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Thermodynamic Properties of Iron—Selenium Alloys

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Selenium vapor pressures of iron—selenium alloys were determined by an isopiestic method between 700 and 1200 K and 50 to 60 at% Se, and activities and partial molar enthalpies of selenium were calculated. By *Gibbs-Duhem* integration activities of iron, and integral *Gibbs* energies were obtained. A theoretical model was successfully applied to interprete the thermodynamic properties of the hexagonal δ-phase with NiAs-structure. Assuming a random distribution of iron vacancies in every transition metal layer of the lattice excellent agreement with experimental data was found. The energy of interaction between iron vacancies was calculated to be 147.0 kJ/g-atom.

(Keywords: Chalcogen systems; Iron—selenium; Non-stoichiometry; Thermodynamic properties)

Thermodynamische Eigenschaften von Eisen—Selen-Legierungen

Die Selendampfdrücke von Eisen—Selen-Legierungen wurden mit Hilfe einer isopiestischen Methode zwischen 700 und 1200 K und zwischen 50 und 60 At% Se bestimmt. Daraus wurden die Aktivitäten und die partiellen molaren Enthalpien von Selen berechnet, und über eine *Gibbs-Duhem*-Integration wurden die Eisen-Aktivitäten und die integralen *Gibbs*'schen Energien erhalten. Ein theoretisches Modell wurde erfolgreich angewendet, um die thermodynamischen Eigenschaften in der hexagonalen NiAs-Phase δ zu interpretieren. Unter der Annahme einer statistischen Verteilung von Eisen-Leerstellen über sämtliche Übergangsmetall-Schichten wurde eine ausgezeichnete Übereinstimmung mit den experimentell gefundenen Daten festgestellt. Die Wechselwirkungsenergie zwischen diesen Leerstellen wurde zu 147,0 kJ/g-atom ermittelt.

Introduction

In a series of publications activities of tellurium and selenium, resp., were determined in the binary systems Ni—Te, Co—Te, Fe—Te, Ni—Se, and Co—Se by an isopiestic method[1–5]. Emphasis was placed on the range of homogeneity of the NiAs-related phases in these

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systems. Since several NiAs-related phases were reported to exist in the iron—selenium system with the phase boundaries still in doubt, the isopiestic method mentioned above was employed to measure the selenium activities. The iron—selenium phase diagram was studied by DTA- and X-ray measurements and the results including the phase boundaries derived from the present isopiestic investigation have been published elsewhere[6].

Various thermodynamic studies have been reported in the iron—selenium system. *Fabre*[7] measured the enthalpy of solution of FeSe in an aqueous bromine solution and calculated the enthalpy of formation as $\Delta H^0_{298} = -77.2$ kJ/mol; using the same basic data a recalculation of *Wagman* et al.[8] yielded a value for $\Delta H^0_{298} = -75.3$ kJ/mol. *Grønvold*[9] determined the enthalpies of formation of $Fe_{1.04}Se$, FeSe, Fe_7Se_8, and Fe_3Se_4 at 1050 K by high temperature reaction calorimetry and derived from it the enthalpies of formation at 298 K. *Svendsen*[10] measured the selenium partial pressures of alloys from 48.7 to 79.5 at% Se using the *Knudsen* effusion method and a quartz spiral manometer and calculated standard enthalpies of formation for FeSe, Fe_7Se_8, Fe_3Se_4, and $FeSe_2$. *Grønvold* and *Westrum*[11, 12] and *Grønvold*[13, 14] performed heat capacity measurements on $Fe_{1.04}Se$, Fe_7Se_8, and Fe_3Se_4 between 5 and 1050 K, and on $FeSe_2$ between 5 and 1000 K. *Svendsen*[15] obtained the enthalpy content of $FeSe_2$ in the range from 300 to 853 K by means of an adiabatic drop calorimeter. A review and compilation of all thermodynamic data of iron—selenium alloys up to 1973 has been published by *Mills*[16].

In the present investigation activities of selenium were derived from isopiestic vaporpressure measurements. Iron specimens were heated in a closed system in a temperature gradient and equilibrated with selenium vapor from a reservoir kept at the temperature minimum of the closed system. Partial and integral thermodynamic properties were calculated and phase boundaries were obtained from discontinuities of the concentration-temperature curves.

Experimental Procedure

Selenium shots (99.999 %Se, ASARCO, New York, U.S.A.) and iron wire with a diameter of 0.2 mm (99.9% Fe, Allied Chemical and Dye Corp., U.S.A.) served as starting materials. The iron wire was coiled into small rings of 12 to 14 turns with about 10 mm diameter, each ring weighing from 120 to 130 mg. The iron samples were degreased with acetone, dried, and weighed with a semimicrobalance to within ± 0.05 mg. Selenium was used without further cleaning, and about 35 to 40 g were taken as reservoir for each run. For run No. 4 the experimental quartz apparatus was the same as previously used for the iron—tellurium system[3]. The other experiments were carried out in a modified quartz system. The height of the quartz crucibles was reduced to 8-10 mm, and top and bottom of the crucibles were ground plane parallel so that the crucible above would serve as the cover for the one below. Further experimental details of the construction of the gradient furnace have been described previously[3]. The temperature was measured with a Pt/Pt-10% Rh thermocouple calibrated at the melting points of high purity Cd, Zn, Sb, and Cu. Reservoir temperature

