Thermodynamic properties of RuSe₂ from 5 to 1500 K

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The heat capacity of RuSe₂ has been measured in the range from 5 to 988 K with adiabatic low- and high-temperature calorimeters. From 882 to 1483 K a drop calorimeter was used to measure enthalpy increments of the compound. Thermodynamic functions have been calculated. Values at 298.15 and 1500 K of the molar heat capacity $C_{p,m}$, standard molar entropy $\Delta_0^T S_m^\circ(T)$, and standard molar function $\Phi_m^\circ(T, 0)$ are 69.87, 80.084, 36.407 $J \cdot K^{-1} \cdot mol^{-1}$, and 90.45, 205.77, 132.86 $J \cdot K^{-1} \cdot mol^{-1}$, respectively. Decomposition pressures for the reaction: RuSe₂(s) = Ru(s) + Se₂(g), have been determined between 1270 and 1480 K by means of a Bodenstein-type silica-glass manometer. The results obtained by the static measurements extend the torsion-effusion measurements accomplished by Murray and Heyding at lower temperatures. The standard molar enthalpy formation for RuSe₂ from Ru(s) and Se(s, hex) at 298.15 K is $-(162.07 \pm 0.72) \, kJ \cdot mol^{-1}$ according to the third-law treatment. The uncertainty given is one standard deviation.

1. Introduction

In earlier communications[1,2] the thermodynamic properties of RuTe₂ and RuS₂ have been studied by means of drop calorimetry and tensimetry. This paper concerns RuSe₂, which together with RuTe₂ and RuS₂ are the only binary solid compounds formed by ruthenium with sulfur, selenium, or tellurium. They are of the pyrite type, but RuTe₂ can under controlled conditions also be obtained as a marcasite-type compound.[3]

In a study by Murray and Heyding,[4] the decomposition pressures of RuSe₂ were measured using the torsion-effusion technique. By means of estimated heat capacities and second-law treatment of the obtained pressures, these authors found a standard molar enthalpy of formation $-(179.5 \pm 14.6) \, kJ \cdot mol^{-1}$ and standard molar entropy 64.9 $J \cdot K^{-1} \cdot mol^{-1}$ at 298.15 K for the compound.

In the present study the heat capacities have been experimentally determined and the decomposition pressures have been measured using a static method.

2. Experimental

The ruthenium diselenide used for the adiabatic low- and high-temperature calorimetric determinations was made from ruthenium powder of purity 99.98 mass per cent from Falconbridge Nikkelverk, Kristiansand, Norway, and selenium of purity 99.998 mass per cent from Boliden Gruvaktiebolag, Sweden. Stoichiometric amounts of the components were weighed into a silica ampoule. After sealing under vacuum the ampoule was gradually heated to 1300 K and kept at this temperature for 24 h. The reaction did not go to completion, and the ampoule was reheated to 1123 K for 4 d, then kept at 1023 K for 7 d, and slowly cooled to room temperature. Unreacted Se and Ru were still present in the ampoule corresponding to mole fractions 0.04743 and 0.02371, respectively, as determined from the enthalpy of fusion of the selenium, see table 5.

The ruthenium diselenide prepared for the drop calorimeter and the tensimetric measurements contained ruthenium of purity 99.99 mass per cent from Johnson Matthey Chemicals and the same selenium as above. Stoichiometric amounts of the components were gradually heated in an evacuated ampoule to 1300 K and kept there for a week, then slowly cooled to room temperature over several days. A small amount of the components did not react. The free selenium was isolated and weighed. The gross composition of the sample without the free selenium was calculated to correspond to $(0.00565Ru + 0.99435RuSe_2) = RuSe_{1.9887}$.

CALORIMETRIC TECHNIQUE

5 to 350 K, *University of Michigan.* The heat capacity of the compound was measured in the Mark II adiabatic calorimetric cryostat described elsewhere.[5] A gold-plated copper calorimeter (W-52, which incorporates a gold-gasketed screw closure and copper vanes) with a volume of 59 cm^3 and a mass of 33.2 g was used. Helium gas was added to the sample space (5.5 kPa at 300 K) to enhance thermal equilibration. The calorimeter was surrounded by a shield system provided with automatic temperature control. Temperatures were measured with a capsule-type strain-free platinum resistance thermometer (laboratory designation A-5) located in a central re-entrant well in the calorimeter. The platinum resistance thermometer had been calibrated by the U.S. National Bureau of Standards. Temperatures are judged to correspond to IPTS-68 within 0.03 K from 4 to 350 K. All masses, electric potentials, resistances, *etc.*, were measured with reference to instruments calibrated by the U.S. National Bureau of Standards.

