SOUTH DAKOTA SCHOOL OF MINES AND TECHNOLOGY
DEPARTMENT OF MATERIALS & METALLURGICAL ENGINEERING

MET 320 Final Exam Dec. 12, 2013

Constants:
R = 1.987 cal/K•gmole = 8.31 J/K•gmole
$\mathcal{F}$ = 23,061 cal/volt•gram equivalent = 96,485 Joule/volt•gram equivalent

1. Pure, liquid LiCl at 900 K is to undergo electrolysis to form Cl_2 gas at a pressure of 0.5 ATM and pure, liquid Li. What cell potential is needed? See the attached data sheets from JANAF for crystalline, liquid, and gaseous LiCl.

	Melting Point, K	Boiling Point, K
LiCl	878	1,655
Li	727	1,615

NOTE: (neg of Table value − ΔG° form) ↓

$LiCl_{(l)} = Li_{(l)} + \frac{1}{2} Cl_{2}(g)$

$\Delta G^{\circ} = +80{,}100 \frac{cal}{gmole\ LiCl}$

$$\Delta G = \Delta G^{\circ} + RT\ln \frac{\overset{\frac{1}{2}\ \sqrt{1/2}}{P_{Cl_2}^{}}\ \overset{1}{a_{Li}}}{\underset{1}{a_{LiCl}}} = (80{,}100 + \tfrac{1}{2} \underset{\uparrow\ 1.987 \frac{cal}{gm\ K}}{R} \overset{900K\ \downarrow}{T} \ln \tfrac{1}{2})$$

$$E = \frac{\Delta G}{-n\mathcal{F}} = \frac{\Delta G\ (\text{in } \frac{cal}{gmol})}{-(1 \frac{eq}{gfw})\ 23{,}061 \frac{\cancel{cal}}{volt\text{-}eq}}$$

$$\boxed{E = \frac{80{,}100 + \frac{1}{2} RT \ln \frac{1}{2}}{-1 * 23{,}061}}\ V$$

$R = 1.987 \frac{cal}{K\text{-}gm}$
$T = 900\ K$

2. How many degrees of freedom are there in a system consisting of $SiO_{2\,(s)}$, $CaO_{(s)}$, $CaCO_{3(s)}$, $CO_{2(g)}$, and $N_{2(g)}$? The silica, lime, and carbonate are all distinct phases.

$$C = \begin{pmatrix} SiO_2 \\ CaO \\ CaCO_3 \\ CO_2 \\ N_2 \end{pmatrix}_5 - (CaO + CO_2 = CaCO_3)_1 - (\text{none})_0 = 4$$

$$P = \begin{pmatrix} SiO_2 \\ CaO \\ CaCO_3 \\ GAS \end{pmatrix}_4 = 4$$

$$F = 4 - 4 + 2 = \underline{\underline{2}}$$

3. Ten moles of an ideal gas at 1 atm and 300 K are adiabatically compressed to 8 atm.
   a) What is the final temperature?

$$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{R/C_p = 2/5} = 300 \times 8^{2/5}\text{ K}$$

   b) How much heat was required?

0 adiabatic

   c) How much work was required?

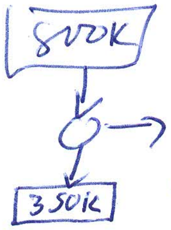
$$\Delta U = -w$$

$$w = -\Delta U = -nC_v\,\Delta T = \boxed{-10\text{ mole}\left(\tfrac{3}{2}R\right)300\left(8^{2/5}-1\right)}$$

$R = 8.31\text{ J/K}\cdot\text{g mole}$

4. What is the maximum amount of work that could be obtained from 100 Joule's of heat from a boiler at 800 K if the coldest heat sink available is at 350 K?

$$\frac{|q_1|}{|q_2|} = \frac{T_1}{T_2}$$



$100\text{J} \times \frac{800}{800}$

$w \Rightarrow \boxed{\frac{450}{850}\,100\text{ J}}$

$100\,\frac{350}{800}\text{ J}$

5. Mercury "boils" at 630 K. What would be its vapor pressure at room temperature (298 K). The heat of vaporization is 61,430 J/gmole.

