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Thermodynamic Properties of Nickel—Selenium Alloys*

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With 7 Figures

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Vapor pressures of selenium in nickel—selenium alloys were determined by an isopiestic method between 450° and 1000 °C and between 45 and 66.6 at% Se. Activities of selenium were evaluated according to three methods. For the NiAs-type $Ni_{1-x}Se$ phase a statistical model was applied assuming random distribution of metal atoms and metal vacancies in the partially vacant (00½) layers of the lattice. Good agreement between experimental and theoretical values was obtained. The interaction energy between nickel vacancies was found to be 8600 cal/g-atom.

In a series of previous publications thermodynamic investigations of the Ni—Te[1], Co—Te[2], and Co—Se[3] systems have been described. This paper is concerned with a similary study of the Ni—Se system.

The Ni—Se phase diagram, as discussed by *Hansen*[4], *Elliott*[5], and *Shunk*[6], is based mainly on thermal analyses and X-ray measurements of *Kuznetsov* et al.[7]. Recently *Komarek* and *Wessely*[8] have studied the Ni—Se system by *DTA*- and X-ray measurements and have constructed the complete phase diagram which is characterized by four compounds: β-Ni_3Se_2 which decomposes peritectically at 785 °C and transforms at 585 °C into α-Ni_3Se_2 which is stable at lower temperatures; Ni_6Se_5 which forms at 400 °C and decomposes by a peritectoid reaction at 648 °C; the B 8(NiAs) phase $Ni_{1-x}Se$ which has a congruent melting point at 53.5 at% Se and 959 °C and a maximum range of homogeneity between 50.5 and 56.8 at% Se; $NiSe_2$ which decomposes peritectically at 853 °C. At lower temperatures superstructures appear in the $Ni_{1-x}Se$ phase[9], and the disordering of vacancies in these structures appears as λ-type transitions in the C_p-curves[10].

Fabre[11] has reported a standard enthalpy of formation, $\Delta H^{\circ}_{298} = -9.2$ kcal/g-atom, for "NiSe" from heat of solution measurements. En-

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* Dedicated to Prof. *O. Hoffmann-Ostenhof* on the occasion of his 60th birthday.

Table 1. *Experimental Isopiestic Results in the* Ni—Se *System*

Number	Temp. (°C)	Composition (at% Se)	$-\log a_{Se}$	$-\Delta\bar{H}_{Se}$	$-\log a_{Se}$	$-\Delta\bar{H}_{Se}$	$-\log a_{Se}$	$-\Delta\bar{H}_{Se}$
			(Method *A*)		(Method *B*)		(Method *C*)	
			Run 1					
1	955	47.78	1.424	—	1.293		1.496	
2	948	48.09	1.412	—	1.280		1.485	
3	940	48.43	1.399	—	1.265		1.471	
4	932	48.63	1.385	—	1.249		1.457	
5	910	52.24	1.344	16.90	1.206	13.77	1.416	13.28
6	892	52.42	1.313	16.89	1.168	13.70	1.364	13.24
7	872	52.55	1.275	16.88	1.125	13.69	1.342	13.20
8	844	52.80	1.220	16.84	1.062	13.65	1.282	13.10
9	820	53.10	1.171	16.74	1.005	13.62	1.225	12.95
10	792	53.45	1.110	16.52	0.935	13.47	1.153	12.76
11	760	53.90	1.037	16.12	0.849	12.90	1.061	12.41
12	739	54.15	0.986	15.85	0.789	12.37	0.994	12.22
13	696	55.00	0.875	15.22	0.659	11.51	0.853	11.62
14	670	55.60	0.804	14.96	0.576	11.30	0.759	11.32
15	623	66.70	0.662	0.25	0.417	0.25	0.568	0.25
16	599	66.88	0.586	0.25	0.339	0.25	0.471	0.25
17	563	67.12	0.462	0.25	0.232	0.25	0.324	0.25
18	550	67.13	0.414	0.25	0.198	0.25	0.270	0.25
19	527	67.20	0.326	0.25	0.143	0.25	0.186	0.25
Res.	452	—						
			Run 2					
1	869	52.97	1.058	16.79	0.911	13.66	1.119	13.32
2	858	53.07	1.036	16.75	0.887	13.62	1.097	13.29
3	851	53.22	1.022	16.67	0.871	13.58	1.082	13.28
4	842	53.33	1.004	16.60	0.850	13.53	1.061	13.26
5	823	53.46	0.964	16.52	0.804	13.47	1.015	12.75
6	811	53.70	0.939	16.32	0.773	13.26	0.986	12.57
7	802	53.82	0.920	16.21	0.753	13.09	0.964	12.47
8	790	54.01	0.894	16.01	0.722	12.70	0.931	12.33
9	771	54.30	0.851	15.70	0.672	12.09	0.878	12.11
10	726	55.10	0.741	15.16	0.546	11.45	0.737	11.55
11	704	55.50	0.685	15.00	0.482	11.32	0.666	11.35
12	685	56.16	0.634	14.80	0.426	11.20	0.601	11.19
13	649	66.77	0.531	0.25	0.320	0.25	0.464	0.25
14	628	66.80	0.467	0.25	0.261	0.25	0.382	0.25
15	603	66.91	0.388	0.25	0.197	0.25	0.289	0.25
16	580	66.95	0.308	0.25	0.145	0.25	0.207	0.25
17	564	66.94	0.254	0.25	0.113	0.25	0.157	0.25
18	552	66.93	0.210	0.25	0.090	0.25	0.120	0.25
Res.	499	—						
			Run 3					
1	975	52.55	0.676		0.564		0.685	
2	972	52.60	0.671		0.559		0.679	

Table 1 (continued)