Table 1. *Experimental isopiestic results in the* Fe—Se *system*

No.	at% Se	T_S, K	phase	$-\ln a_{Se}$ (T_S)	$-\Delta \bar{H}_{Se}$ kJ (g-atom)$^{-1}$	$-\ln a_{Se}$ (873 K)	$-\ln a_{Se}$ (973 K)
Run 1			$T_R = 719$ K			Duration: 15 days	
1	53.90	1110	δ	3.070	42.9	4.332	3.725
2	53.97	1104	δ	3.033	42.3	4.252	3.654
3	54.08	1097	δ	2.989	41.5	4.157	3.569
4	54.12	1089	δ	2.939	41.2	4.065	3.482
5	54.19	1080	δ	2.881	40.7	3.956	3.379
6	54.26	1076	δ	2.855	40.3	3.903	3.332
7	54.29	1072	δ	2.828	40.1	3.854	3.286
8	54.36	1067	δ	2.795	39.6	3.787	3.226
9	54.39	1062	δ	2.762	39.5	3.731	3.171
10	54.43	1056	δ	2.721	39.2	3.675	3.102
11	54.53	1050	δ	2.680	38.5	3.574	3.029
12	54.56	1044	δ	2.639	38.4	3.506	2.962
13	54.63	1039	δ	2.604	38.1	3.443	2.903
14	54.69	1032	δ	2.555	37.7	3.355	2.821
15	54.78	1025	δ	2.505	37.4	3.269	2.740
16	54.85	1018	δ	2.454	37.0	3.180	2.656
17	54.95	1010	δ	2.395	36.6	3.079	2.561
18	55.07	1001	δ	2.328	35.9	2.961	2.452
19	55.18	992	δ	2.260	35.6	2.848	2.344
20	55.30	985	δ	2.202	35.2	2.753	2.255
21	55.45	971	δ	2.096	(34.7)	—	2.087
22	55.82	960	δ	2.008	(33.6)	—	1.952
23	56.36	946	γ'	1.892	(32.4)	—	1.778
24	57.17	934	γ	1.791	28.9	2.051	—
25	57.39	917	γ	1.638	25.8	1.809	1.443
26	57.71	901	γ	1.499	21.8	1.592	1.284
27	57.92	886	γ	1.361	19.5	1.400	1.124
28	58.19	869	γ	1.200	17.1	1.189	0.947
29	58.61	854	γ	1.056	14.0	1.013	0.815
30	58.93	842	γ	0.939	12.2	0.877	0.704
31	59.39	831	γ	0.833	10.4	0.761	—
32	59.76	821	γ	0.733	9.5	0.650	—
Run 2			$T_R = 715$ K			Duration: 28 days	
1	53.98	1084	δ	2.943	43.2	4.102	3.490
2	54.06	1079	δ	2.910	41.7	4.007	3.416
3	54.19	1065	δ	2.817	40.7	3.828	3.252
4	54.28	1056	δ	2.752	40.1	3.714	3.142
5	54.34	1049	δ	2.707	39.7	3.625	3.063
6	54.36	1043	δ	2.662	39.6	3.551	2.991
7	54.42	1037	δ	2.623	39.2	3.477	2.922
8	54.47	1033	δ	2.594	38.8	3.422	2.873
9	54.60	1026	δ	2.540	38.2	3.325	2.784
10	54.67	1019	δ	2.493	37.8	3.239	2.704

Table 1 (continued)

No.	at% Se	T_S, K	phase	$-\ln a_{Se}$ (T_S)	$-\Delta \bar{H}_{Se}$ kJ (g-atom)$^{-1}$	$-\ln a_{Se}$ (873 K)	$-\ln a_{Se}$ (973 K)
11	54.72	1012	δ	2.441	37.5	3.151	2.620
12	54.86	1004	δ	2.381	36.9	3.044	2.522
13	54.95	997	δ	2.324	36.6	2.951	2.433
14	54.99	988	δ	2.258	36.4	2.842	2.326
15	55.13	977	δ	2.171	35.8	2.696	2.189
16	55.48	953	δ	1.975	(34.6)	—	1.885
17	55.97	941	δ	1.873	(33.2)	—	1.733
18	57.03	927	γ	1.747	31.2	1.997	—
19	57.37	913	γ	1.627	25.9	1.783	1.417
20	57.48	896	γ	1.471	24.5	1.558	1.211
21	57.76	880	γ	1.319	21.1	1.342	1.043
22	58.06	867	γ	1.194	18.1	1.177	0.921
23	58.31	851	γ	1.037	16.2	0.979	0.750
24	58.71	840	γ	0.929	13.3	0.857	0.669
25	59.11	831	γ	0.836	11.4	0.757	0.595
26	59.53	822	γ	0.755	10.0	0.670	—
27	62.12	815	$\gamma + \varepsilon$	0.685	—	—	—
Run 3			$T_R = 588$ K			Duration: 27 days	
1	52.16	1140	δ	4.950	61.2	6.925	6.058
2	52.26	1131	δ	4.896	60.1	6.785	5.934
3	52.31	1122	δ	4.841	59.4	6.657	5.816
4	52.36	1117	δ	4.810	58.7	6.577	5.745
5	52.51	1106	δ	4.741	57.1	6.398	5.590
6	52.61	1095	δ	4.668	55.8	6.227	5.437
7	52.68	1088	δ	4.626	54.9	6.121	5.343
8	52.70	1082	δ	4.583	54.7	6.039	5.264
9	52.74	1074	δ	4.534	54.2	5.932	5.164
10	52.81	1066	δ	4.480	53.4	5.812	5.056
11	52.91	1058	δ	4.425	52.4	5.687	4.945
12	52.96	1049	δ	4.362	51.7	5.557	4.825
13	53.02	1039	δ	4.292	51.0	5.415	4.693
14	53.11	1030	δ	4.227	50.1	5.279	5.470
15	53.20	1021	δ	4.161	49.1	5.142	4.446
16	53.32	1010	δ	4.075	48.1	4.974	4.293
17	53.45	996	δ	3.971	46.8	4.767	4.105
18	53.58	982	δ	3.861	45.6	4.558	3.913
19	53.74	967	δ	3.739	44.1	4.330	3.705
20	53.95	949	δ	3.583	42.5	4.052	3.450
21	54.20	931	δ	3.430	40.6	3.779	3.204
22	54.31	909	δ	3.230	39.9	3.448	2.883
23	54.68	890	δ	3.049	37.7	3.148	2.614
24	55.59	869	$\gamma' + \gamma$	2.834	(34.3)	—	2.327
25	56.92	843	γ	2.561	33.3	2.398	—
26	57.05	825	γ	2.367	30.9	2.119	—
27	57.38	805	γ	2.129	25.9	1.828	1.461