The heat capacity of the empty calorimeter was determined in a separate series of experiments. It represented less than 26 per cent of the total. Small adjustments were applied for temperature excursions of the shields from the calorimeter temperature and for "zero drift" of the calorimeter temperature. Further small corrections were applied for differences in masses of the gold gasket, helium gas, and Apiezon-T grease. The mass of sample used was 171.64 g. Buoyancy correction was made on the basis of a crystallographic density of 8.23 g·cm^{-3}.

300 to 1000 K, *University of Oslo.* The calorimetric apparatus and measuring technique have been described.[6] The calorimeter was intermittently heated and

surrounded by electrically heated and electronically controlled adiabatic shields. The substance was enclosed in an evacuated and sealed silica-glass tube of about 50 cm^3 volume, fitted into the silver calorimeter. A central well in the tube served for the heater and platinum resistance thermometer. Calibration of the thermometer was carried out locally at the ice, steam, tin, zinc, and antimony points. Temperatures are judged to correspond to IPTS-68 within 0.05 K from 300 to 900 K and within 0.1 K above. The heat capacity of the empty calorimeter was determined in a separate series of experiments. It represented about 65 per cent of the total after correction for differences in mass of the silica-glass containers. The mass of sample used was 173.87 g.

880 to 1483 K, *University of Oslo*. Enthalpy increments relative to 298.15 K were measured in an adiabatic drop calorimeter operating in air. Details of the construction have been described.[7]

The enthalpy determinations were performed on 9.4155 g of RuSe$_{1.9887}$ sealed in a silica ampoule of mass 3.0730 g which was placed in a container of (Pt + 10 mass per cent Rh) of mass 26.0260 g. Separate determinations were performed on an evacuated empty ampoule of the same mass as the sample ampoule. The enthalpy of the sample represented about 28 per cent of the total. The temperature in the furnace used to heat the ampoules was measured with a Pt-to-(Pt + 10 mass per cent Rh) thermocouple. The uncertainty in the temperature readings is ± 0.7 K below 1000 K and ± 1.2 K above this temperature.

The decomposition pressures were measured with a silica-glass spiral gauge of Bodenstein type. The experimental arrangement follows mainly the description given by Biltz and Juza.[8] The furnace temperature was kept within ± 0.5 K of the set-point temperature by means of a Eurotherm LP96-PID controller. The sample temperature was measured by means of a calibrated Pt-to-(Pt + 10 mass per cent Rh) thermocouple with an uncertainty of ± 1.2 K. The sample container was charged with (0.5567 g of RuSe$_{1.9887}$ + 0.3046 g of Se) which gave a gross composition RuSe$_{3.777}$. Thirteen series of pressure measurements with decreasing selenium contents were performed with an uncertainty of ± 0.13 kPa in the readings. Series 1 to 3 were discarded on account of impurity tension.

The lattice constant of RuSe$_2$ as a function of temperature was determined with a Guinier-Simon camera in the temperature interval 93 to 293 K with an uncertainty of ± 10 K, and with a 19 cm diameter Unicam high-temperature camera in the temperature interval 298 to 1273 K with an uncertainty of ± 3 K. The lattice constants from the Unicam camera were calculated from back reflections and extrapolated to $\theta = \pi/2$ by the Nelson-Riley method.

3. Selenium vapour

The thermodynamic functions for the Se$_2$(g) molecule were calculated by standard methods[9] from the molecular constants,[10-13] adjusted to the natural relative molecular mass, see table 1. The excitation energy for the a$^1\Delta_g$ state was taken from Drowart et al.[14,15] and the vibrational and rotational constants for this state were estimated by comparison with the corresponding state for the diatomic sulphur

TABLE 1. Molecular constants for $Se_2(g)$, $M = 157.92$ g·mol^{-1}

State	g	T_e/cm^{-1}	ω_e/cm^{-1}	$x_e\omega_e/cm^{-1}$	B_e/cm^{-1}	$10^3\alpha_e/cm^{-1}$
$X^3\Sigma0_g^+$	1	0	387.69	0.9904	0.09100	0.299
$X^3\Sigma1_g$	2	511.0	389.52	0.9757	0.09117	0.289
$a^1\Delta_g$	2	(4500)	(370)	—	(0.09)	—
$b^1\Sigma_g^+$	1	7957.1	357.21	1.1086	0.08875	0.338

TABLE 2. Thermodynamic function values for $Se_2(g)$. $M = 157.92$ g·mol^{-1}; $R = 8.3143$ J·K^{-1}·mol^{-1};

$$\Phi_m^\circ(T, T') \stackrel{\text{def}}{=} \Delta_0^T S_m^\circ(T) - \Delta_{T'}^T H_m^\circ(T)/T;\ T' = 298.15\ \text{K}$$