Number	Temp. (°C)	Composition (at% Se)	$-\log a_{Se}$	$-\Delta\bar{H}_{Se}$	$-\log a_{Se}$	$-\Delta\bar{H}_{Se}$	$-\log a_{Se}$	$-\Delta\bar{H}_{Se}$
			(Method A)		(Method B)		(Method C)	
3	966	52.97	0.661		0.548		0.669	
4	959	53.58	0.650	16.41	0.535	13.37	0.656	12.65
5	949	53.75	0.633	16.27	0.517	13.20	0.638	12.52
6	938	53.80	0.614	16.23	0.497	13.12	0.620	12.49
7	928	53.90	0.597	16.11	0.478	12.90	0.603	12.41
8	912	54.10	0.569	15.90	0.447	12.47	0.575	12.26
9	882	54.55	0.514	15.50	0.387	11.78	0.519	11.92
10	836	55.26	0.423	15.14	0.293	11.39	0.423	11.47
11	818	55.44	0.385	15.02	0.256	11.34	0.382	11.39
12	785	56.15	0.313	14.80	0.190	11.20	0.301	11.19
13	765	65.10	0.268	0.25	0.153	0.25	0.247	0.25
14	746	66.25	0.222	0.25	0.120	0.25	0.163	0.25
15	722	66.90	0.163	0.25	0.082	0.25	0.136	0.25
16	711	66.92	0.134	0.25	0.065	0.25	0.112	0.25
17	701	66.95	0.107	0.25	0.050	0.25	0.086	0.25
Res.	662	—						
Run 4								
1	985	50.51	1.004		0.887		1.054	
2	982	50.54	0.999		0.882		1.050	
3	977	50.61	0.991		0.873		1.041	
4	972	50.73	0.983		0.864		1.032	
5	966	50.85	0.973		0.852		1.021	
6	952	51.05	0.950		0.827		0.998	
7	940	52.82	0.930	16.84	0.805	13.69	0.977	13.09
8	920	53.04	0.895	16.76	0.766	13.64	0.944	13.00
9	915	53.28	0.886	16.63	0.756	13.55	0.933	12.87
10	896	53.40	0.851	16.56	0.716	13.50	0.896	12.78
11	881	53.50	0.824	16.48	0.685	13.44	0.868	12.71
12	838	54.22	0.739	15.78	0.590	12.22	0.776	12.17
13	808	54.65	0.676	15.41	0.519	11.70	0.704	11.86
14	787	55.01	0.630	15.21	0.467	11.50	0.649	11.62
15	750	55.65	0.544	14.94	0.373	11.29	0.540	11.30
16	725	56.20	0.482	14.80	0.310	11.20	0.461	11.19
17	694	66.85	0.401	0.25	0.271	0.25	0.365	0.25
18	673	66.91	0.343	0.25	0.187	0.25	0.295	0.25
19	649	66.94	0.274	0.25	0.138	0.25	0.212	0.25
Res.	565	—						
Run 5								
1	958	51.87	0.810		0.691		0.841	
2	937	53.30	0.775	16.62	0.652	13.54	0.804	12.85
3	924	53.45	0.752	16.52	0.627	13.47	0.780	12.75
4	900	53.70	0.709	16.31	0.579	13.26	0.737	12.57
5	861	54.25	0.635	15.75	0.497	12.17	0.659	12.14
6	845	54.40	0.603	15.61	0.462	11.96	0.627	12.05

Table 1 (continued)

Number	Temp. (°C)	Composition (at% Se)	$-\log a_{Se}$	$-\Delta \bar{H}_{Se}$	$-\log a_{Se}$	$-\Delta \bar{H}_{Se}$	$-\log a_{Se}$	$-\Delta \bar{H}_{Se}$
			(Method *A*)		(Method *B*)		(Method *C*)	
7	815	54.90	0.541	15.27	0.394	11.54	0.556	11.70
8	793	55.41	0.493	15.03	0.343	11.35	0.500	11.40
9	758	56.17	0.413	14.80	0.263	11.20	0.403	11.19
10	737	65.48	0.362	0.25	0.217	0.25	0.341	0.25
11	712	66.84	0.299	0.25	0.165	0.25	0.266	0.25
12	697	66.84	0.259	0.25	0.137	0.25	0.222	0.25
13	674	66.94	0.196	0.25	0.096	0.25	0.157	0.25
Res.	609	—						
				Run 6				
1	937	47.40	1.518		1.381		1.592	
2	921	47.81	1.490		1.350		1.562	
3	888	52.09	1.430	16.90	1.282	13.78	1.500	13.30
4	875	52.25	1.405	16.89	1.254	13.77	1.474	13.28
5	830	52.72	1.316	16.86	1.151	13.71	1.375	13.14
6	799	53.16	1.248	16.70	1.073	13.60	1.296	12.93
7	772	53.54	1.189	16.46	1.004	13.41	1.222	12.69
8	730	54.15	1.087	15.85	0.883	12.37	1.091	12.41
9	699	54.60	1.008	15.46	0.789	11.74	0.989	11.90
10	642	55.90	0.846	14.86	0.598	11.24	0.769	11.22
11	612	66.72	0.753	0.25	0.491	0.25	0.648	0.25
12	559	66.80	0.571	0.25	0.307	0.25	0.418	0.25
13	530	66.99	0.462	0.25	0.220	0.25	0.292	0.25
Res.	427	—						
				Run 7				
1	917	47.11	1.572		1.430		1.635	
2	913	47.40	1.565		1.422		1.628	
3	908	47.58	1.556		1.411		1.617	
4	901	47.71	1.543		1.397		1.605	
5	890	51.80	1.523	16.90	1.374	13.80	1.583	13.35
6	870	52.10	1.485	16.90	1.331	13.78	1.543	13.30
7	860	52.14	1.466	16.90	1.309	13.77	1.523	13.29
8	840	52.49	1.426	16.89	1.263	13.75	1.477	13.22
9	826	52.55	1.397	16.88	1.229	13.74	1.445	13.19
10	809	52.70	1.361	16.85	1.188	13.72	1.404	13.14
11	776	53.06	1.288	16.75	1.102	13.64	1.314	12.97
12	756	53.42	1.241	16.55	1.047	13.49	1.253	12.78
13	730	53.80	1.177	16.22	0.972	13.13	1.170	12.50
14	681	54.55	1.047	15.50	0.817	11.78	1.003	11.92
15	651	55.20	0.963	15.12	0.716	11.42	0.887	11.50
16	619	56.20	0.865	14.80	0.600	11.20	0.756	11.19
17	565	66.76	0.683	0.25	0.398	0.25	0.521	0.25
18	539	66.81	0.568	0.25	0.307	0.25	0.398	0.25
19	511	66.86	0.475	0.25	0.221	0.25	0.272	0.25
Res.	410	—						

