

Thermodynamic Stability of the γ -Co_{1-x}Se Phase by CaF₂ Electrolyte Galvanic Cell Method

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The partial molar free enthalpy of cobalt, $\Delta \bar{G}_{\text{Co}}$, and the molar free enthalpy of formation of Co_xSe alloy phase, $\Delta G_f^0(\text{Co}_x\text{Se})$ at 873 K, were determined by the solid CaF₂ electrolyte galvanic cell method for $x = 0.725$ to 0.956. $\Delta \bar{G}_{\text{Co}}$ was observed to be a monotonic function of the mole fraction X_{Co} in the composition region of the investigation with an inflexion point at $X_{\text{Co}} = 0.455$. The measurements were extended down to a temperature of 710 K and a partial Co—Se phase diagram was evaluated from the resultant data.

Untersuchung der thermodynamischen Stabilität der γ -Co_{1-x}Se Phase mittels galvanischer Zelle mit CaF₂ Elektrolyt

Die partiellen molaren freien Enthalpien von Kobalt ($\Delta \bar{G}_{\text{Co}}$) und die molaren freien Bildungsenthalpien der Co_xSe Legierungsphase [$\Delta G_f^0(\text{Co}_x\text{Se})$ bei 873 K] wurden mittels galvanischer Zelle (CaF₂ Fest-Elektrolyt) für $x = 0,725$ —0,956 bestimmt. $\Delta \bar{G}_{\text{Co}}$ wurde im untersuchten Bereich als monotone Funktion vom Molenbruch X_{Co} , mit einer Inflexion bei $X = 0,455$, gefunden. Die Messungen wurden bis zu einer Temperatur von 710 K ausgedehnt und die Daten wurden zur Erstellung eines partiellen Co—Se-Phasendiagramms ausgewertet.

Introduction

Thermodynamic investigations¹⁻⁷ as well as phase diagram studies^{8,9} have confirmed the existence of Co_{1-x}Se phase having a considerable composition homogeneity above 800 K. But the resultant thermodynamic data are in significant disagreement. There are many reasons for this disagreement. In the work of Laffitte and Cerclier⁴ eutectic formation¹⁰ between CoCl₂(s) and BaCl₂(s) at 768 K could have introduced some indeterminate errors into the a_{Co} while the results of

Matlasevich et al.^{5,6} could have been affected by the increased solubility of the Co—Se alloy in the molten LiCl—KCl electrolyte. A comparison of either of these two investigations with the results of *Jelinek and Komarek*⁷ requires both the extrapolation of data with respect to temperature and the *Gibbs—Duhem* integration of the measured activity of selenium. A need, therefore, existed for an independent measurement of the $\Delta \bar{G}_{\text{Co}}$ or $\Delta \bar{G}_{\text{Se}}$ of these alloys to establish the thermodynamic state of this system. Hence the present investigation was undertaken to obtain better values for the ΔG_f^0 of Co_{1-x}Se phase by measuring the a_{Co} using single crystal $\text{CaF}_2(\text{s})$ as the solid electrolyte.

Experimental

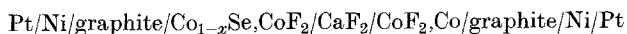
Materials

Co—Se alloys of different compositions were prepared by direct reactions of the elements. Co metal powder was heated in a stream of hydrogen at 800 K for about 2 h to remove any oxide contamination. The Se powder was spectrochemically analysed to be 99.99 percent pure. Both the Co and Se powders were supplied by the Pure Materials Section of this Division. The calculated amounts were weighed, mixed and compacted into pellets of about 10 mm diameters. These green pellets were heated at 875 K for a week in an evacuated sealed silica tube. The resultant products were ground and heated again for two more weeks at 930 K and quenched. The phases present were identified by X-ray diffraction technique.

The reference electrodes of $\text{Co} + \text{CoF}_2$ were prepared by mixing the hydrogen reduced Co powder and the CoF_2 (Ozark-Mahoning Co., 99.9 percent pure) in the mole ratio of 2:1 and pressing the mixture into pellets of 6 mm diameter and 2 mm thick and sintering in a flow of HF/Ar gas at 900 K. The alloys electrodes were made by mixing the powdered alloy of the desired compositions with the $\text{CoF}_2(\text{s})$ sample in the mole ratio of 1:1 and pressing the mixture into pellets of 6 mm diameter by 2 mm thick. A 17 mm diameter, 5 mm thick single crystal CaF_2 disc (Technical Physics Division, BARC) was used as the fluoride ion conducting electrolyte.

Procedure

The galvanic cells of the following type



were assembled for each alloy composition and the *emf* outputs were recorded for several heating and cooling cycles. Except for minor modifications other experimental details like the cell assembly, inert gas purification, furnace and the *emf* recording instrumentation etc. were essentially similar to those described earlier¹¹.

There was the possibility of preferential volatilization of Se from the alloy-pellet electrode if it was directly exposed to the inert gas (argon) stream. This would affect the alloy composition during the *emf* measurement. This was eliminated by placing the electrode pellets inside the tightly fitting cavities of graphite cups in such a way that argon gas had a minimum direct contact with the two electrode pellets surfaces (Fig. 1).