$$\frac{d\ln P}{d\,1/T} = -\frac{\Delta H_v^0}{R}$$

$$\boxed{\ln P_2/\underset{1}{p_1} = -\frac{\Delta H_v^0}{R}\left(\frac{1}{\underset{298K}{T_2}} - \frac{1}{\underset{630K}{T_1}}\right)}$$

where

$\Delta H_v^0 = 61{,}430\ \frac{J}{gmol}$

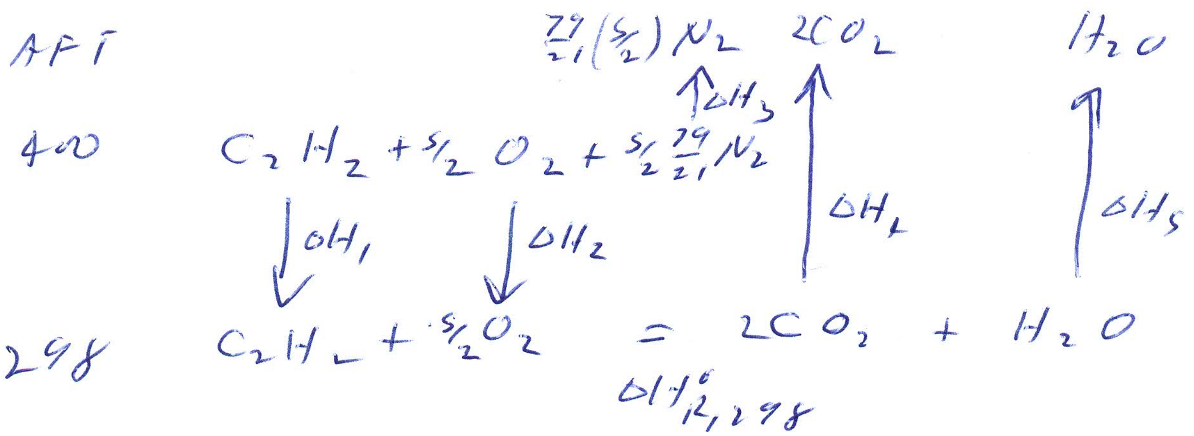
$R = 8.31\ \frac{J}{gmol\,K}$

Solve for P_2

6. Find the adiabatic flame temperature for the combustion of C_2H_2. With air (21% O_2 and 79% N_2). The air and the C_2H_2 are initially at 400 K. Use the data provided below only.

$$C_2H_2\,(g) + 2.5O_2(g) = 2CO_2\,(g) + H_2O(g)$$

Species	Heats of Formation (calories/g mole at 298°K)	Cp (cal/ gmole °K)
$C_2H_2(g)$	54,190	19.0
$H_2O(g)$	-57,800	10.5
$CO_2(g)$	-94,000	13.6
$O_2(g)$		8.6
$N_2(g)$		7.0



$\Sigma \Delta H's = 0$

$$\Delta H_1 + \Delta H_2 = \int_{400\,K}^{298\,K} \left(Cp_{C_2H_2} + \frac{5}{2} Cp_{O_2}\right) dT$$

see table of Cp for values

$$= \left(Cp_{C_2H_2} + \frac{5}{2} Cp_{O_2}\right)(298 - 400) < 0$$

$$\Delta H_3 = \frac{79}{21}\frac{5}{2}\int_{400}^{AFT} Cp_{N_2}\, dT = \frac{79}{21} \times \frac{5}{2} Cp_{N_2}\left(T_{AFT} - 400\right) > 0$$

$$\Delta H^0_{R,298} = 2\Delta H^0_{f,CO_2} + \Delta H^0_{f,H_2O} - \Delta H^0_{f,C_2H_2} - \frac{5}{2}\overset{0}{\cancel{\Delta H^0_{f,O_2}}} < 0$$

$$\Delta H_4 + \Delta H_5 = \int_{298}^{AFT} \left(2Cp_{CO_2} + Cp_{H_2O}\right) dT = \left(2Cp_{CO_2} + Cp_{H_2O}\right) * \left(T_{AFT} - 298\right)$$

$\hookrightarrow \Sigma = 0 = F(T_{AFT})$ solve T_{AFT}

7. Would a gas with a partial pressure of Cl_2 of 10^{-10} atm react with solid Mg to form solid $MgCl_2$ at 600 K? Show your work.