Table 1 (continued)

No.	at% Se	T_S, K	phase	$-\ln a_{Se}$ (T_S)	$-\Delta \bar{H}_{Se}$ kJ (g-atom)	$-\ln a_{Se}$ (873 K)	$-\ln a_{Se}$ (973 K)
28	57.54	786	γ	1.904	23.7	1.543	1.207
29	57.91	770	γ	1.695	19.6	1.334	1.056
30	58.91	753	$\gamma + \varepsilon$	1.486	(12.3)	—	—
Run 4			$T_R = 645$ K			Duration: 36 days	
1	53.04	1104	δ	3.903	51.5	5.388	4.658
2	53.09	1100	δ	3.877	50.2	5.304	4.593
3	53.14	1095	δ	3.845	49.7	5.233	4.530
4	53.28	1082	δ	3.761	48.3	5.046	4.363
5	53.51	1062	δ	3.627	46.1	4.757	4.105
6	53.60	1047	δ	3.523	45.4	4.563	3.920
7	53.78	1032	δ	3.416	43.9	4.348	3.726
8	54.03	1009	δ	3.241	41.9	4.019	3.426
9	54.34	981	δ	3.027	39.7	3.629	3.067
10	54.80	949	δ	2.758	37.2	3.168	2.642
11	56.65	907	$\gamma' + \gamma$	2.386	(32.0)	—	—
12	57.27	861	γ	1.933	27.3	1.881	—
13	57.81	824	γ	1.535	20.6	1.366	1.075
14	58.66	789	γ	1.134	13.7	0.933	0.739
Run 5			$T_R = 506$ K			Duration: 101 days	
1	50.71	1228	δ	7.035	80.8	10.253	9.109
2	50.77	1223	δ	7.010	79.8	10.156	9.026
3	50.83	1218	δ	6.984	79.0	10.067	8.948
4	50.86	1208	δ	6.929	78.7	9.936	8.822
5	50.91	1202	δ	6.897	78.0	9.838	8.734
6	50.99	1196	δ	6.864	76.9	9.725	8.636
7	51.01	1189	δ	6.826	76.6	9.631	8.546
8	51.06	1182	δ	6.788	76.1	9.529	8.451
9	51.09	1175	δ	6.749	75.4	9.419	8.351
10	51.17	1167	δ	6.707	74.3	9.286	8.234
11	51.20	1159	δ	6.661	73.9	9.173	8.127
12	51.26	1151	δ	6.615	73.2	9.051	8.014
13	51.29	1142	δ	6.562	72.7	8.921	7.892
14	51.32	1132	δ	6.502	72.4	8.784	7.759
15	51.46	1122	δ	6.439	70.5	8.595	7.596
16	51.53	1110	δ	6.367	69.5	8.411	7.427
17	51.66	1098	δ	6.288	67.9	8.205	7.244
18	51.80	1083	δ	6.194	65.8	7.952	7.020
19	51.91	1070	δ	6.104	64.5	7.740	6.827
20	51.98	1054	δ	5.994	63.6	7.499	6.598
21	52.06	1036	δ	5.867	62.6	7.224	6.338
22	52.28	1016	δ	5.724	59.6	6.880	6.036
23	52.45	994	δ	5.556	57.8	6.525	5.707
24	52.71	970	δ	5.364	54.6	6.116	5.343
25	52.97	944	δ	5.141	51.5	5.675	4.945

Table 1 (continued)