After the cell was assembled and evacuated ($p \approx 0.1$ to 1.0 Pa) it was back filled with purified argon and an argon flow of about $20 \text{ cm}^3 \text{ min}^{-1}$ was maintained through both electrode chambers during the *emf* measurements. This cell assembly was gradually brought up to 900 K and was allowed to equilibrate overnight at this temp. before making the *emf* measurements. The *emf* was continuously recorded for about 3-4 h at each set temperature and the steady reading of $E \pm 0.5 \text{ mV}$ during this period was considered as the cell *emf*. The reversibility of the cell reactions was ascertained each time in the usual way. The *emf* recording of each cell was generally continued for 10-12 days.

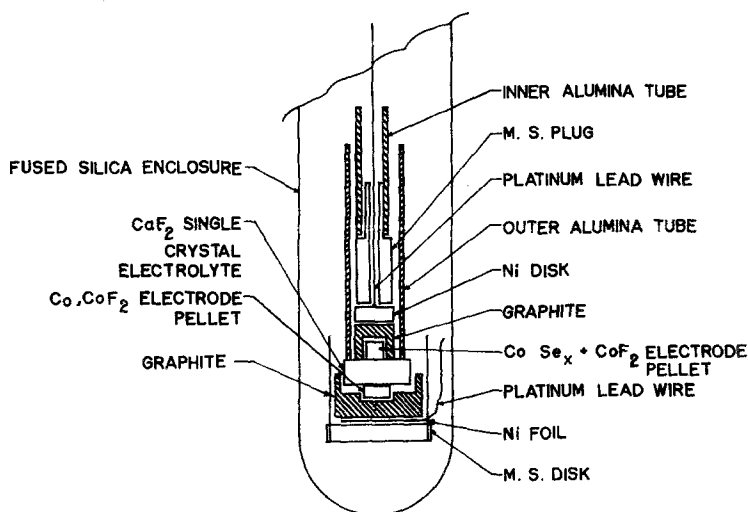


Fig. 1. Details of cell assembly

Results and Discussion

Table 1 presents the initial compositions and the results of the X-ray identification of the phases present in the air quenched samples (equilibration temperature = 930 K).

The alloy sample of $\text{Co/Se} = 0.49_6$ showed the presence of only the δ - CoSe_2 phase, while alloys of $0.69_6 \leq \text{Co/Se} \leq 0.72_5$ compositions in addition contained the monoclinic γ' - Co_{1-x}Se phase. The samples of the stoichiometry, $0.73_1 \leq \text{Co/Se} \leq 0.83_5$, contained the single γ' -phase only. Those alloys containing Co/Se between 0.90_8 and 0.95_6 were found to contain only the single hexagonal γ -phase.

These results indicate two *two-phase* regions. The δ and γ' phases co-exist between $\text{Co/Se} = 0.69_6$ and 0.72_5 while the γ' and γ phases co-exist from $\text{Co/Se} = 0.85_0$ to 0.90_8 . However, whether these composition limits refer to the annealing temperature of 930 K or to some lower

temperature can not be established from the examination of the quenched samples only. For example, *Bøhm et al.*⁸ on samples annealed at 673 K and quenched reported a value of $0.83 \geq \text{Co/Se} \geq 0.75$ for the homogeneity range for γ' -phase and $\text{Co/Se} = 0.93$ for the phase boundary limit of γ -phase. Hence additional information gathered from the isopiestic experiments and *emf* data have to be utilized to decide this phase boundary compositions.

Table 1. *X-ray identification of phases present in the quenched samples.*
(Annealing temperature = 930 K, Iron K_{α} -X-radiations)

Sample number	Co, % (<i>w/w</i>)	Composition of the sample		
		X_{Co}	Co/Se	identified
1	27.0	0.33 ₂	0.49 ₆	δ -CoSe ₂ only
14	34.2	0.41 ₂	0.69 ₆	δ -CoSe ₂ + γ' -Co _{<i>x</i>} Se
5	35.1	0.42 ₀	0.72 ₅	δ -CoSe ₂ + γ' -Co _{<i>x</i>} Se
16	35.3	0.42 ₄	0.73 ₁	γ' -Co _{<i>x</i>} Se only
17	35.5	0.42 ₅	0.73 ₈	γ' -Co _{<i>x</i>} Se only
18	35.9	0.42 ₉	0.75 ₀	γ' -Co _{<i>x</i>} Se only
19	36.2	0.43 ₂	0.76 ₀	γ' -Co _{<i>x</i>} Se only
13	36.9	0.43 ₉	0.78 ₄	γ' -Co _{<i>x</i>} Se only
20	37.3	0.44 ₄	0.79 ₇	γ' -Co _{<i>x</i>} Se only
4	38.0	0.45 ₁	0.82 ₁	γ' -Co _{<i>x</i>} Se only
11	38.4	0.45 ₅	0.83 ₅	γ' -Co _{<i>x</i>} Se only
12	38.8	0.45 ₉	0.85 ₀	γ' -Co _{<i>x</i>} Se + γ -Co _{<i>y</i>} Se
21	39.4	0.46 ₆	0.87 ₁	γ' -Co _{<i>x</i>} Se + γ -Co _{<i>y</i>} Se
23	40.4	0.47 ₆	0.90 ₈	γ -Co _{<i>y</i>} Se only
3	40.9	0.48 ₀	0.92 ₇	γ -Co _{<i>y</i>} Se only
22	41.2	0.48 ₂	0.93 ₇	γ -Co _{<i>y</i>} Se only
8	41.7	0.48 ₉	0.95 ₆	γ -Co _{<i>y</i>} Se only
6	42.3	—	0.98 ₂	γ -Co _{<i>y</i>} Se + β -Co ₉ Se ₈ ^a