$$Mg(s) + Cl_{2(g)} = MgCl_2(s)$$

see data sheet

$$\Delta G^0 = -603,200 + 121.43\underset{\underset{600\,K}{\uparrow}}{T}$$

$$\Delta G = \Delta G^0 + RT\ln\frac{\overset{=1}{a_{MgCl_2}}}{\underset{10^{-10}}{P_{Cl_2}}\;\underset{1}{a_{Mg}}} = \Delta G^0 + \underset{8.31}{R}\,\underset{600}{T}\ln 10^{+10}$$

$$\Delta G = -603,200 + 121.43(600) + 2.303RT(10)$$

appears to be < 0

$\therefore \longrightarrow$

8. Show on the attached Ellingham Diagram for Ti and TiO_2 at 1000°C
   a) the equilibrium pressure of O_2

   10^{-25} atm

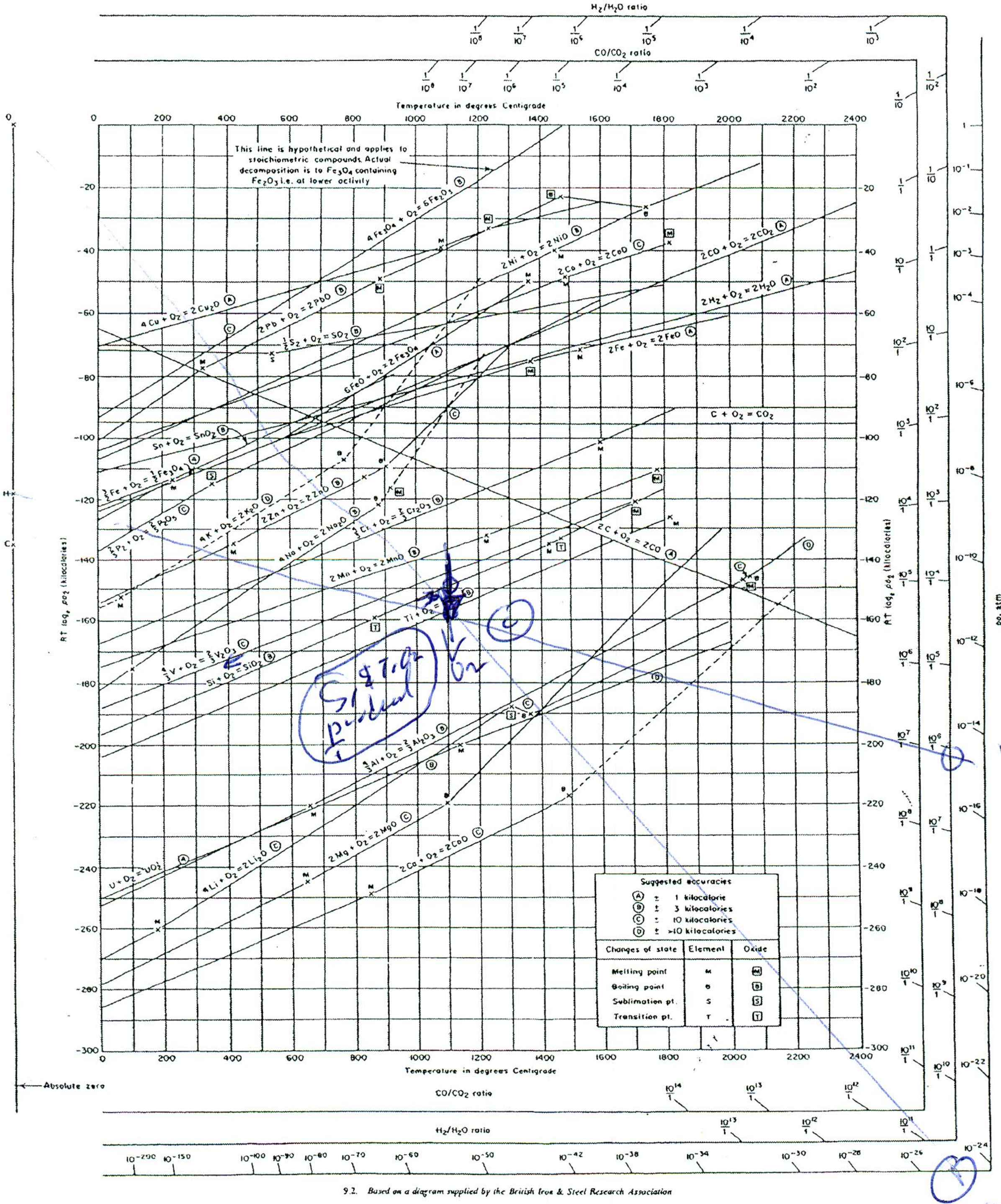
   b) the equilibrium H_2/H_2O ratio

   $10^{6.1}/1$

   c) in the presence of Si and SiO_2, if Ti or Si will be produced.