No.	at% Se	T_S, K	phase	$-\ln a_{Se}$ (T_S)	$-\Delta \overline{H}_{Se}$ kJ (g-atom)$^{-1}$	$-\ln a_{Se}$ (873 K)	$-\ln a_{Se}$ (973 K)
26	53.26	915	δ	4.886	48.6	5.193	4.505
27	53.62	886	δ	4.605	45.2	4.696	4.056
28	53.94	857	δ	4.310	42.6	4.200	3.597
29	54.34	829	δ	4.006	39.7	3.716	3.154
30	56.72	800	γ	3.668	(31.9)	—	—
31	57.06	773	γ	3.331	30.8	2.782	—
32	57.20	747	γ	2.990	28.4	2.330	—
33	57.34	723	γ	2.640	26.3	1.888	1.516
34	58.80	700	$\gamma + \varepsilon$	2.289	(12.9)	—	—
Run 6		$T_R = 610$ K				Duration: 27 days	
1	52.66	1098	δ	4.356	55.3	5.917	5.134
2	52.69	1094	δ	4.327	54.8	5.852	5.076
3	52.80	1087	δ	4.284	53.5	5.735	4.978
4	52.85	1083	δ	4.258	53.1	5.677	4.925
5	52.94	1078	δ	4.225	51.9	5.585	4.850
6	52.96	1073	δ	4.192	51.7	5.520	4.788
7	53.04	1067	δ	4.151	51.5	5.441	4.712
8	53.12	1061	δ	4.111	50.0	5.332	4.624
9	53.18	1056	δ	4.073	49.4	5.252	4.553
10	53.27	1050	δ	4.031	48.4	5.155	4.470
11	53.31	1043	δ	3.985	48.1	5.065	4.384
12	53.34	1037	δ	3.942	47.7	4.981	4.306
13	53.43	1030	δ	3.892	47.0	4.879	4.214
14	53.52	1023	δ	3.840	46.0	4.769	4.118
15	53.61	1015	δ	3.781	45.3	4.654	4.013
16	53.66	1008	δ	3.725	44.9	4.554	3.918
17	53.75	999	δ	3.656	44.0	4.421	3.789
18	53.86	990	δ	3.589	43.3	4.294	3.681
19	53.96	980	δ	3.510	42.4	4.148	3.547
20	54.05	970	δ	3.424	41.8	4.000	3.408
21	54.19	958	δ	3.325	40.7	3.823	3.246
22	54.33	945	δ	3.218	39.8	3.636	3.072
23	54.48	933	δ	3.109	38.7	3.452	2.904
24	54.69	917	δ	2.969	37.7	3.218	2.684
25	54.94	899	δ	2.801	36.6	2.947	2.429
26	56.61	879	$\gamma' + \gamma$	2.606	(32.1)	—	—
27	56.99	857	γ	2.381	31.9	2.299	—
28	57.25	835	γ	2.144	27.8	1.970	—
29	57.49	811	γ	1.872	24.4	1.615	1.270
30	57.91	787	γ	1.585	19.6	1.290	1.012
31	60.01	764	$\gamma + \varepsilon$	1.298	(9.1)	—	—
Run 7		$T_R = 546$ K				Duration: 63 days	
1	51.30	1182	δ	5.914	72.6	8.529	7.501
2	51.32	1177	δ	5.889	72.4	8.465	7.440

Table 1 (continued)

No.	at% Se	T_S, K	phase	$-\ln a_{Se}$ (T_S)	$-\Delta \bar{H}_{Se}$ kJ (g-atom)$^{-1}$	$-\ln a_{Se}$ (873 K)	$-\ln a_{Se}$ (973 K)
3	51.38	1172	δ	5.861	71.5	8.374	7.362
4	51.45	1168	δ	5.835	70.6	8.292	7.292
5	51.49	1157	δ	5.772	69.9	8.136	7.146
6	51.57	1151	δ	5.738	68.8	8.027	7.053
7	51.62	1145	δ	5.702	68.3	7.937	6.970
8	51.67	1138	δ	5.661	67.5	7.827	6.871
9	51.77	1131	δ	5.619	66.3	7.703	6.764
10	51.85	1123	δ	5.573	65.3	7.576	6.651
11	51.88	1117	δ	5.533	64.8	7.483	6.566
12	51.95	1109	δ	5.484	63.8	7.355	6.451
13	51.98	1101	δ	5.433	63.6	7.248	6.347
14	52.05	1092	δ	5.378	62.7	7.110	6.223
15	52.11	1083	δ	5.320	61.9	6.974	6.097
16	52.18	1074	δ	5.260	61.0	6.833	5.969
17	52.25	1064	δ	5.192	60.2	6.681	5.828
18	52.37	1055	δ	5.127	58.6	6.520	5.690
19	52.39	1044	δ	5.050	58.4	6.368	5.541
20	52.55	1033	δ	4.975	56.4	6.179	5.380
21	52.66	1021	δ	4.887	55.3	5.991	5.208
22	52.80	1007	δ	4.782	53.5	5.763	5.005
23	52.92	994	δ	4.678	52.3	5.555	4.815
24	53.04	980	δ	4.567	51.5	5.342	4.613
25	53.24	961	δ	4.411	48.8	5.027	4.336
26	53.44	943	δ	4.258	46.9	4.738	4.074
27	53.72	923	δ	4.080	44.4	4.411	3.783
28	53.97	901	δ	3.881	42.3	4.062	3.463
29	54.28	876	δ	3.636	40.1	3.655	3.087
30	54.66	857	δ	3.436	37.9	3.339	2.802
31	56.72	829	γ	3.131	(31.9)	—	—
32	57.10	806	γ	2.872	30.0	2.528	—
33	57.21	783	γ	2.591	28.1	2.146	—
34	57.44	760	γ	2.286	25.0	1.774	1.420
35	58.40	735	γ + ε	1.949	(15.4)	—	—

and the temperature gradient were determined by raising and lowering of the thermocouple with an accuracy of ± 1 K, and were checked several times during an experiment. After equilibration the samples were reweighed, and the selenium content calculated from the weight increase. The composition of several samples was also determined by chemical analysis, and it agreed with the weight increase within ± 0.5%. The method of chemical analysis and of X-ray analysis have been already described in more detail elsewhere[6].