^a Note: This sample was annealed at 673 K.

In Figs. 2*a*, 2*b*, and 2*c*, the *emf* values of the cells with Co—Se alloys of compositions $\text{Co/Se} = 0.98_2$ to 0.49_6 are plotted as a function of the temperature. The straight line portion of each plot is the linear least squares of the data. On the assumption that these parameters of the least squares expression were $\Delta \bar{H}_{\text{Co}}$ and $\Delta \bar{S}_{\text{Co}}$ and the $\Delta \bar{H}_{\text{Co}}$ and $\Delta \bar{S}_{\text{Co}}$ for homogeneous phase alloys were temperature independent, they were calculated from the least squares fitted lines (Table 2).

ΔG_{Co} vs. composition isotherms at 873, 843, 803, 773, 748, and 723 K were evaluated from the *emf* vs. temperature plots. From these

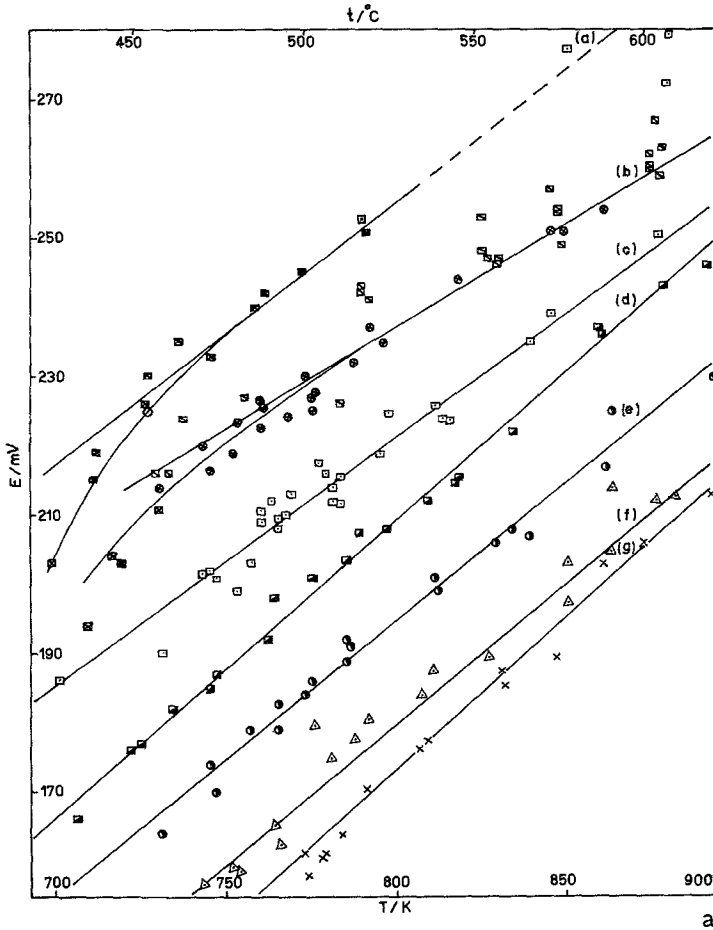


Fig. 2a. E.M.F. vs. temperature

isotherms, the miscibility gap of γ and γ' phases as well as the $\delta\text{-}\gamma'$ two phase field were calculated. Above 740 K, the alloy of Se content higher than $\text{Co/Se} = 0.49_6$ is single phase $\delta\text{-CoSe}_2$ as the E vs. T plot for this is linear (curve *a* of Fig. 2a). This composition is probably the lower Se-limit of this phase. This was further inferred from the following observation:

When the electrode pellet containing this alloy composition was thermal cycled below 800 K, it yielded the curve (a) of Fig. 2a but when the cell assembly was first equilibrated at higher temperature (24–40 h at 873 K) prior to measurement of *emf*, the resultant *emf* values were