$SiO_2 \rightarrow O_2 + \boxed{Si}$ produced

$O_2 + Ti = TiO_2$



9.2. *Based on a diagram supplied by the British Iron & Steel Research Association*

b $\frac{H_2}{H_2O}$ $\frac{10^{6.1}}{1}$

a

P_{O_2} =

(a) 10^{-25}

9. Fill in the blank.

To obtain in a binary alloy	Given	Use Method or Equation
The Integral Molar Quantity	The Partial Molar Quantities	Tangent-Intercept method
The Partial Molar Quantity #1	The Partial Molar Quantity #2	Gibbs-Duhem eq Integration
Both Partial Molar Quantities	The Integral Molar Quantity	$\Sigma X_i Q_i = Q_i$

10. Show how to find the equilibrium mole fraction of Cu in a Ag-Cu alloy at 1423 K through which air is blown to form pure, liquid Cu_2O.

$2Cu_{(l)} + 0.5\ O_{2\ (g)} = Cu_2O_{(l)}$ (See data sheet for ΔG° data.)

Activity data for liquid
Ag-Cu Alloys at 1423 K

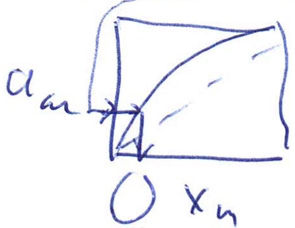
X_{Cu}	a_{Cu}
0.0	0.000
0.1	0.260
0.2	0.422
0.3	0.535
0.4	0.616
0.5	0.679
0.6	0.731
0.7	0.782
0.8	0.841
0.9	0.912
1.0	1.000

$$\Delta G^\circ = -\overset{8.31}{R}\ \underset{1423K}{T} \ln K_{EQ} = -188{,}300 + 88.48T \ \frac{J}{gm}$$

$$K_{EQ} = \frac{a_{Cu_2O}}{a_{Cu}^2\, p_{O_2}^{1/2}} \qquad p_{O_2}^{1/2} \rightarrow \sqrt{0.21}$$

$$\text{Find} \rightarrow \boxed{a_{Cu}} = \left(\frac{1}{K_{EQ}\sqrt{0.21}}\right)^{1/2} = \gamma_{Cu} X_{Cu}$$

plot



read off $\boxed{X_{Cu}}$

Lithium Chloride (LiCl)

(Liquid) Mol. Wt. = 42.397

T, °K.	cal. mole^{-1}deg.$^{-1}$			kcal. mole^{-1}			Log K_p
	C_p°	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	
0							
100							
200							
298	11,479	18,745	18,745	,000	- 93,394	- 88,965	65,210
300	11,495	18,816	18,745	,021	- 93,391	- 88,938	64,788
400	12,182	22,224	19,205	1,207	- 93,241	- 87,476	47,792
500	12,749	25,004	20,095	2,454	- 93,839	- 85,976	37,578
600	16,179	27,435	21,116	3,792	- 93,649	- 84,417	30,747
700	15,953	29,912	22,201	5,398	- 93,181	- 82,917	25,886
800	15,727	32,028	23,300	6,982	- 92,732	- 81,481	22,259
900	15,501	33,867	24,374	8,544	- 92,307	- 80,100	19,450
1000	15,275	35,489	25,406	10,082	- 91,905	- 78,766	17,214
1100	15,049	36,934	26,390	11,599	- 91,525	- 77,471	15,391
1200	14,822	38,234	27,324	13,092	- 91,170	- 76,210	13,879
1300	14,596	39,411	28,209	14,563	- 90,836	- 74,977	12,604
1400	14,370	40,485	29,048	16,011	- 90,525	- 73,768	11,515
1500	14,143	41,468	29,844	17,437	- 90,235	- 72,582	10,575
1600	13,914	42,374	30,599	18,840	- 89,967	- 71,413	9,754
1700	13,691	43,211	31,316	20,220	- 124,768	- 68,933	8,862
1800	13,467	43,987	31,999	21,578	- 124,363	- 65,659	7,972
1900	13,242	44,709	32,649	22,913	- 123,981	- 62,407	7,178
2000	13,015	45,382	33,269	24,226	- 123,623	- 59,177	6,466