Results and Discussion

A total of seven successful experiments with reservoir temperatures between 506 and 719 K and specimen temperatures between 700 and

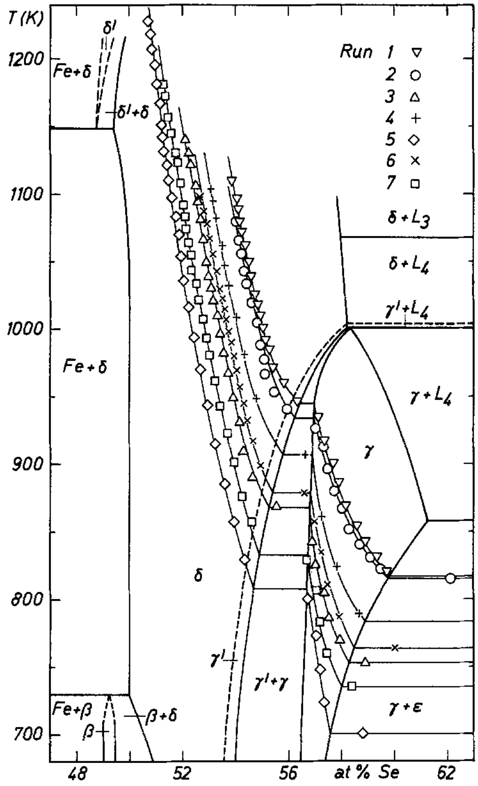

Fig. 1. Specimen composition as a function of specimen temperature in the partial Fe—Se phase diagram

1 228 K were evaluated. The duration of the runs to achieve equilibration ranged between 15 and 101 days. The results and the experimental conditions (specimen- and reservoir temperatures, duration of runs) are listed in Tab. 1. The equilibration curves superimposed on the partial phase diagram are shown in Fig. 1. From the discontinuities of the equilibration curves accurate values for the phase boundaries $\gamma'/(\gamma' + \gamma)$, $(\gamma' + \gamma)/\gamma$, and $\gamma/(\gamma + \varepsilon)$ could be obtained which have been already used to construct the phase diagram[6]. The one-phase λ-type transition $\delta \rightleftharpoons \gamma'$ did not show in the equilibration curves.

The large majority of specimens contained only one phase excepting sample 24 of run No. 3, sample 11 of run No. 4, and sample 26 of run No. 6 which were two-phase $\gamma' + \gamma$, obviously due to small temperature fluctuations in the gradient furnace. In addition a number of specimens were found in the two-phase field $\gamma + \varepsilon$. X-ray analysis of sample 31 of run No. 6 before crushing the specimen showed that a surface layer of $FeSe_2$ had formed on the wire. In the powdered sample in addition to orthorhombic ε-$FeSe_2$ the monoclinic γ-phase was found. Apparently a very dense non-porous layer of $FeSe_2$ is formed on the surface which acts as a barrier to the diffusion of selenium into the interior of the sample so that equilibration could not be achieved for specimens in the $FeSe_2$-field. Similar problems were encountered with orthorhombic $CoTe_2$[2], cubic $CoSe_2$[5], and orthorhombic $FeTe_2$[3], but not with cubic $NiSe_2$[4]. In one experiment the reservoir temperature was originally set to 508 K but the rate of evaporation of selenium from the reservoir was apparently too low so that after 35 days the samples were not in equilibrium. Therefore run No. 6 was first kept for 14 days at a reservoir temperature of 615 K to obtain equilibration, then the reservoir temperature was lowered to 506 K, and held for 87 days. Selenium evaporated from the samples and equilibration could be readily achieved.

In an isopiestic experiment the total pressure in the closed system is determined by the pure volatile component of the reservoir kept at the lowest temperature. At equilibrium the vapor pressure of the volatile component above each alloy is equal to the vapor pressure of the pure volatile component at the given reservoir temperature T_R. The activity a_i of the volatile component at the specimen temperature T_S is given by

$$a_i = \left(\frac{p_{i_n}(T_S)}{p^0_{i_n}(T_S)}\right)^{1/n} \tag{1}$$

with i_n indicating the molecular species in the gas phase containing n atoms. The composition of the selenium vapor and the partial vapor pressures of the various molecular species have been studied by a number of authors[17–24]. According to recent measurements of *Keller* et al.[25] all species between Se_2 and Se_8 are present in varying amounts in the selenium vapor. The total vapor pressure is thus given by the sum of all partial vapor pressures:

$$p = p_{Se_2} + p_{Se_3} + p_{Se_4} + p_{Se_5} + p_{Se_6} + p_{Se_7} + p_{Se_8} = \sum p_{Se_x} \tag{2}$$

To calculate the activity of selenium one single species has to be selected. Se_2 was chosen for that purpose since according to[25] the dissociation equilibria of the various selenium molecules in the gas phase are shifting with increasing temperatures towards Se_2. The activity of selenium is therefore expressed as

$$a_{Se} = \left(\frac{p_{Se_2}}{p^0_{Se_2}}\right)^{1/2} \tag{3}$$

Table 2. *Thermodynamic properties of iron—selenium alloys [standard states:* $Fe_{(s)}$ *and* $Se_{(l)}$*]*