Table 1 (continued)

Number	Temp. (°C)	Composition (at% Se)	$-\log a_{Se}$	$-\Delta \overline{H}_{Se}$	$-\log a_{Se}$	$-\Delta \overline{H}_{Se}$	$-\log a_{Se}$	$-\Delta \overline{H}_{Se}$
			(Method *A*)		(Method *B*)		(Method *C*)	
Run 8								
1	892	46.25	1.793		1.640		1.847	
2	882	46.56	1.775		1.619		1.829	
3	870	51.61	1.752		1.593	13.80	1.804	13.36
4	857	51.68	1.726		1.564	13.80	1.777	13.35
5	845	51.80	1.702		1.536	13.80	1.750	13.34
6	828	51.97	1.668		1.496	13.79	1.710	13.32
7	813	52.10	1.636		1.459	13.78	1.674	13.30
8	789	52.42	1.582		1.397	13.77	1.609	13.25
9	770	52.60	1.540		1.347	13.74	1.557	13.18
10	739	53.13	1.466		1.260	13.61	1.459	12.94
11	711	53.36	1.395		1.176	13.52	1.371	12.81
12	660	54.20	1.255		1.007	12.26	1.185	12.18
13	637	54.70	1.187		0.924	11.66	1.088	11.82
14	605	55.50	1.086		0.802	11.32	0.956	11.36
15	561	66.65	0.935	0.25	0.621	0.25	0.758	0.25
16	531	66.75	0.822	0.25	0.492	0.25	0.606	0.25
17	503	66.80	0.709	0.25	0.376	0.25	0.464	0.25
18	470	66.84	0.564	0.25	0.257	0.25	0.301	0.25
19	451	66.89	0.475	0.25	0.199	0.25	0.223	0.25
Res.	364	—						
Run 9								
1	763	50.77	2.597		2.382		2.579	
2	755	50.92	2.579		2.361		2.554	
3	745	50.97	2.555		2.332		2.522	
4	735	51.10	2.530		2.303		2.488	
5	720	51.20	2.491	16.90	2.257	13.82	2.442	13.40
6	702	51.36	2.446	16.90	2.202	13.81	2.382	13.39
7	691	51.53	2.415	16.90	2.165	13.80	2.341	13.37
8	665	51.74	2.344	16.90	2.079	13.80	2.253	13.35
9	648	51.91	2.294	16.90	2.019	13.79	2.179	13.33
10	616	52.50	2.196	16.89	1.899	13.75	2.045	13.22
11	594	52.98	2.124	16.79	1.810	13.66	1.950	13.06
12	555	53.71	1.987	16.31	1.640	13.25	1.771	12.57
13	526	54.19	1.876	15.81	1.501	12.27	1.621	12.19
14	481	55.45	1.688	15.02	1.263	11.34	1.371	11.38
15	376	66.75	1.147	0.25	0.597	0.25	0.679	0.25
16	352	66.58	0.998	0.25	0.450	0.25	0.574	0.25
17	333	66.31	0.872	0.25	0.351	0.25	0.386	0.25
18	304	66.50	0.659	0.25	0.228	0.25	0.250	0.25
Res.	228	—						
Run 10								
1	838	44.70	2.168		1.991		2.187	
2	833	44.95	2.159		1.980		2.176	

Table 1 (continued)

Number	Temp. (°C)	Composition (at% Se)	$-\log a_{Se}$ (Method *A*)	$-\Delta\bar{H}_{Se}$ (Method *A*)	$-\log a_{Se}$ (Method *B*)	$-\Delta\bar{H}_{Se}$ (Method *B*)	$-\log a_{Se}$ (Method *C*)	$-\Delta\bar{H}_{Se}$ (Method *C*)
3	821	51.02	2.134		1.951		2.149	
4	814	51.14	2.118		1.933		2.130	
5	804	51.39	2.096	16.90	1.908	13.81	2.105	13.39
6	796	51.40	2.080	16.90	1.888	13.81	2.085	13.39
7	782	51.47	2.048	16.90	1.852	13.80	2.045	13.38
8	760	51.70	1.997	16.90	1.792	13.80	1.981	13.36
9	750	51.85	1.972	16.90	1.762	13.79	1.948	13.34
10	737	51.90	1.942	16.90	1.726	13.79	1.909	13.30
11	714	52.24	1.882	16.90	1.655	13.77	1.832	13.28
12	695	52.43	1.832	16.89	1.595	13.75	1.766	13.24
13	659	53.10	1.733	16.73	1.475	13.62	1.636	12.96
14	634	53.50	1.658	16.50	1.385	13.44	1.529	12.72
15	596	54.40	1.537	15.61	1.236	11.96	1.372	12.04
16	568	54.85	1.439	15.30	1.114	11.57	1.243	11.72
17	526	56.22	1.281	14.74	0.918	11.20	1.030	11.50
Res.	295	—						

thalpies of formation of nickel selenides at 1,050 K by reaction calorimetry have been determined by *Grønvold*[12]. Heat capacities of three samples within the homogeneity range of the $Ni_{1-x}Se$ phase have been measured at low[13] and at high[10] temperatures, and the heat capacity of $NiSe_2$ at low temperatures[14]. *Cerclier* and *Laffitte*[15, 16] determined activities of Ni in Ni—Se alloys between 400 and 600 °C with a solid electrolyte *emf* method. The literature data[10–14] were critically evaluated by *Mills*[17].