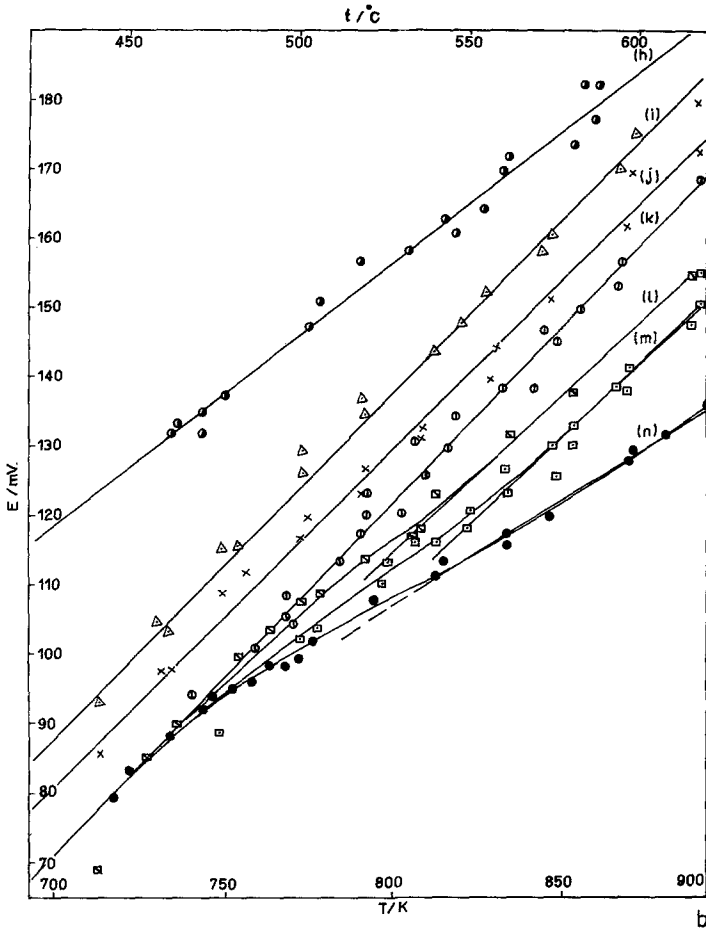


Fig. 2b. E.M.F. vs. temperature

nearly equal to those obtained for alloys identified to contain ($\delta + \gamma'$) mixture, i.e., curve (b) of Fig. 2a. It was, therefore, concluded that the alloy, $\text{Co}_{0.496}\text{Se}$, represents the cobalt-rich end of the δ -phase above 740 K.

Even though the X-ray examination of the alloy, $\text{Co}/\text{Se} = 0.696$ showed the presence of both δ - and γ' -phases, the measured E vs. T was linear within the experimental errors above 770 K. The temperature dependence of the cell containing alloy of $\text{Co}/\text{Se} = 0.725$ (curve c of Fig. 2a) was linear in the entire temperature range of measurement suggesting a single, homogeneous phase. But the X-rays examination

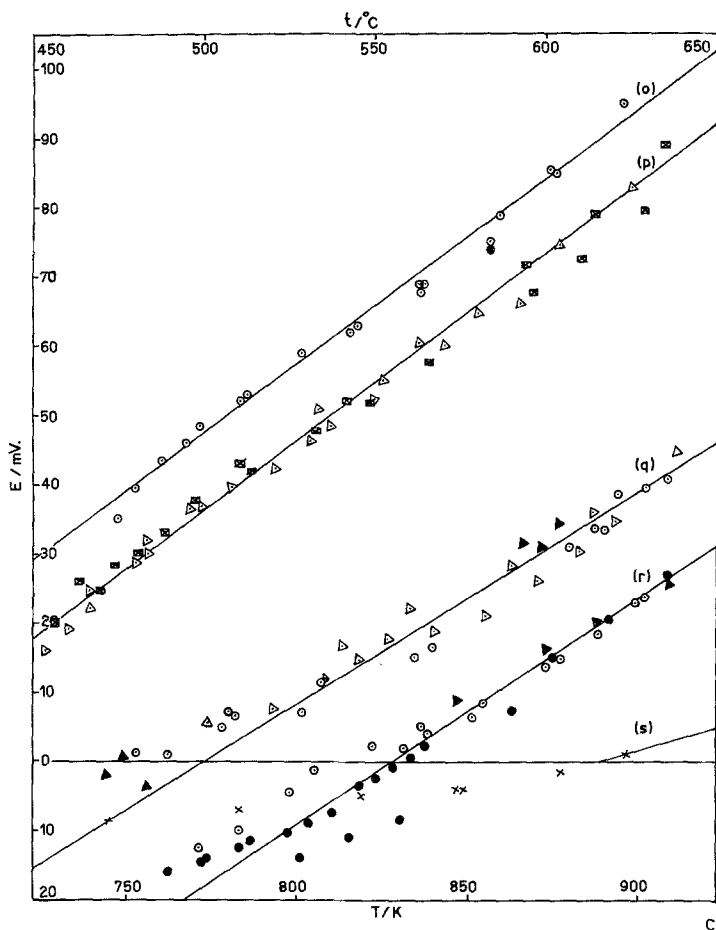


Fig. 2c. E.M.F. vs. temperature

of the quenched samples showed a trace of δ -phase in addition to the γ' -phase. It was concluded that this composition probably forms the selenium-rich boundary of the γ' -phase. This conclusion is supported by isopiestic equilibration measurements.