at% Se	$-\ln a_{Se}$ (873 K)	$-\ln a_{Se}$ (873 K) theor.	$-\ln a_{Fe}$ (873 K)	$-\ln a_{Se}$ (973 K)	$-\ln a_{Se}$ (973 K) theor.	$-\ln a_{Fe}$ (973 K)	$-\Delta G$ (973 K) kJ (g-atom)$^{-1}$	$-\Delta \overline{H}_{Se}$ kJ (g-atom)$^{-1}$	$-\Delta \overline{H}_{Se}$ theor. kJ (g-atom)$^{-1}$
50.0	11.82	∞	0	11.02	∞	0	44.6	90.7	82.4
50.5	10.63	10.90	1.23	9.67	9.73	1.39	45.1	83.7	76.6
51.0	9.45	9.44	2.42	8.45	8.37	2.62	45.3	76.7	71.1
51.5	8.37	8.31	3.54	7.37	7.31	3.77	45.5	69.9	65.8
52.0	7.33	7.33	4.67	6.40	6.40	4.79	45.5	63.3	60.6
52.5	6.42	6.44	5.68	5.60	5.58	5.70	45.7	57.2	55.7
53.0	5.57	5.61	6.61	4.84	4.82	6.52	45.5	51.2	51.0
53.5	4.80	4.84	7.49	4.14	4.11	7.35	45.5	46.2	46.4
54.0	4.12	4.12	8.28	3.47	3.45	8.09	45.3	42.1	42.1
54.5	3.48	3.42	9.01	2.90	2.82	8.77	45.1	38.6	37.9
55.0	2.97	2.77	9.66	2.42	2.22	9.35	44.8	36.3	33.8
55.5	2.70	—	9.99	2.09	1.65	9.76	44.5	—	—
56.0	2.70	—	9.99	1.85	1.11	10.06	44.2	—	—
56.5	2.70	—	9.99	1.68	0.59	10.28	43.9	—	—
57.0	2.16	—	10.70	1.61	0.01	10.37	43.5	31.7	—
57.5	1.62	—	11.42	1.37	—	10.68	43.1	24.3	—
58.0	1.27	—	11.90	1.01	—	11.18	42.7	18.7	—
58.5	1.02	—	12.25	0.75	—	11.55	42.3	14.7	—
59.0	0.84	—	12.51	0.57	—	11.80	41.9	11.8	—
59.5	0.71	—	12.69	0.50	—	11.90	41.4	10.1	—
60.0	0.61	—	12.84	0.50	—	11.90	40.9	9.2	—

Table 3. *Comparison of thermodynamic data with previously reported values*

at% Se	ΔG_{973} this work	ΔG_{973} *Svendsen*[10,*]	ΔH^0_{298} this work [kJ (g-atom)$^{-1}$]	ΔH^0_{298} *Svendsen*[10]	ΔH^0_{298} *Grønvold*[9]
53.33	—45.5	—41.7 ± 1.7	—40.8	—35.7 ± 2.9 —34.2 ± 4.9	—30.9 ± 0.2
57.14	—43.5	—39.7 ± 2.9	—41.6	—36.8 ± 3.8 —34.3 ± 4.7	—30.3 ± 0.2

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* Converted values (see text).

The relationship between the various selenium molecules and Se_2 in the gas phase is given by six equations of the kind

$$Se_x\,(g) = \frac{x}{2} Se_2\,(g) \tag{4}$$

each with an equilibrium constant

$$K_x = (p_{Se_2})^{x/2}/p_{Se_x} \tag{5}$$

Combining Eqs. (2) and (5) we get for the total vapor pressure

$$p = p_{Se_2} + \sum_{x=3}^{8} (p_{Se_2})^{x/2}/K_x \tag{6}$$

Applying the *Gibbs-Helmholtz* equation with the limits of integration T_R and T_S the relation

$$K_x\,(T_S) = K_x\,(T_R) \exp\left[-\frac{\Delta H_x{}^0}{R}\left(\frac{1}{T_S}-\frac{1}{T_R}\right)\right] \tag{7}$$

is obtained with $\Delta H_x{}^0$ the enthalpies of dissociation corresponding to the various equilibria of Eq. (4). The equilibrium constant K_x can be calculated at the reservoir temperature with Eq. (5). The saturation partial pressures of the various selenium molecules listed by *Keller* et al.[25] at certain temperatures were plotted and from a straight line drawn through the points values for p_{Se_x} at the temperatures T_R were taken. The dissociation enthalpies $\Delta H_x{}^0$ were taken from Tab. 3 of *Jelinek* and *Komarek*[5]. Since the total pressure p in the system is fixed by the reservoir temperature T_R, the partial pressure of Se_2, p_{Se_2}, in equilibrium with the specimen can be calculated by combining Eqs. (6) and (7). The result is an equation of the eighth order which was solved with an iterative *Newton* method by a computer program. The physically meaningful values of p_{Se_2} were selected and combined with the saturation partial pressure of Se_2 at the specimen temperature, $p^o_{Se_2}$, to calculate the activity of selenium by Eq. (3); $p^o_{Se_2}$ was determined by linear extrapolation of the values given by *Keller* et al.[25]:

$$\log p^o_{Se_2} = -\frac{6702.413}{T_S} + 6.759 \text{ (atm)} \tag{8}$$

The natural logarithms of the activities of selenium thus calculated are given in Tab. 1, and are plotted in Fig. 2 as a function of the reciprocal specimen temperatures. Specimen temperatures for certain selected compositions were obtained by interpolation of the equilibration curves in Fig. 1, and their reciprocal values were also marked in Fig. 2. For a given composition these points fell on straight lines corresponding to the equation

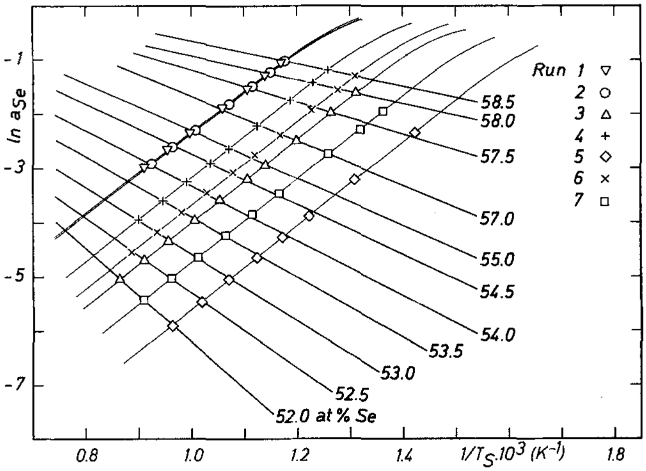

Fig. 2. Activity of selenium as a function of temperature

$$\ln a_{Se}\,(T_2) - \ln a_{Se}\,(T_1) = \frac{\Delta \overline{H}_{Se}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{9}$$