In the present investigation vapor pressures of selenium of mostly solid Ni—Se alloys were determined by an isopiestic method by equilibrating Ni samples in a temperature gradient with selenium vapor from a reservoir kept at the temperature minimum of the sealed reaction tube. After quenching the compositions of the equilibrated samples were determined and the activities of selenium calculated.

Experimental Procedure

The materials used in this investigation were 99.999% selenium shots (American Smelting and Refining Corp., New York, U.S.A.) and 0.05 mm thick 99.99% nickel foil (Vacuum Metals Corp., Syracuse, U.S.A.).

The preparation of the samples and the experimental procedure have been previously described[3]. The analysis of the nickel content followed closely the procedure for cobalt[3], the only differences being the use of ammonia as a buffer and that of murexide as an indicator. X-ray powder patterns were taken using CoK_α-radiation with a Fe-filter.

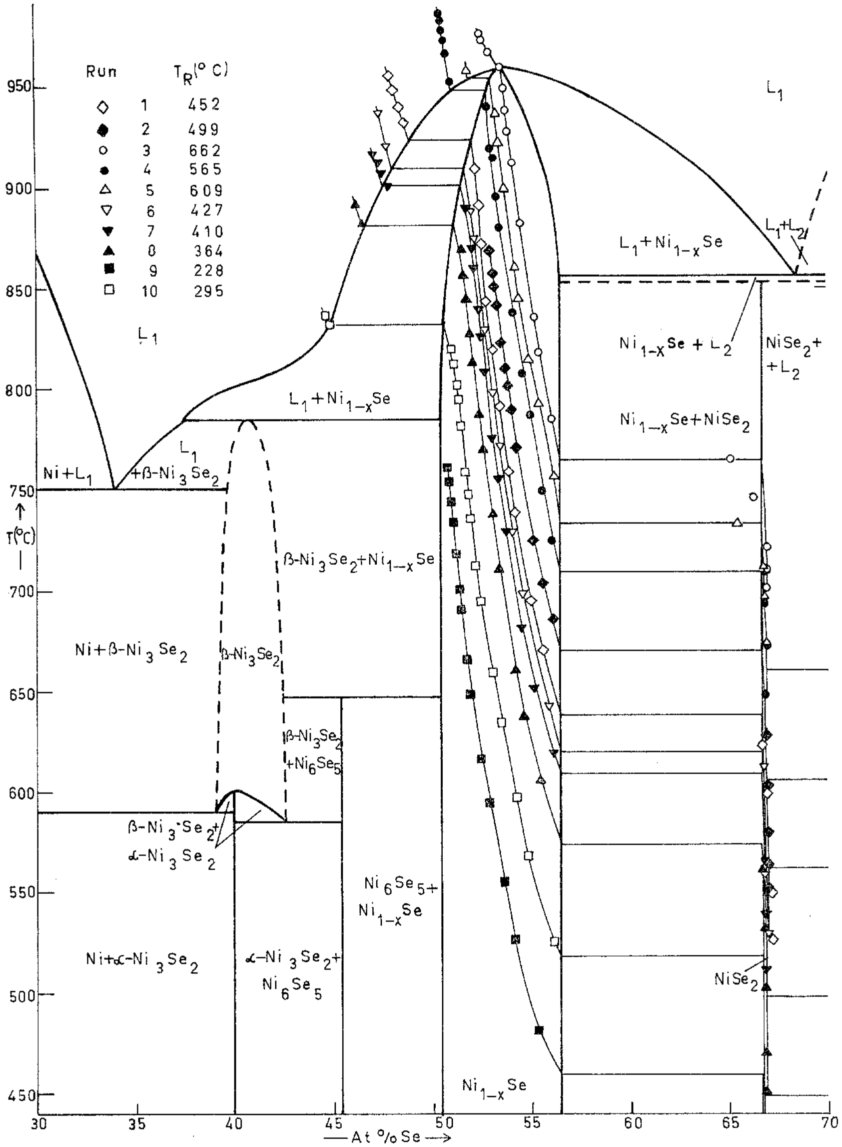

Fig. 1. Specimen composition vs. specimen temperature and partial Ni—Se phase diagram