In one set of experiment, 153.695 ± 0.002 mg of the sample $\text{Co/Se} = 0.696$ and 236.652 ± 0.002 mg of the sample $\text{Co/Se} = 0.725$ were placed inside the same silica vial, evacuated to a pressure of 10^{-3} Pa and sealed. The sealed vial was then heated at 890 ± 2 K for two weeks and then slowly pulled out of the furnace to cool. Both samples on reweighing showed net losses (0.130 ± 0.002 mg for the first sample and

Table 2. Partial molar quantities of cobalt in γ -CoSe alloys evaluated from the emf data

X_{Co}	$\frac{E/\text{mV} = a + bT/\text{K}}{b}$	$\pm \delta E/\text{mV}$	$-\Delta G_{\text{Co}}(723 \text{ K})$ kJ mol ⁻¹	$-\Delta G_{\text{Co}}(873 \text{ K})$ kJ mol ⁻¹	$\frac{\Delta S_{\text{Co}}}{\text{J mol}^{-1} \text{K}^{-1}}$	$\frac{\Delta H_{\text{Co}}}{\text{kJ mol}^{-1}}$
0.42 ₀	-67.16	1.6	37.4	47.7	69.6 ± 5.4	13.0
0.42 ₁	-135.07	1.8	34.0	46.5	83.1 ± 4.6	26.1
0.42 ₅	-125.09	2.3	31.7	43.2	77.2 ± 6.2	24.1
0.42 ₉	-147.01	2.1	28.6	40.6	78.8 ± 5.4	28.2
0.43 ₂	-180.13	1.3	26.9	39.7	85.3 ± 3.5	34.8
0.43 ₉	-147.41	2.1	24.6	35.5	73.3 ± 5.4	28.5
0.44 ₁	-254.33	1.9	19.3	33.6	94.6 ± 6.2	49.0
0.45 ₁	-247.26	1.7	17.9	31.8	90.8 ± 4.4	47.5
0.45 ₅	-278.70	2.3	16.1	30.6	96.7 ± 6.2	53.8
0.45 ₉	visual fit	—	16.0	27.3	88.8	50.2
0.46 ₆	visual fit	—	16.0	24.9	61.8	29.0
0.47 ₆	-237.86	1.5	5.6	16.2	71.7 ± 3.8	45.9
0.48 ₀	-240.75	2.2	—	14.0	69.2 ± 5.8	46.5
0.48 ₂	-220.45	2.0	—	6.0	55.6 ± 5.8	42.5
0.48 ₉	-233.35	1.0	—	2.9	54.6 ± 6.2	44.8
0.49 ₅	—	—	—	0.0	—	—

0.157 ± 0.002 mg for the second) indicating that the selenium activity in both was the same. Therefore, both samples at 890 K belong to the $\delta + \gamma'$ two phase field. Small losses of weight of both samples might have been the result of selenium vapour condensing on the inner wall of the silica tube during quenching. When the isopiestic equilibration was repeated at the same temperature with samples of Co/Se = 0.725 and

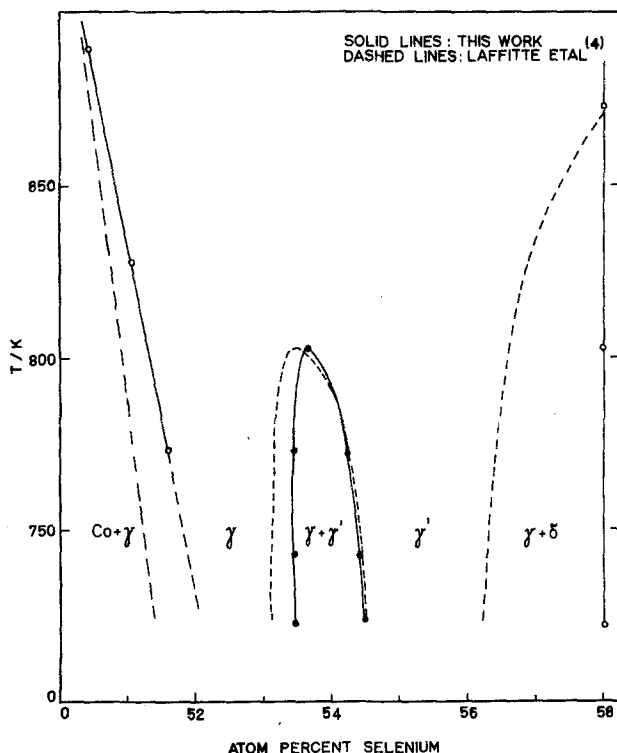


Fig. 3. Phase diagram of Co_{1-x}Se phase field

0.731, the former lost weight (initially 236.485 mg, loss 0.630 mg) while the latter sample gained it (initially 227.650 mg gain 0.380 mg). Thus the a_{Se} in the sample of 0.725 is higher than the corresponding activity in the sample of 0.731.

The X-ray diffraction results of the quenched samples and the linear dependence of the observed *emf* on temperature from 700 to 890 K (curves *d-k* in Fig. 2) clearly established that they all belong to the single homogeneous γ' -alloy phase field. The isopiestic result established the fact that the selenium-rich limit of the γ' -phase cannot exceed

Co/Se = 0.725. The observed fact that E vs. T for the cell with this alloy composition electrode was linear from 700–890 K indicates that the upper phase boundary composition of the γ' -phase between 700 and 890 K is Co/Se \approx 0.725 and is essentially temperature independent in this range.