From the slope of these curves partial molar enthalpies $\Delta \overline{H}_{Se}$ were calculated, and the values listed in Tab. 1 and plotted as a function of composition in Fig. 3. Whith these $\Delta \overline{H}_{Se}$ values activities of selenium were calculated for 873 and 973 K using Eq. (9) which are also given in Tab. 1. They have been plotted in Figs. 4 and 5 as a function of composition, and smooth curves extrapolated to 50 at% Se have been

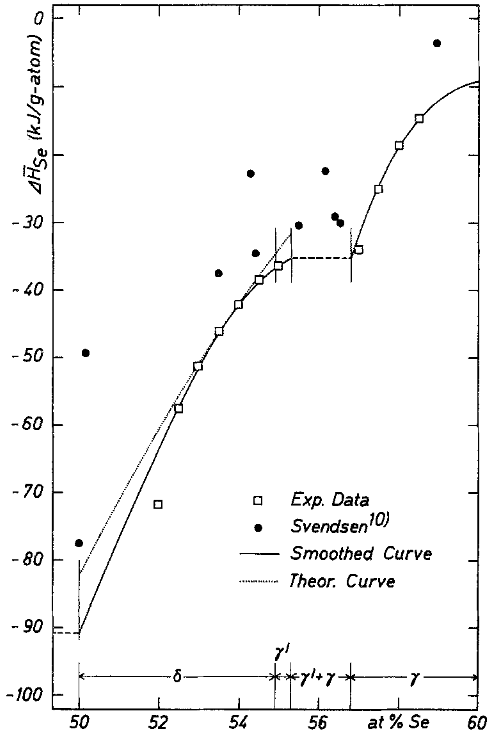

Fig. 3. Partial molar enthalpy of selenium as a function of composition

drawn through the experimental points. Activities of iron were calculated from the smoothed selenium activities by a *Gibbs-Duhem* integration. According to *Kullerud*[26] the solid solubility of selenium in iron at 1 200 K is < 0.5 at%. For the integration a solubility of 0.001 at% Se was assumed but a solubility up to 0.5 at% Se would result only in slightly different iron activities. The natural logarithms of the smoothed selenium activities, the activities of iron, and the integral *Gibbs* energies are given in Tab. 2. Iron activities as function of composition are included in Figs. 4 and 5.

The thermodynamic data of the present investigation can be compared with the values published by *Svendsen*[10]. His partial pressures, p_{Se_2}, in the concentration range of our results were converted to activities using the saturation partial pressures, $p^0_{Se_2}$, calculated from Eq. (8) which were then transformed to 973 K with $\Delta\overline{H}_{Se}$-values from Fig. 3 and Tab. 2, resp. They are also shown in Fig. 5. The agreement

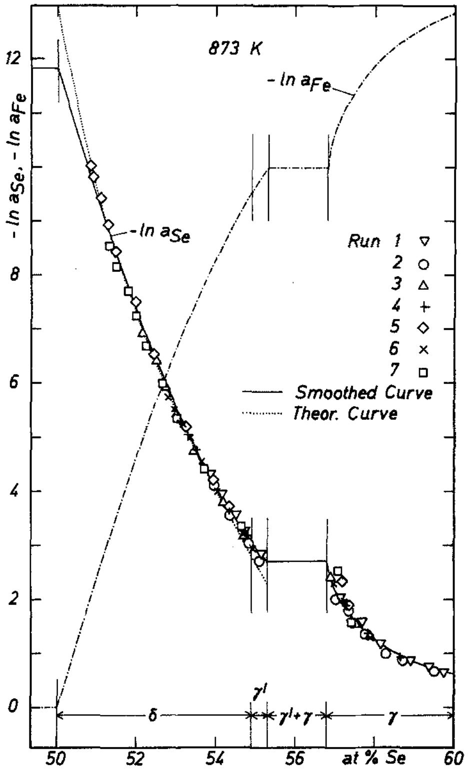

Fig. 4. Activity of selenium and iron as a function of composition at 873 K (— smoothed a_{Se}, --- theoretical a_{Se}, -·-· a_{Fe})

between the two sets of data is very satisfactory except in the range near 50 at% Se. This can be explained by the uncertainty in the $\Delta \bar{H}_{Se}$-values which in that range were obtained by extrapolation. For a comparison of the partial molar enthalpies of selenium the values of *Svendsen*[10] with gaseous selenium as standard state were transformed to liquid selenium as standard state using $\Delta H_v{}^0 = 107.1$ kJ/mol[27] as enthalpy of evaporation. Agreement is less satisfactory as can be seen in Fig. 3 but values for the enthalpy of evaporation of selenium quoted in literature differ widely so that one has to assign a considerable limit of uncertainty to these data.