Experimental Results

Ten experiments with temperature gradients between 310° and 540 °C, with sample temperatures between 300° and 1,000 °C, and with reservoir temperatures between 228° and 662 °C lasting from three to four weeks were carried out. The time was in all cases sufficient to equilibrate the samples, contrary to the Co—Se system[3] where much longer times were needed to equilibrate samples in the $CoSe_2$ phase field. The experimental data are listed in Table 1, and sample compositions and sample and reservoir temperatures, superimposed on the partial phase diagram[8], are shown in Fig. 1. From the discontinuities of the various experimental curves in Fig. 1 phase boundaries can be determined. For the Ni-rich liquidus curve of congruent melting $Ni_{1-x}Se$ the following values were obtained: 833 °C (45 at% Se), 865 °C (46 at% Se), 889 °C (47 at% Se), 908 °C (48 at% Se). The shoulder of the liquidus curve, indicated by these values, was later verified by thermal analyses[8]. The maximum melting point of $Ni_{1-x}Se$ of 959 °C at 53.58 at% Se is in excellent agreement with the previous results[8]. By extrapolation the Ni-rich phase boundary of $Ni_{1-x}Se$ at 785 °C was found to be 50.5 at% Se; the Se-rich boundary of $Ni_{1-x}Se$ between 500° and 750 °C was found to be 56.7 at% Se, both values in very good agreement with the data in the literature[8, 9, 15]. For $NiSe_2$ a small homogeneity range from 66.7 to 67.0 at% Se was obtained. No isopiestic $NiSe_2$ sample had a Ni content higher than the stoichiometric composition of 66.7 at% Se which contradicts the X-ray data by *Grønvold* and *Jacobsen*[9] who assumed a narrow homogeneity range on the Ni-rich side of $NiSe_2$. The compositions of our $NiSe_2$ samples, determined by weight increase and by complexometric titration, agreed within 0.1 at% Se supporting the assumption of a homogeneity range on the Se-rich side. Similar results were obtained with $CoSe_2$[3]. According to X-ray analyses all samples contained already known compounds and were mostly one-phase. Only sample 13 of run 3 and sample 10 of run 5 were in the $Ni_{1-x}Se$—$NiSe_2$ two-phase region, probably due to temperature fluctuations[3].

The reciprocal reservoir temperatures (T_R) are plotted versus the reciprocal specimen temperatures (T_S) in Fig. 2. Equi-composition points lie on straight lines indicating that the results are consistent. Further evaluation of the results to compute activities of Se is somewhat involved because of the complexity of the Se vapor. As in the previous paper[3] three different methods of calculation have been employed. In method A it was assumed that only Se_2 molecules are present in the vapor using the results of *Baker*[18] for the total vapor pressure of Se. Method B made use of empirical equations derived by *Rau*[19], and method C was based on measurements of the saturation partial pressures of *Keller* et al.[20] at lower temperatures. Details of the three methods have been described elsewhere[3]. The activities obtained from the equations are listed in Table 1 and were plotted as $\log a_{Se}$ versus $1/T$. For selected compositions temperatures were interpolated on the equilibration curves in Fig. 1 and their reciprocal values plotted on the log a_{Se} versus $1/T$ curves. For a given composi-

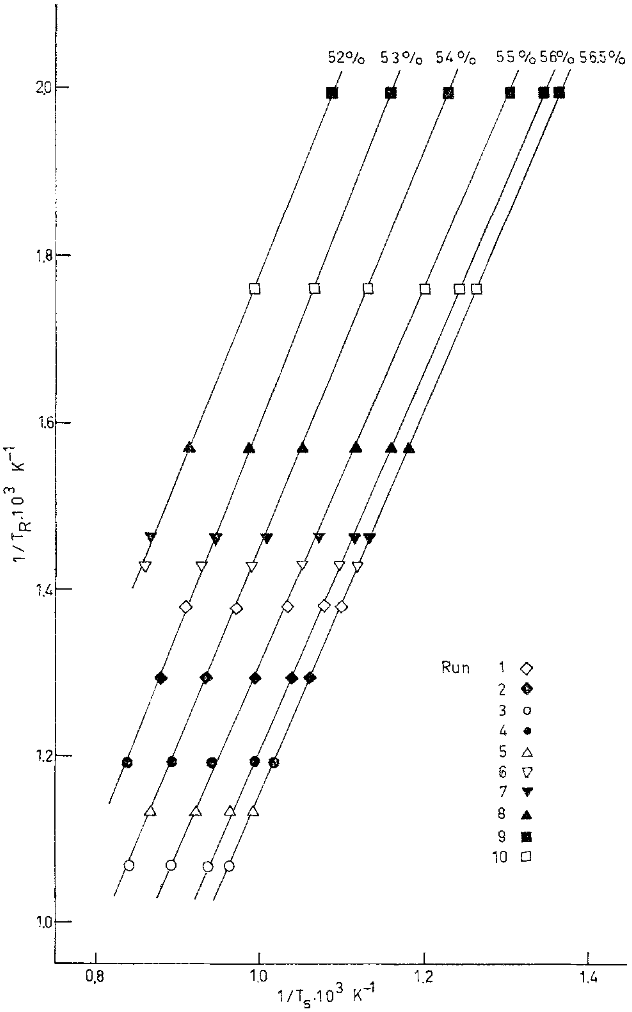

Fig. 2. Reciprocal reservoir temperature vs. reciprocal sample temperature

tion these points lie on a straight line according to the *Gibbs—Helmholtz* equation. The $\Delta \bar{H}_{Se}$ values in kcal/g-atom, calculated from the slopes of these lines are listed in Table 1 and are shown in Fig. 3. Due to the small homogeneity range of $NiSe_2$ the $\Delta \bar{H}_{Se}$ values could not be determined and an estimated value of — 0.25 kcal/g-atom was used for the $NiSe_2$ compound to correct the activities of Se. Activities were calculated at 600° and 875 °C with the $\Delta \bar{H}_{\mathrm{Se}}$ values from Table 1 and are plotted in Fig. 4. Only the data points for method *B* and *C* are shown in the figure. Since the $\Delta \bar{H}_{\mathrm{Se}}$ values obtained by method *B* and *C* are the same within the limits of error (Fig. 3), there is no relative shift of the two activity curves "*B*" and "*C*" with respect to each other with changing temperature. Activities obtained by method *C* are given preference since this method is based on actual measurements of partial pressures[20].