$\dfrac{T}{K}$	$\dfrac{C_{p,m}^\circ(T)}{R}$	$\dfrac{\Delta_{T'}^T H_m^\circ(T)}{R \cdot K}$	$\dfrac{\Phi_m^\circ(T, T')}{R}$	$\dfrac{\Delta_0^T S_m^\circ(T)}{R}$	$\dfrac{T}{K}$	$\dfrac{C_{p,m}^\circ(T)}{R}$	$\dfrac{\Delta_{T'}^T H_m^\circ(T)}{R \cdot K}$	$\dfrac{\Phi_m^\circ(T, T')}{R}$	$\dfrac{\Delta_0^T S_m^\circ(T)}{R}$
298.15	5.0161	0	29.7404	29.7404	900	4.7054	2910.5	31.8886	35.1225
300	5.0175	9.3	29.7406	29.7715	1000	4.7065	3380.9	32.2372	35.6182
400	4.9844	510.7	29.9376	31.2143	1100	4.7178	3852.2	32.5652	36.0612
500	4.8868	1004.3	30.3075	32.3160	1200	4.7359	4324.7	32.8744	36.4785
600	4.8051	1488.6	30.7183	33.1994	1300	4.7585	4799.4	33.1665	36.8584
700	4.7500	1966.3	31.1269	33.9356	1400	4.7833	5276.6	33.4430	37.2119
800	4.7184	2439.4	31.5183	34.5677	1500	4.8091	5756.1	33.7054	37.5428

molecule.[16] Since the molecular parameters for the $a^1\Delta_g$ state in the $Se_2(g)$ molecule have not yet been experimentally verified, the calculations of the thermodynamic functions for the molecule are limited to 1500 K, where the contribution from this state is small, see table 2. The standard molar enthalpy of formation was calculated by the third-law method from pressure measurements,[17-19] performed independently on the molecule: $\Delta_f H_m^\circ(Se_2, g, 298.15\ K) = (144.197 \pm 0.410)$ kJ·mol^{-1}. Experimentally, one measures the total vapour pressure in the decomposition reaction for $RuSe_2$. Therefore the equilibrium constants between the Se_2 molecule and the other different gaseous species of selenium molecules must be known so as to obtain the partial pressures of the Se_2 molecule referred to in the decomposition equation. The equilibrium constants as function of temperature for the six gaseous reactions:

$$Se_i(g) = (i/2)Se_2(g),\quad (i = 3\ \text{to}\ 8),$$
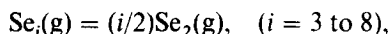
are given in the form:

$$\lg(K_i/\text{kPa}^{\frac{1}{2}i-1}) = -A(K/T) - B\lg(T/K)$$
$$+ C(T/K) + D(T/K)^{3/2} + E(K/T)^2 + F,\quad (i = 3\ \text{to}\ 8).$$

The six terms in the logarithmic polynomial originate from the four-term $C_{p,m}$ polynomial used for the $Se_2(g)$ molecule:

$$C_{p,m}(Se_2, g) = a_1 + a_2(T/K) + a_3(K/T)^2 + a_4(T/K)^{3/2}.$$

Since the $C_{p,m}(Se_2, g)$ values have a minimum at about 950 K, at least a three-term polynomial should be applied. But the four terms used give a better fit and were

therefore chosen. For the gaseous species Se_i ($i = 3$ to 8), estimated two-term expressions[20] are available:

$$C_{p,m}(Se_i, g, i = 3 \text{ to } 8) = b_1 + b_2(T/K).$$

For each of the six gaseous reactions the heat capacity was integrated to obtain the change in the enthalpy and the entropy. The integration constants were determined by means of the standard enthalpy of formation and standard entropy for the molecules, estimated[20] for $Se_i(g)$ ($i = 3$ to 8). The equilibrium constants are finally given by the equation: $-RT \ln K_r^\circ = (\Delta_r H_m^\circ - T\Delta_r S_m^\circ)$. There are six equations with six i.e. 36 coefficients to be determined by the least-squares programme in which the first calculated values are used as starting values. 170 experimentally obtained saturated vapour pressures[19,21-29] were then compared with calculated total pressures at the same temperatures. Calculated values of $p(Se_2)$ for the reaction: $2Se(s \text{ or } l) = Se_2(g)$, were obtained from a third-law treatment:

$$p(Se_2)/p^\circ = \exp\{-\Delta_f H_m^\circ(Se_2, g, 298.15 \text{ K})/RT\}\exp\{\Delta_r \Phi_m^\circ(T, 298.15 \text{ K})/R\},$$

with $p^\circ = 101.325$ kPa, and interpolated values of Φ_m° from heat-capacities[30,31] for solid and liquid selenium, see table 3. The sum p of the partial pressures of the