LITHIUM CHLORIDE (LiCl) (LIQUID) MOL. WT. = 42.397

$\Delta H_f^\circ{}_{298.15}$ = -93.394 kcal. mole^{-1}

$S^\circ_{298.15}$ = 18.745 cal. deg.$^{-1}$ mole^{-1}

T_m = 883 ± 2°K

ΔH_m = 4.74 ± 0.10 kcal. mole^{-1}

T_b(equilibrium mixture) = 1656°K

T_b(monomeric gas) = 1701°K

Heat of Formation.

Obtained from that of the crystal by adding ΔH_m and $H_{883}-H_{298}$(c) and subtracting $H_{883}-H_{298}$(l).

Heat Capacity and Entropy.

The heat capacity from the melting point to 1100°K and 1200°K has been reported by E. N. Rodigina, K. Z. Gomelski, and V. F. Luginina, Zhur. Neorg. Khim. 4, 975 (1959) and T. B. Douglas, J. L. Dever, and A. W. Harman, quoted in Natl. Bur. of Standards Report 6297. The equation given by the former authors for the enthalpy of the liquid does not agree with their measurements and has been replaced by $H_T-H_{293.15} = 18.000T - 1.5 X 10^{-3}T^2 - 2279$ cal. mole^{-1}, which fits to ± 0.3%. The two sets of results were averaged and the equations were assumed to hold up to the normal boiling point. The entropy was calculated from that of the crystal in a manner analogous to the heat of formation.

Melting.

See table for crystal.

Boiling.

The equilibrium boiling point was taken from H. von Wartenburg and H. Schultz, Z. Electrochem. 27, 568 (1921) and the boiling point of the monomeric gas is defined as the temperature at which it reaches 1 atm. pressure. This was obtained from the free energy crossover between liquid and monomeric gas. The heat of vaporization to the monomeric gas was found from the tables to be 38.8 kcal. mole^{-1}.

Lithium Chloride (LiCl)