Svendsen[10] has also reported standard *Gibbs* energies of formation for Fe_7Se_8 (53.33 at% Se) at 934 K, $\Delta G^0_{934} = -90.4 \pm 3.6$ kJ/mol, and for Fe_3Se_4 (57.14 at% Se) at 1020 K, $\Delta G^0_{1020} = -88.0 \pm 6.7$ kJ/mol. With standard entropies[13,28] the data were converted to 973 K and

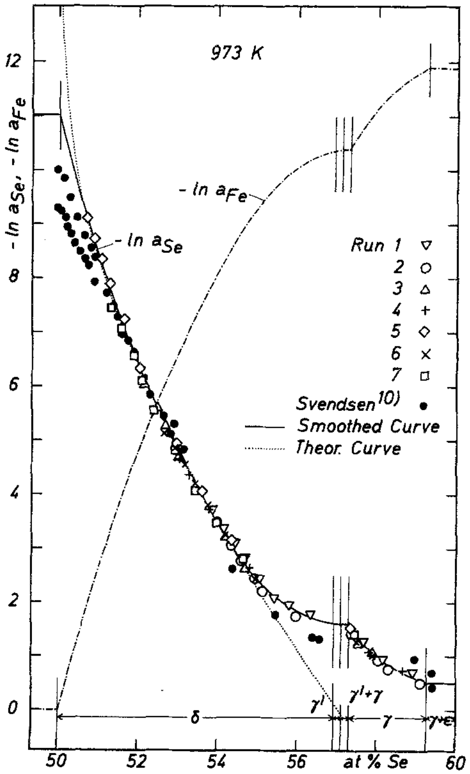

Fig. 5. Activity of selenium and iron as a function of composition at 973 K (— smoothed a_{Se}, ... theoretical a_{Se}, -·-·- a_{Fe}, • *Svendsen*[10])

changed to liquid selenium as the standard state. As can be seen from Tab. 3 agreement with the integral *Gibbs* energies obtained in the present investigation is satisfactory. From the *Gibbs* energies the standard enthalpies of formation at 298 K were derived by the equation

$$\Delta H^{\circ}_{298} = \Delta G^{\circ}_{T} - T \Delta (fef)_{T} \qquad (10)$$

with the free energy function

$$(fef)_{T} = [(H^{\circ}_{T} - H^{\circ}_{298})/T] - S^{\circ}_{T} \qquad (11)$$

taken from literature[13, 28]. These ΔH°_{298}-values agree within the limits of error with the data of *Svendsen*[10], but not with those of *Grønvold*[9] which have been already considered as being too positive[10] (Tab. 3).

Using published standard entropies[13,28] and the ΔH°_{298} data *Gibbs* standard energies were calculated:

$$\Delta G^{\circ}_{298}\,(53.33\,\mathrm{at\%\,Se}) = -42.5\,\mathrm{kJ/g\text{-}atom};$$
$$\Delta G^{\circ}_{298}\,(57.14\,\mathrm{at\%\,Se}) = -42.8\,\mathrm{kJ/g\text{-}atom}.$$

Ettenberg et al.[1] and *Geffken* et al.[2] developed a theoretical model to describe the thermodynamic properties of phases with NiAs-structure. This model based on the assumption of a random distribution of vacancies in every other transition metal layer was quite succesfully applied to several transition metal—chalcogen systems[1–5]. *Ipser* and *Komarek*[3] modified the model by assuming a random distribution of vacancies in every transition metal layer, and derived the following equations:

$$\ln a_{Fe} = \ln\left(\frac{1-x_{Se}}{2x_{Se}-1}\right) - \frac{2E_i}{RT}\left(\frac{2x_{Se}-1}{x_{Se}}\right) - \ln K - \frac{E_v}{RT} \qquad (12)$$

$$\ln a_{Se} = \ln\left(\frac{x_{Se}-0.5}{x_{Se}}\right) + \frac{E_i}{RT}\left(\frac{2x_{Se}-1}{x^2_{Se}}\right) + \mathit{const.} \qquad (13)$$

$$\Delta\overline{H}_{Se} = E_i\left(\frac{2x_{Se}-1}{x^2_{Se}}\right) + \mathit{const.} \qquad (14)$$

$$\Delta\overline{S}_{Se} = -R\ln\left(\frac{x_{Se}-0.5}{x_{Se}}\right) + \mathit{const.} \qquad (15)$$

E_i is the interaction energy between vacancies, E_v the energy of formation of a vacancy, and K the term for the non-configurational contributions.

Both models were applied to the δ-phase of the iron—selenium system but the results were nearly identical. Since in this concentration range the iron vacancies at higher temperatures (above ≈ 400 °C) are supposedly randomly distributed in every transition metal layer[29], theoretical data based on the modified model[3] are listed in Tab. 2. This model was also successfully applied by *Lin* et al.[30] to the pyrrhotite-phase of the iron-sulfur system.

The interaction energy was calculated from the slope of the plot $\ln a_{Se}$ (*experiment.*) $-\ln[(x_{Se}-0.5)/x_{Se}]$ vs. $[(2x_{Se}-1)/x^2_{Se}]$ as $E_i = 147.0$ kJ/g-atom. The constants in Eqs. (13) and (14) were evaluated by fitting a_{Se} (*theoret.*) to a_{Se} (*experiment.*) at 52.0 at% Se, and $\Delta\overline{H}_{Se}$ (*theoret.*) to $\Delta\overline{H}_{Se}$ (*experiment.*) at 54.0 at% Se. Theoretical activities of selenium at 873 and 973 K, and theoretical partial molar enthalpies are presented in Tab. 2 and plotted in Figs. 3, 4, and 5. The agreement between experimental and theoretical values is generally excellent which lends weight to the basic assumption of the model. Deviations near the selenium-rich boundary of the δ-phase and in the γ'-phase can be explained by the increasingly monoclinic distortion of the NiAs-structure.

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