t - 650)$	−950
30 $PbCl_2$–70 CsCl–0 NaCl	$1.3223 - 493 \cdot 10^{-6}\ (t - 675)$	−4500
–52.5 CsCl–17.5 NaCl	$1.3020 - 480 \cdot 10^{-6}\ (t - 675)$	−3530
–35 CsCl–35 NaCl	$1.2798 - 474 \cdot 10^{-6}\ (t - 675)$	−2500
–17.5 CsCl–52.5 NaCl	$1.2605 - 499 \cdot 10^{-6}\ (t - 675)$	−1670
100 $PbCl_2$	$1.2320 - 596 \cdot 10^{-6}\ (t - 575)$	
	$1.2028 - 585 \cdot 10^{-6}\ (t - 625)$	
	$1.1881 - 580 \cdot 10^{-6}\ (t - 650)$	
	$1.1734 - 575 \cdot 10^{-6}\ (t - 675)$	

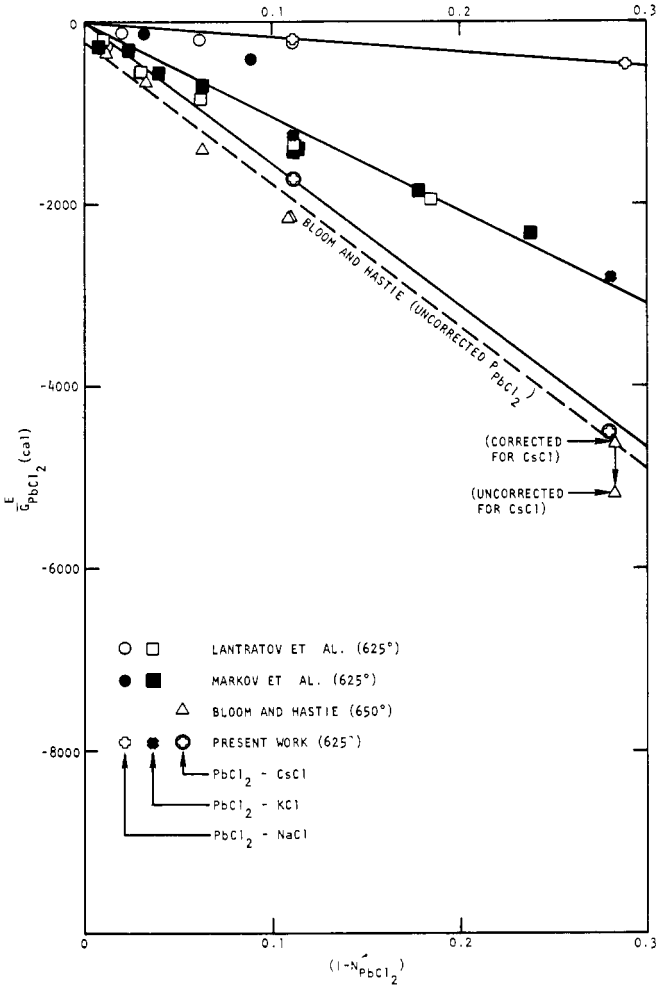

Figure 7. Plot of $\bar{G}_{PbCl_2}^E$ vs. $(1 - N_{PbCl_2}')^2$ at 625°C

$N_{PbCl_2}'\left(= \frac{2\,n_{PbCl_2}}{n_{ACl} + 2\,n_{PbCl_2}}\right)$ is the equivalent fraction of $PbCl_2$

Table III. Partial Excess Thermodynamic Quantities of $PbCl_2$ at 665°C and at N_{PbCl_2} Equals 0.5

System	$\bar{H}_{PbCl_2}^E$, cal[a]	$\bar{G}_{PbCl_2}^E$, cal[b]	$\bar{S}_{PbCl_2}^E$, cal/deg
$PbCl_2$–NaCl	−125	−280	0.2
$PbCl_2$–KCl	−750	−1200	0.5
$PbCl_2$–CsCl	−1540	−1810	0.3

[a] Reference *15*. [b] Extrapolated from present data.

LITERATURE CITED

(1) Barton, J. L., Bloom, H., *Trans. Faraday Soc.*, **55**, 1792 (1959).
(2) Blander, M., "Some Fundamental Concepts in the Chemistry of Molten Salts," in "Molten Salts," ed. by G. Mamantov, Marcel Dekker, New York, N.Y., and London, 1969.
(3) Bloom, H., Hastie, J. W., *J. Phys. Chem.*, **72**, 2361 (1968).
(4) Delimarksii, Yu. K., Roms, Yu. G., *Ukr. Khim. Zh.*, **29**, 781 (1963).
(5) Flengas, S. N., Ingraham, T. R., *J. Electrochem. Soc.*, **106**, 714 (1959).
(6) Førland, T., *J. Phys. Chem.*, **59**, 152 (1955).
(7) Guion, J., Blander, M., Hengstenberg, D., Hagemark, K., *ibid.*, **72**, 2086 (1968).
(8) Hagemark, K., *ibid.*, **72**, 2316 (1968).
(9) Hagemark, K., Hengstenberg, D., *J. Chem. Eng. Data*, **11**, 596 (1966).
(10) Hamby, Drannan C., Scott, Allen B., *J. Electrochem. Soc.*, **115** (7), 704 (1968).
(11) Hildebrand, J. H., Ruhle, G. C., *J. Amer. Chem. Soc.*, **49**, 722 (1927).
(12) JANAF Thermochemical Tables, Dow Chemical Co., Midland, Mich., 1961.
(13) Lantratov, M. F., Alabyshev, A. F., *Z. Prikl. Khim.*, **26**, 263 (1953) (Russian).
(14) Markov, B. F., Delimarskii, Yu. K., Panchenko, T. D., *Zh. Fiz. Khim.*, **28**, 1987 (1954).
(15) McCarty, F. G., Kleppa, O. J., *J. Phys. Chem.*, **68**, 3846 (1964).

RECEIVED for review May 13, 1971. Accepted November 1, 1971.