(Ideal Gas) Mol.• Wt. = 42.397

T, °K.	C_p°	S°	$-(F^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_p
	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
0	,000	,000	INFINITE	-2,166	-46,742	-46,742	INFINITE
100	6,978	42,859	57,562	-1,470	-46,516	-48,366	105,700
200	7,412	47,800	51,575	-,755	-46,601	-50,197	54,850
298	7,946	50,864	50,864	,000	-46,778	-51,926	38,061
300	7,954	50,913	50,864	,015	-46,782	-51,958	37,850
400	8,312	53,255	51,181	,829	-47,003	-53,651	29,312
500	8,534	55,135	51,790	1,673	-48,004	-55,208	24,130
600	8,677	56,705	52,482	2,534	-48,291	-56,620	20,623
700	8,775	58,050	53,184	3,407	-48,557	-57,988	18,104
800	8,847	59,227	53,867	4,288	-48,811	-59,319	16,204
900	8,901	60,272	54,522	5,175	-49,059	-60,617	14,719
1000	8,945	61,212	55,145	6,068	-49,304	-61,889	13,525
1100	8,981	62,067	55,736	6,964	-49,544	-63,135	12,543
1200	9,012	62,849	56,296	7,864	-49,782	-64,361	11.721
1300	9,040	63.572	56,828	8,766	-50.017	-65,566	11.022
1400	9,064	64,243	57,334	9,672	-50,248	-66,753	10,420
1500	9,087	64,869	57,816	10,579	-50,477	-67,925	9,896
1600	9,108	65,456	58,275	11,489	-50,702	-69,080	9,435
1700	9,128	66,009	58,714	12,401	-85,972	-68,893	8,856
1800	9,147	66,531	59,134	13,315	-86,010	-67,886	8,242
1900	9,165	67,026	59,537	14,230	-86,048	-66,877	7,692
2000	9,182	67,497	59,923	15,148	-86,086	-65,868	7,197
2100	9,199	67,945	60,294	16,067	-86,123	-64,858	6,750
2200	9,215	68,373	60,652	16,987	-86,162	-63,844	6,342
2300	9,232	68,783	60,997	17,910	-86,199	-62,828	5,970
2400	9,247	69,177	61,329	18,834	-86,238	-61,811	5,628
2500	9,263	69,554	61,651	19,759	-86,279	-60,792	5,314
2600	9,278	69,918	61,962	20,686	-86,320	-59,773	5,024
2700	9,294	70,268	62,263	21,615	-86,365	-58,752	4,755
2800	9,309	70,607	62,555	22,545	-86,411	-57,727	4,506
2900	9,324	70,934	62,838	23,477	-86,462	-56,703	4,273
3000	9,338	71,250	63,113	24,410	-86,515	-55,675	4,056
3100	9,353	71,556	63,381	25,344	-86,574	-54,645	3,852
3200	9,368	71,854	63,641	26,280	-86.636	-53,615	3,662
3300	9,382	72,142	63,894	27,218	-86,704	-52,582	3,482
3400	9,397	72,422	64,141	28,157	-86,776	-51,545	3,313
3500	9,411	72,695	64,382	29,097	-86,854	-50,510	3,154
3600	9,425	72,960	64,616	30,039	-86,939	-49,470	3,003
3700	9,440	73,219	64,845	30,982	-87,030	-48,429	2,860
3800	9,454	73,471	65,069	31,927	-87,127	-47,382	2,725
3900	9,468	73,716	65,287	32,873	-87,232	-46,334	2,596
4000	9,482	73,956	65,501	33,820	-87,344	-45,285	2,474
4100	9,496	74,191	65,710	34,769	-87,464	-44,232	2,358
4200	9,511	74,420	65,915	35,720	-87,592	-43,178	2,247
4300	9,525	74,644	66,115	36,672	-87,728	-42,118	2,141
4400	9,539	74,863	66,312	37,625	-87,872	-41,053	2,039
4500	9,553	75,077	66,504	38,579	-88,027	-39,989	1,942
4600	9,567	75,287	66,693	39,535	-88,191	-38,920	1,849
4700	9,581	75,493	66,878	40,493	-88,365	-37,848	1,760
4800	9,595	75,695	67,059	41,451	-88,550	-36,773	1,674
4900	9,609	75,893	67,238	42,412	-88,747	-35,691	1,592
5000	9,623	76,087	67,413	43,373	-88,955	-34,605	1,512
5100	9,636	76,278	67,585	44,336	-89,177	-33,513	1,436
5200	9,650	76,465	67,754	45,300	-89,413	-32,420	1,362
5300	9,664	76,649	67,920	46,266	-89,663	-31,325	1,292
5400	9,678	76,830	68,083	47,233	-89,929	-30,221	1,223
5500	9,692	77,008	68,244	48,202	-90,212	-29,111	1,157
5600	9,706	77,183	68,402	49,172	-90,511	-28,001	1,093
5700	9,720	77,354	68,557	50,143	-90,830	-26,881	1,031
5800	9,734	77,524	68,711	51,116	-91,169	-25,754	,970
5900	9,748	77,690	68,861	52,090	-91,528	-24,625	,912
6000	9,761	77,854	69,010	53,065	-91,909	-23,486	,855

June 30, 1962

LITHIUM CHLORIDE (LiCl) (IDEAL GAS) MOL. WT. = 42.397

ΔH_{f0}° = -46.742 kcal. mole^{-1}

Ground State Configuration $^1\Sigma$

$\Delta H_{f\ 298.15}^\circ$ = -46.778 ± 3.0 kcal. mole^{-1}

$S^\circ_{298.15}$ = 50.864 cal. deg.$^{-1}$ mole^{-1}

ω_e = 641.1 ± 3.0 cm.$^{-1}$

B_e = 0.7053 cm.$^{-1}$

$\omega_e x_e$ = 4.2 ± 0.3 cm.$^{-1}$

α_e = 0.0067 cm.$^{-1}$

σ = 1

r_e = 2.022 Å

Heat of Formation.