From the E vs. T plots, it was concluded that the lower phase composition limit of the γ' -phase between 700–890 K is Co/Se = 0.835. Alloys of the compositions Co/Se = 0.850, 0.853, and 0.871 represent a mixture of γ' - and γ -phases below 823 K and probably homogeneous single phase at higher temperatures. Based on the linear E vs. T behaviour over the entire temperature range of measurement and the results of the X-ray examination of the quenched sample of the composition Co/Se = 0.908 it is concluded that this composition is the single phase γ -CoSe alloy.

The partial Co—Se phase diagram thus evaluated is presented in the Fig. 3. For comparison, data of *Laffitte* and *Cerclier*⁴ are also shown. There is agreement between the two sets of measurements with respect to the shape of the phase boundaries and the width of the γ and γ' miscibility gap. However, according to the present investigation all phase boundary compositions need to be shifted towards the Se side. A possible reason for the difference could be, as stated earlier, the increased composition uncertainties due to electrode dissolution in the BaCl₂(s) and CoCl₂(s) eutectic used by them.

Though an upper critical solution temperature and the critical solution composition could not be calculated unambiguously, a temperature of 803 ± 10 K and a composition of Co/Se = 0.866 ± 0.005 was assigned on the basis of this investigation.

The determination of the cobalt-rich phase boundary composition of γ -phase was inconclusive. Alloys of Co/Se = 0.908, 0.927, 0.939, and 0.956 all yielded linear E vs. T plots (Fig. 2c) and were identified to contain only the γ -phase in the quenched samples. But on careful examination it is observed that the E vs. T plots for Co/Se = 0.939 below 773 K and for the Co/Se = 0.956 sample below 828 K, change sign suggesting that the cobalt activity in the alloy co-existing with CoF₂ is higher than the corresponding Co activity existing in the mixture of Co metal and CoF₂(s). This is unacceptable thermodynamically for an equilibrium state situation. A probable explanation is that in these alloy compositions, on thermal cycling, in addition to the Co metal and the γ -CoSe phase, the Co₉Se₈ phase might also be formed resulting in the metastable co-existence of these three solid phases. The slow rates of formation and dissociation of Co₉Se₈ phase at these temperatures may result in the persistence of such a metastable ternary mixture. Thus in these measurements the true equilibrium states were not achieved.

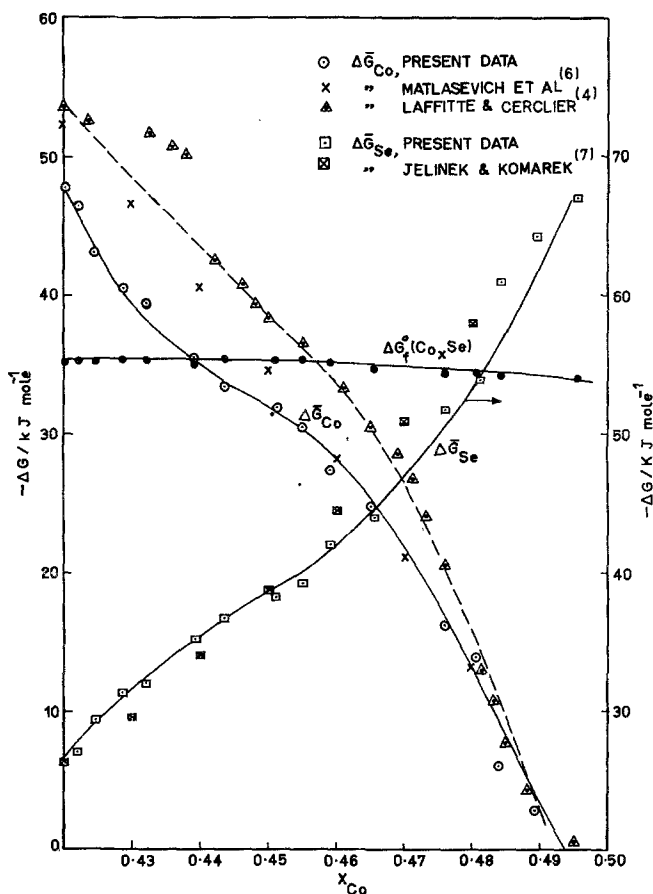


Fig. 4. ΔG vs. X_{Co} for the single phase $Co_{1-x}Se$ alloys at 873 K. $\Delta \bar{G}_{Se}$ right scale

The net reaction of cell I is a virtual transport of Co from the Co—CoF₂ electrode to CoF₂-alloy electrode. Assuming a unit activity for Co in the Co—CoF₂ mixture, the measured *emf* of the cell directly yields a_{Co} and hence $\Delta \bar{G}_{Co}$.