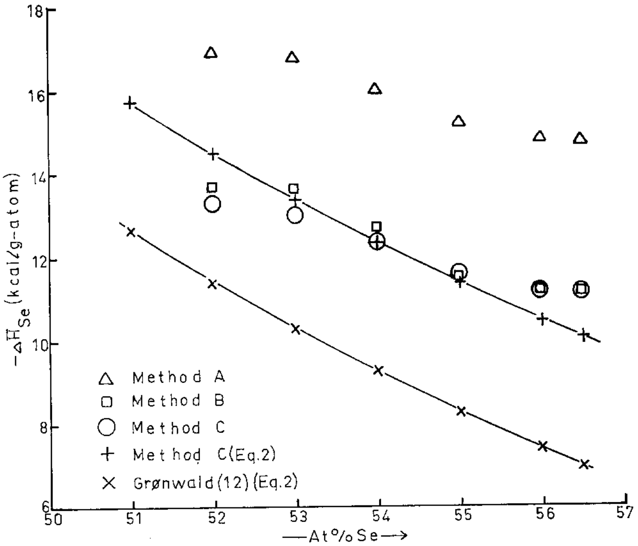

Fig. 3. Partial molar enthalpy of Se in the $Ni_{1-x}Se$ phase

The only activity measurements reported in the literature are those of *Cerclier* and *Laffitte*[15, 16]. These authors determined activities of nickel between 400° and 600 °C by an *emf* method using a solid $BaCl_2$ electrolyte and calculated the activities of Se by *Gibbs—Duhem* integration. The values at 600 °C[15] are plotted in Fig. 5 for comparison with our data at the same temperature. The curves have qualitatively similar shapes but the activities of the present work are significantly smaller, i.e. log a_{Se} is more negative. The two solid lines in Fig. 5 represent the smoothed experimental data from Fig. 4. Activities of Se were also calculated from a model assuming a statistical distribu-

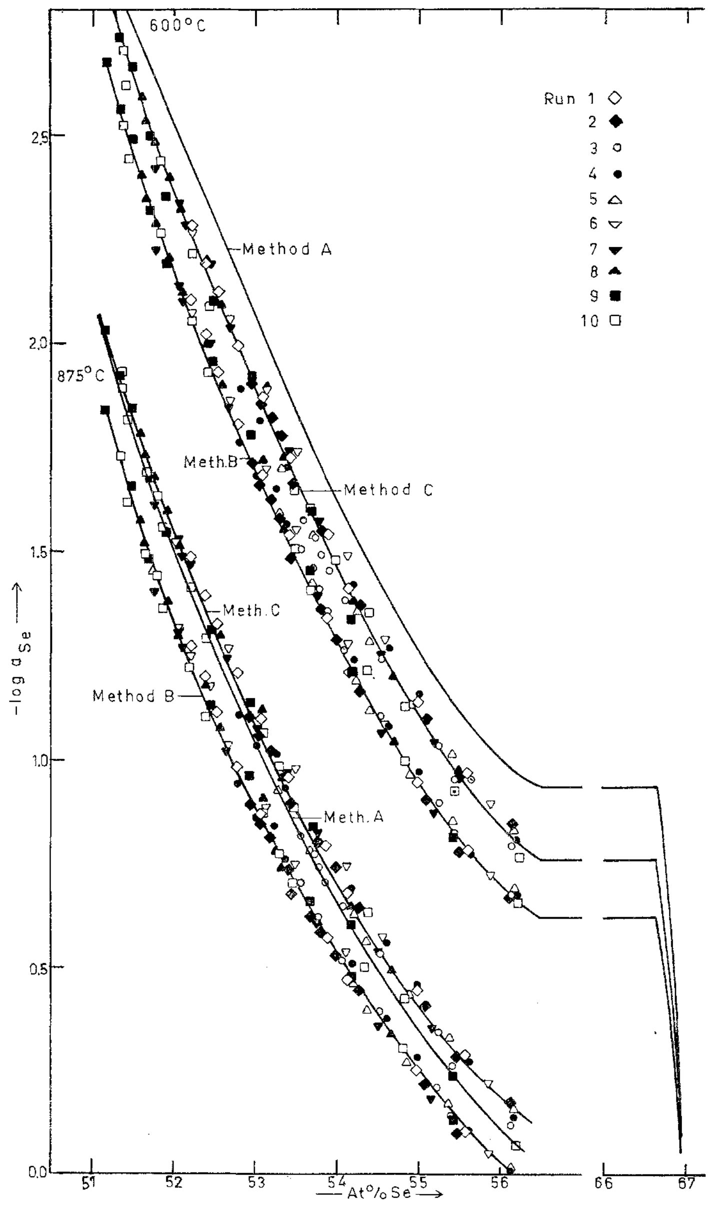

Fig. 4. Activity of Se as a function of composition at 600° and 875 °C

tion of transition metal atoms and transition metal vacancies in the (00½) layers of the hexagonal NiAs lattice allowing for a certain interaction between the vacancies. The equations for the partial molar quantities of Se, previously derived[3], are as follows:

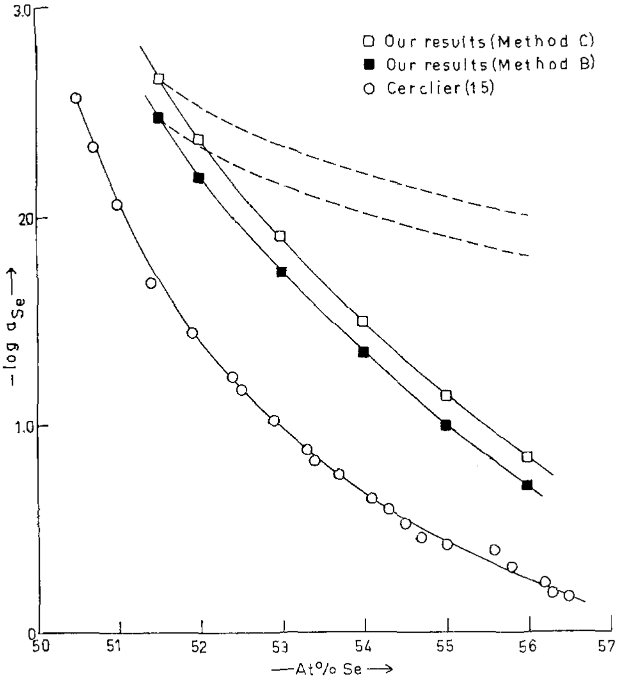

Fig. 5. Activity of Se as a function of composition at 600 °C

$$\ln a_{Se} = \ln\left\{\frac{(N_{Se} - 0.5)}{[N_{Se}\,(0.666 - N_{Se})]^{1/2}}\right\} - \frac{4\,E_i}{RT}\left(\frac{1-2\,N_{Se}}{2\,N_{Se}^2}\right) + \text{const} \qquad (1)$$

$$\Delta \overline{H}_{Se} = -4\,E_i\left(\frac{1-2\,N_{Se}}{2\,N_{Se}^2}\right) + \text{const} \qquad (2)$$

$$\Delta \overline{S}_{Se} = -R\ln\left\{\frac{(N_{Se} - 0.5)}{[N_{Se}\,(0.666 - N_{Se})]^{1/2}}\right\} + \text{const.} \qquad (3)$$

The values, represented by the square boxes (□ and ■) in Fig. 5, were obtained from Eq (1) with an interaction energy, E_i, of 8,600 cal/g-atom (method *C*) and 8,220 cal/g-atom (method *B*), resp., by using the experimental activity at 51.5 at% Se as reference point. The dashed curves in Fig. 5 represent the values without interaction between the vacancies, i.e. ignoring the term containing E_i in Eq (1). As can be seen in Fig. 5, there is excellent agreement between experimental and theoretical activities when the interaction between vacancies is taken into account. Heat capacity measurements of *Grønvold*[10] from room temperature to 777 °C on three Ni—Se alloys in the $Ni_{1-x}Se$ phase field, at 51.3, 53.3, and 55.5 at% Se, revealed no transition at 51.3 at% Se, one λ-type transition at 230 °C at 53.3 at% Se, and two λ-type transitions, at 316° and 722 °C, resp., at 55.5 at% Se.

Table 2. *Thermodynamic Properties of the* $Ni_{1-x}Se$ *Phase at* 600 °C *[Standard states:* $Ni_{(s)}$ *and* $Se_{(l)}$*]*

Composition (at% Se)	$-\log a_{Se}$ (exp., B)	$-\log a_{Se}$ (exp., C)	$-\Delta \bar{H}_{Se}$ (exp., B)	$-\Delta \bar{H}_{Se}$ (exp., C)	$-\Delta \bar{H}_{Se}$ (calc., C)	$-\Delta H^{M}$* (calc., Eq. 5)	$-\Delta \bar{H}_{Se}$* (calc., Eq. 2)
51.5	2.47	2.66	—	—	—	—	—
52.0	2.19	2.37	13.72	13.30	14.50	9.83	11.42
53.0	1.73	1.90	13.65	13.03	13.37	9.85	10.29
54.0	1.34	1.49	12.71	12.33	12.33	9.84	9.25
55.0	0.99	1.13	11.51	11.62	11.36	9.82	8.28
56.0	0.70	0.84	11.22	11.22	10.48	9.78	7.40
56.5	—	—	11.17	11.18	10.06	9.74	6.98

* Based on the data of *Grønvold*[12].

These transitions were interpreted as being due to ordering in the partially vacant metal layers. Our measurements were carried out above these temperatures, so that the assumption of a statistical distribution in the defected layers appears to be justified. Similar measurements on Co—Se alloys[3] gave a very similar interaction energy ($E_i = 7{,}780$ cal/g-atom). The activities of Se in the Co—Se system at 600 °C were, however, more than one order of magnitude smaller, and the partial molar enthalpies of Se 6 to 7 kcal more negative than the corresponding properties in the Ni—Se system. $\Delta \bar{H}_{Se}$ values were calculated with Eq (2) using the experimental value at 54 at% (Table 2, method C) to solve for the constant (— 17,043). The results are listed in Table 2 and shown in Fig. 3.

The partial molar enthalpy of Se can be combined with the partial molar enthalpy of Ni[3]

$$\Delta \bar{H}_{Ni} = 4\, E_i \left(\frac{1-2\, N_{Se}}{N_{Se}}\right) - E_v \qquad (4)$$

to obtain the molar enthalpy of mixing

$$\Delta H^M = N_{Se}\,\Delta \bar{H}_{Se} + N_{Ni}\,\Delta \bar{H}_{Ni} =$$

$$= 8\,E_i\,\frac{(N_{Se} - 0.5)^2}{N_{Se}} + (\text{const} + E_v)\,N_{Se} - E_v \qquad (5)$$

with E_v the energy of formation of a nickel vacancy and "const." the same constant as in Eq. (2). *Grønvold*[12] has determined ΔH^M of Ni—Se alloys at 777 °C by high temperature reaction calorimetry. His results for the $Ni_{1-x}Se$ phase are plotted in Fig. 6 and a smooth curve was drawn through the data points ignoring two points which seem to be somewhat off. The curve passes through a very shallow minimum at 53.5 at% Se which coincides with the composition of the maximum melting point of $Ni_{1-x}Se$. With $E_i = 8{,}600$ and with two ΔH^M values, taken from the smooth curve at 52 and 56 at% Se, Eq. (5) was solved. E_v was found to be 5,458 cal, and the constant — 13,958. With these values Eq. (5) was solved at various compositions and the results are listed in Table 2 and Fig. 6. The calculated points fall on the smooth curve and are in perfect agreement with the data of *Grønvold*[12]. His ΔH^M results (in cal/g-atom) can therefore be expressed by the equation