W. Klemperer, W. G. Norris, A. Büchler and A. G. Emslie, J. Chem. Phys. 33, 1534 (1960) quote a private communication from W. H. Evans at the National Bureau of Standards giving D_0° = 4.85 e.v., which corresponds to ΔH_{f0}° = -45.3 ± 2.4 kcal. mole^{-1}. A third law analysis of the vapor pressure data of An. N. Nesmeyanov and L. A. Sazonov, Zhur. Neorg. Khim. 4, 231 (1960) in conjunction with the relative concentration of monomer, dimer, and trimer at 870°K from the work of R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956) and 27, 981 (1957) leads to a monomer heat of sublimation at 298° of 52.56 kcal. mole^{-1}, this gives $\Delta H_{f\ 298.15}^\circ$ = -45.02 kcal. mole^{-1}. These values lead, however, to partial vapor pressures of the monomer which are less than half of the total vapor pressure near the boiling point. From the data of Miller and Kusch loc. cit. it would be expected that the monomer would be the predominant species near the boiling point, a fact also substantiated by the work of C. Beusman, AEC Report ORNL-2323 (1957), on the average molecular weight of the vapor. Thus it was decided to change the heat of sublimation so as to give the correct normal boiling point and vapor pressures in the region 1400-1600°K and to approximate the relative concentrations of monomer, dimer, and trimer as found by Miller and Kusch at 870°K. A monomer heat of sublimation at 298° of 50.8 kcal. mole^{-1} was chosen, which gives $\Delta H_{f\ 298.15}^\circ$ = -46.778 kcal. mole^{-1}. The normal boiling point was taken as 1656°K as determined by H. von Wartenburg and H. Schulz, Z. Electrochem 27, 568 (1921) and the boiling point of LiCl(g) was found as 1701°K from the free energy crossover between liquid and gas.

Heat Capacity and Entropy.

The spectroscopic constants were taken from Klemperer et al. loc. cit. The value of α_e was calculated from the value of a_1 given by the Rittner potential function and the equation given by Klemperer et al. The value of r_e was taken from the Natl. Bur. of Standards Report 6297 (1959).

Lithium Chloride (LiCl)

(Crystal) Mol. Wt. = 42.397

	cal. mole⁻¹deg.⁻¹			kcal. mole⁻¹			
T, °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
0	.000	.000	INFINITE	- 2.224	- 97.600	- 97.600	INFINITE
100	8,679	3.247	23,574	- 2,033	- 97.878	- 95,768	209,290
200	10,361	9,810	15,191	- 1,076	- 97,722	- 93,720	102,408
298	11,479	14,173	14,173	,000	- 97,578	- 91,786	67,278
300	11,495	14,244	14,173	,021	- 97,575	- 91,751	66,837
400	12,182	17,652	14,633	1.207	- 97,425	- 89,831	49,079
500	12,749	20,432	15,523	2,454	- 98,023	- 87,874	38,408
600	13,287	22,804	16,544	3,756	- 97,868	- 85,857	31,272
700	13.810	24,892	17,590	5,111	- 97,652	- 83,873	26,185
800	14,325	26,769	18,622	6,518	- 97,380	- 81,923	22,379
900	14,833	28,486	19,624	7,976	- 97,058	- 80,009	19,428
1000	15,337	30,075	20,590	9,485	- 96,687	- 78,134	17,075
1100	15,839	31,560	21,521	11,043	- 96,265	- 76,299	15,158
1200	16,338	32,960	22,416	12,652	- 95,794	- 74,505	13,569
1300	16,838	34,287	23,279	14,311	- 95,272	- 72,752	12,230
1400	17,336	35,553	24,111	16,020	- 94,700	- 71,040	11,089
1500	17,831	36,766	24,914	17,778	- 94,078	- 69,372	10,107
1600	18,323	37,933	25,692	19,586	- 93,405	- 67,746	9,253
1700	18,817	39,059	26,445	21,443	- 127,730	- 64,836	8,335
1800	19,311	40,148	27,176	23,349	- 126,776	- 61,162	7,426
1900	19,805	41,205	27,887	25,305	- 125,773	- 57,543	6,619
2000	20,298	42,234	28,579	27,310	- 124,723	- 53,980	5,898

LITHIUM CHLORIDE (LiCl) (CRYSTAL) MOL. WT. = 42.397

$\Delta H^\circ_{f\ 298.15} = -97.578 \pm 0.273$ kcal mole^{-1}

$S^\circ_{298.15} = 14.173 \pm 0.015$ cal deg^{-1} mole^{-1}

$T_m = 883 \pm 2$°K

$\Delta H_m = 4.74 \pm 0.10$ kcal mole^{-1}

Heat of Formation

The heat of formation was obtained as follows:

ΔH_{298}(kcal mole^{-1})

(1) $LiOH \cdot 100H_2O + HCl \cdot 100H_2O \rightarrow LiCl \cdot 201H_2O$ -13.704 ± 0.014
T. W. Richards and A. W. Rowe J. Am. Chem. Soc. 44, 684 (1922).