$$\ln a_{Co} = -2FE/RT = \frac{\Delta \bar{G}_{Co}}{RT} \quad (1)$$

The $\Delta \bar{G}_{Co}$ thus calculated at 873 K is plotted in the Fig. 4. The $\Delta \bar{G}_{Co}$ thus evaluated is a monotonic function of the Co mole fraction (X_{Co}) from $X_{Co} = 0.420$ to 0.496 . There is however an inflexion around $X_{Co} =$

= 0.445, i.e., corresponding to an alloy composition of $\text{Co}_{0.802}\text{Se}$. This confirms that there is no measurable miscibility gap in going from monoclinic $\text{Co}_{0.725}\text{Se}$ to hexagonal $\text{Co}_{0.956}\text{Se}$. The different curvature of the plot on either side of the inflexion point suggested different functional dependence of $\Delta \bar{G}_{\text{Co}}$ on X_{Co} for Co_xSe in the two composition regions. In other words, the type of nearest neighbour interaction in the two regions are distinctly different. Neither *Matlasevich et al.*⁵ nor *Laffitte and Cerclier*⁴ have reported this inflexion point (Fig. 4).

The corresponding $\Delta \bar{G}_{\text{Se}}$ were calculated by *Gibbs—Duhem* integration with the help of *Darken's* α -function method and then the ΔG_f^0 of the single phase Co_xSe alloys were computed. These are also presented in Fig. 4. Unlike the two partial molar quantities, ΔG_f^0 was found to be relatively composition independent.

*Laffitte and Cerclier*⁴ have reported more negative values for $\Delta \bar{G}_{\text{Co}}$ for all alloy compositions while the results of *Matlasevich et al.*⁵ (extrapolated from 823 K, their highest temperature of measurement) were intermediate in behaviour. The agreement is better at the cobalt-rich side. The difference in the $\Delta \bar{G}_{\text{Co}}$ values between the present investigation and those of *Laffitte and Cerclier*⁴ increases with the increase of Se content. One probable reason for this difference is that at 873 K, there could have been a film of CoCl_2 and BaCl_2 eutectic formed between the electrolyte and the electrode interface in their experiments. If it was present, it could have affected their *emf* data firstly by reducing the activity of the CoCl_2 from unity and secondly by the increased solubility of the alloy components in the eutectic thus altering the compositions of the alloys. Both these influences would have higher contributions at selenium-rich regions. But an unambiguous analysis is difficult. These complications were absent in the present investigations as no known eutectic or compound formation between CoF_2 and CaF_2 is observed.

Direct comparison with the results of *Jelinek and Komarek*⁷ was not possible. They have measured a_{Se} in the selenium-rich end at temperatures above 873 K. Both their measurements and this investigation covered only a limited composition range, a direct comparison of their measured a_{Se} with the *Gibbs—Duhem* integrated data of the present investigation was difficult. Hence, for an internal consistency check, the activity, a_{Se} for $\text{Co}_{0.724}\text{Se}$ was assumed to be equal to the value reported by *Jelinek and Komarek*⁷ for this alloy and the $\Delta \bar{G}_{\text{Se}}$ for alloys of other compositions were computed by the method of *Darken*. The good agreement (Fig. 4) between the $\Delta \bar{G}_{\text{Se}}$ thus computed and their directly measured ones lends support to the reliability of the data of this investigation at lower temperatures.

$\Delta \bar{S}_{\text{Co}}$ and $\Delta \bar{H}_{\text{Co}}$ presented in Table 2 were calculated from the E vs.

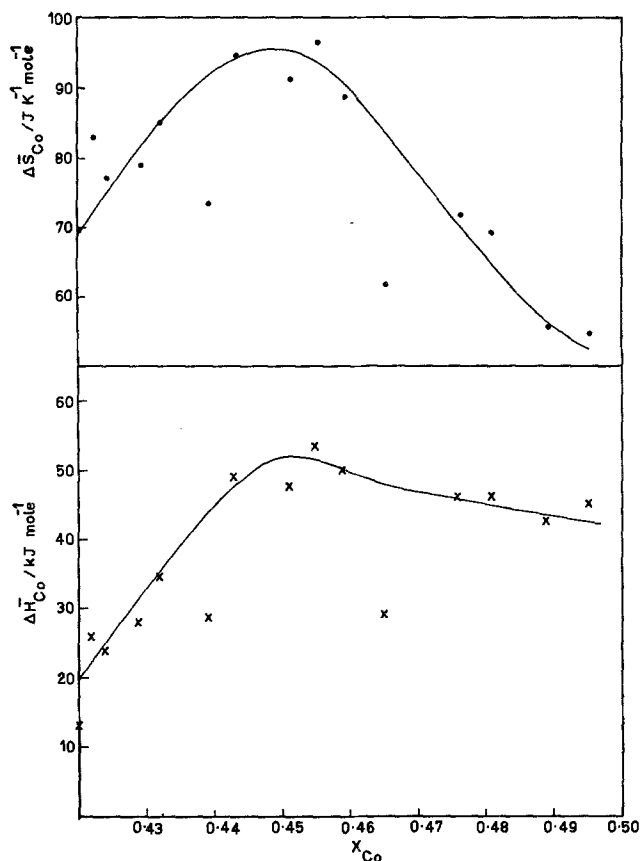
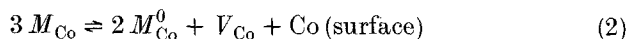


Fig. 5. $\Delta \bar{H}_{\text{Co}}$ and $\Delta \bar{S}_{\text{Co}}$ vs. X_{Co} for the single phase Co_{1-x}Se alloys at 873 K.