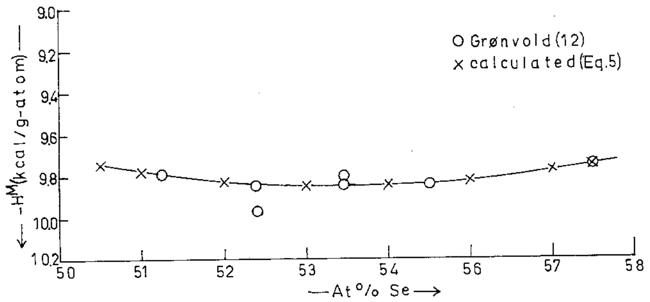

Fig. 6. Enthalpy of formation of $Ni_{1-x}Se$ at 777 °C

$$\Delta H^M = 68{,}800\,\frac{(N_{Se} - 0.5)^2}{N_{Se}} - 8{,}500\,N_{Se} - 5{,}458 =$$

$$= 60{,}300\,N_{Se} - 17{,}200\,N_{Se}^{-1} - 74{,}258. \qquad (6)$$

With $E_i = 8{,}600$ and "const." $= - 13{,}958$ the $\Delta \bar{H}_{Se}$ values were calculated using Eq. (2). These data, based on the calorimetrically

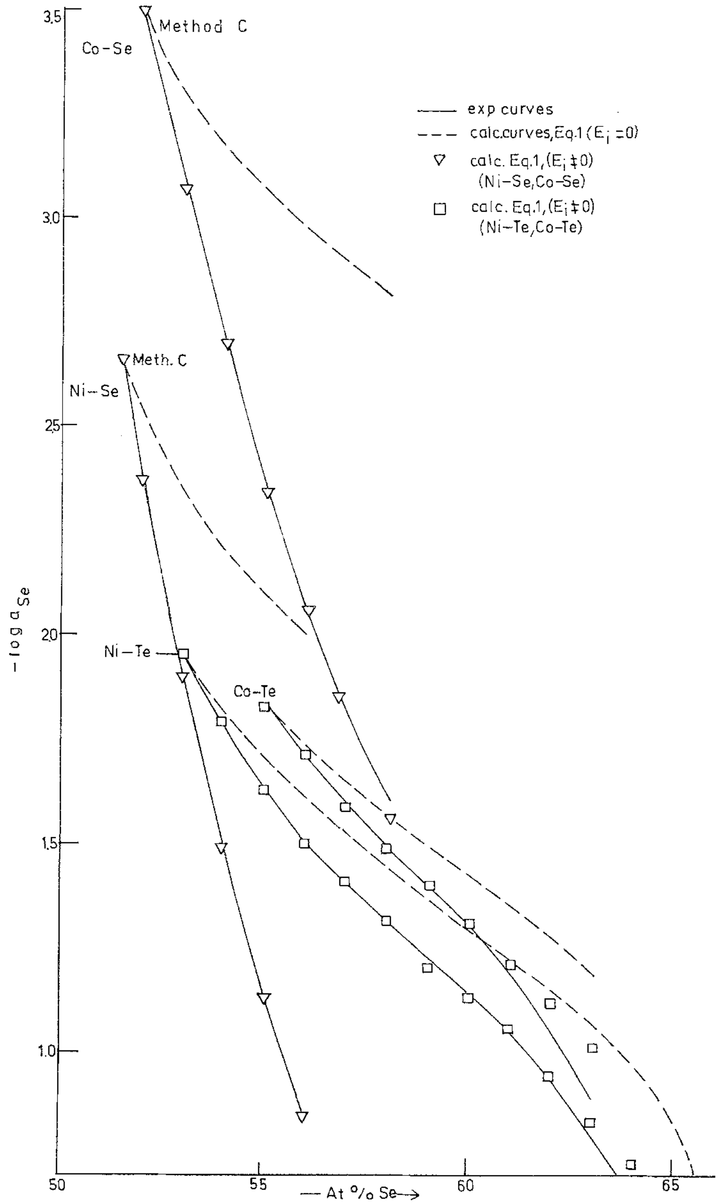

Fig. 7. Chalcogen activities in the NiAs phases of the Co—Se, Ni—Se, Co—Te, and Ni—Te systems at 600 °C

determined ΔH^{M}[12], are listed in Table 2 (last column) and are plotted in Fig. 3. The curve is 3 kcal less negative than the calculated curve drawn through our data points.

Finally in Fig. 7 the activity curves at 600 °C of the NiAs phases of all the systems so far investigated[1–3] are shown. In the Te systems (Co—Te, Ni—Te) the homogeneity range is wider and the activities show less change with composition than in the Se systems (Co—Se, Ni—Se). Consequently the interaction energy E_i is significantly higher in the Se systems than in the Te systems. The interaction energy is practically the same in the Te systems ($\approx$ 1 kcal), and very similar in the Se systems ($\sim$ 7.8 kcal in Co—Se, $\approx$ 8.6 kcal in Ni—Se). For a given chalcogen the activities in the Co system are smaller—i.e. log a_x more negative—than the activities in the Ni system. For all systems the activities at elevated temperatures can be well explained by a model assuming statistical distribution of metal vacancies and metal atoms in the defected (00½) layers of the NiAs structure.

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