(2) $Li(c) + 100H_2O(\ell) \rightarrow LiOH \cdot 100H_2O + 1/2\ H_2(g)$ $-53.142 \pm .019$
S. R. Gunn and L. G. Green J. Am. Chem. Soc. 80, 4782 (1958).

(3) $LiOH \cdot 1000H_2O \rightarrow LiOH \cdot 100H_2O + 900H_2O(\ell)$ 0.153 ± 0.040
T. W. Richards and A. W. Rowe, J. Am. Chem. Soc. 43, 770 (1921).

(4) $1/2\ H_2(g) + 1/2\ Cl_2(g) \rightarrow HCl(g)$ -21.97 ± 0.09
JANAF Tables.

(5) $HCl(g) + 100H_2O(\ell) \rightarrow HCl \cdot 100H_2O$ -17.575 ± 0.100
C. M. Slansky, J. Am. Chem. Soc. 62, 2430 (1940), and
J. M. Sturtevant, J. Am. Chem. Soc. 62, 3265 (1940).

(6) $LiCl \cdot 201H_2O \rightarrow LiCl(c) + 201H_2O(\ell)$ 8.660 ± 0.010
E. Lange and F. Dürr, Z. phys. Chem. 121, 361 (1926).

(1) + (2) + (3) + (4) + (5) + (6) gives $Li(c) + 1/2\ Cl_2(g) \rightarrow LiCl(c)$ -97.578 ± 0.273

A direct calorimetric determination by H. Siemonsen and U. Siemonsen, Z. Electrochem. 56, 643 (1952) gave -94.8 ± 0.6 kcal mole^{-1}. However, the solution route was thought to be inherently more accurate and was adopted.

Heat Capacity and Entropy

The heat capacity between 15° and 325°K has been measured by D. A. Shirley, J. Am. Chem. Soc. 82, 3841 (1960) and by F. L. Oetting, W. E. Hatton and G. C. Sinke, unpublished work, Thermal Laboratory, Dow Chemical Company. The two sets of data are in substantial agreement and were plotted together and used to evaluate the entropy at 298°. The extrapolation to 0°K was done assuming a T^3 law and yielded $S_{15} = 0.019$ e.u. Above 298° T. B. Douglas, J. L. Dever and A. W. Harman, quoted in Natl. Bur. Standards Report 6297, have made enthalpy measurements to 1200°K. E. N. Rodigina, K. Z. Gomelski, and V. F. Luginina, Zhur. Neorg. Khim. 4, 975 (1959) also made enthalpy determinations to 1100°K. These two sets of measurements were averaged and joined smoothly to the low temperature values.

Melting and Transition Data

The melting point has been reported as follows: 880°K., Douglas et. al., loc. cit.; 883°K., Rodigina et al., loc. cit.; 883°K., H. M. Haendler, P. S. Bennett, and C. M. Wheeler, J. Electrochem. Soc. 106, 264 (1959); 879°K., H. Flood, O. Fykse and S. Urnes, Z. Electrochem. 59, 364 (1955); 879°K., H. von Wartenberg and H. Schulz, Z. Electrochem. 27, 568 (1921). The highest value of 883°K. was taken as representing the most pure samples. At this temperature the enthalpy equations of Douglas et al. yield a heat of fusion of 4.718 kcal mole^{-1}, those of Rodigina et al., 4.669 kcal mole^{-1}. A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 64, 269 (1960) report a value of 4.76 ± 0.10 kcal mole^{-1} and quote 4.83 kcal mole^{-1} from a private communication from D. F. Smith. The average value $\Delta H_m = 4.74 \pm 0.10$ kcal mole^{-1} was adopted.

A transition at 838°K has been reported by Kislova andd Bergman, Russ. J. Inorg. Chem. 5, 1210 (1960) but is not supported by the enthalpy measurements quoted above.