T plots for various alloys. Both of these relatively large positive values exhibit (Fig. 5) maxima but the large scatter renders any unambiguous predictions based on these rather uncertain.

Comparison With Defect Models of Co_{1-x}Se

Two models have been proposed to account for the observed wide composition homogeneity of the Co_xSe above the upper critical solution temperature. *Laffitte* and *Cerclier*⁴ proposed the following defect equilibrium as the principal one.



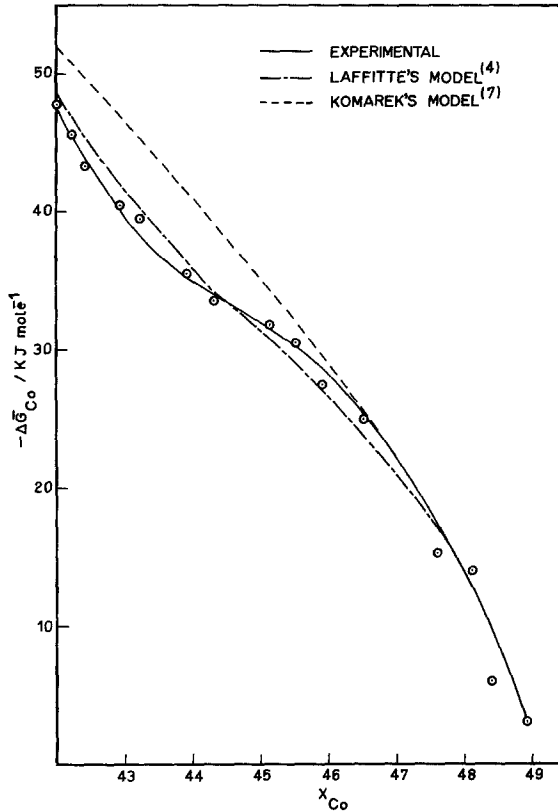


Fig. 6. The comparison of models of *Komarek et al.* and *Laffitte and Cerclier* with the results of this investigation

M_{Co} is the Co atom on the metal sub-lattice, M_{Co}^0 is similar to M_{Co} except it has one d-electron less. V_{Co} is the metal vacancy. They derived the expression (3) for the a_{Co} .

$$\ln a_{\text{Co}} = 3 \ln \frac{1-3\delta}{\delta} + 8 \frac{\epsilon_{V-V}}{RT} \delta + \frac{(g_{V_{\text{Co}}} + 2g_{M_{\text{Co}}^0})}{RT} - \ln 4 \quad (3)$$

where, $\delta = (N_{V_{\text{Co}}})/N$, ϵ_{V-V} = the energy of interaction of one Co vacancy with another, and $(g_{V_{\text{Co}}} + 2g_{M_{\text{Co}}^0})$ is the free enthalpy of formation of the defect pair.

With $\epsilon_{V-V} = 15.2 \text{ kJ}$, the one given by *Cerclier* and *Laffitte*⁴ and the measured a_{Co} in this investigation at $\text{Co}_{0.956}\text{Se}$. the quantity $(g_{V_{\text{Co}}} + 2g_{M_{\text{Co}}^0})$ was calculated at this composition. Employing this

calculated value as constant, the a_{Co} at other compositions were evaluated, Fig. 6 shows these values along with the corresponding a_{Co} measured directly.

Jelinek and *Komarek*⁷ assumed the Co vacancies to be statistically distributed only in (00 1/2) layers of the hexagonal lattice and derived the expression (4) for the absolute activity λ_{Co} .

$$\ln \lambda_{\text{Co}} = \ln \frac{(1 - 6 \Delta N_{\text{Se}})}{8 \Delta N_{\text{Se}}} - \frac{16 E_i}{RT} \left(\frac{\Delta N_{\text{Se}}}{1 + 2 \Delta N_{\text{Se}}} \right) - \left(\ln K + \frac{E_v}{RT} \right) \quad (4)$$

$\Delta N_{\text{Se}} = N_{\text{Se}} - 0.5$, E_i = vacancy—vacancy interaction energy, E_v is the energy of formation of V_{Co} , and K related to the non-configurational entropy.

Assuming the E_i value given by *Jelinek* and *Komarek*⁷ at Co_{0.956}Se and the a_{Co} measured in this study, the term $(\ln K + E_v/RT)$ was evaluated. Then considering this term as composition independent, a_{Co} for other compositions were calculated. The agreement between the a_{Co} thus computed and measured directly was good on the cobalt-rich end in both cases, but not so at selenium rich one. Further neither model accounts for the observed inflexion point. At the present status of theoretical development and the available accuracy of the experimental data, it is not possible to answer which model is more appropriate.

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