TABLE 3. The function $\Phi_m^\circ(T, T')$ for $Se(s \text{ or } l)$ for $T' = 298.15$ K

T/K	$\Phi_m^\circ(T, T')/R$	T/K	$\Phi_m^\circ(T, T')/R$	T/K	$\Phi_m^\circ(T, T')/R$	T/K	$\Phi_m^\circ(T, T')/R$
298.15	5.0840	500	5.4540	800	6.8897	1000	(7.6384)
400	5.2043	600	5.9823	900	7.2801	1060	(7.8402)
494.33	5.4222	700	6.4594	958.00	7.4916		

different gaseous molecules is expressed by means of the calculated $p(Se_2)$ and the calculated equilibrium constants:

$$p(\text{calc.}) = p(Se_2) + \sum_{i=3}^{8} \{p(Se_2)\}^{i/2}/K_i\}.$$

The sum of the squared difference $\{p - p(\text{calc.})\}$ was minimized by successively changing the 36 coefficients. With 170 pressures from 458 and 983 K the overall average relative deviation from the equations is 8.5 per cent. The coefficients are given in table 4.

TABLE 4. Equilibrium constants for the reaction $Se_i(g) = (i/2)Se_2(g)$: $\lg(K_i/kPa^{1-i}) = -A(K/T) - B \lg(T/K) + C(T/K) + D(T/K)^{3/2} + E(K/T)^2 + F$

i	A	B	$10^4 C$	$10^3 D$	E	F
1	−34437.4	−0.039653	8.02732	7.28711	14372.8	−11.6366
3	1720.0	0.77788	7.09690	1.00140	566.5	2.6284
4	6678.3	0.17431	7.90080	0.99936	6820.6	10.8639
5	10616.8	0.13517	8.46816	1.01672	25891.8	14.0417
6	15369.1	1.07755	−10.26210	0.003849	29958.5	23.0651
7	17595.3	0.35801	−0.46582	−0.11910	33388.4	27.6585
8	21666.8	1.54055	13.14600	−0.13071	36834.3	36.6913

If one reduces the six-term polynomial to a three-term polynomial which is often used:

$$\lg K^\circ = -C_1(K/T) + C_2 \lg(T/K) + C_3,$$

the overall average relative deviation from the equations was found to be 31.0 per cent, which reflects the difficulty in accommodating the large span of vapour pressures to a less complex equation.

Table 4 also contains the equilibrium-constant coefficients for the dissociation of the $Se_2(g)$ molecule based on $D_m^\circ(Se_2, g, 0) = 329071 \text{ J} \cdot \text{mol}^{-1}$.[32]

4. Results and discussion

The experimental heat capacities from low- and high temperature ranges, corrected for free Ru and Se, are presented in table 5 and displayed in figure 1. The enthalpy increments relative to 298.15 K, obtained from the drop calorimetry, corrected for free Ru content, are presented in table 6. A comparison of smoothed enthalpies in the overlap region is given in table 7.

The heat capacities from the low- and high temperature series were fitted to polynomials of the form: $C_{p,m} = \{a_1 + a_2(T/K) + a_3(K/T)^2 + \ldots + a_i(T/K)^{i-1}\}$ by the method of least squares, and integrated to yield values of thermodynamic functions at selected temperatures. To combine the high-temperature heat capacities

TABLE 5. Heat capacity of $RuSe_2$, $M = 258.99 \text{ g} \cdot \text{mol}^{-1}$

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
				Low-temperature results (Ann Arbor)							
Series I		255.78	8.0799	Series II		152.55	6.47739	14.50	0.02899	34.03	0.4004
155.33	6.5561	269.42	8.1943	67.48	2.3475	162.70	6.73731	16.03	0.03861	37.79	0.5486
166.80	6.7373	283.01	8.3002	75.96	2.9205	Series III		17.57	0.05003	42.90	0.7891
178.88	7.0896	296.96	8.4084	84.24	3.4729	5.68	0.00261	19.25	0.0654	48.52	1.0975
191.27	7.3151	311.24	8.5251	94.13	4.0697	7.24	0.00505	21.11	0.0868	53.62	1.4126
203.93	7.5138	325.41	8.5768	106.27	4.7145	8.73	0.00838	23.25	0.1168	58.84	1.7563
216.61	7.6763	337.20	8.6273	119.09	5.3110	10.42	0.01174	25.28	0.1610	64.43	2.1393
229.38	7.8298	345.89	8.6237	130.92	5.7847	11.75	0.01636	28.07	0.2179		
242.39	7.9622			142.00	6.16480	13.06	0.02117	30.90	0.2971		
				High-temperature results (Oslo)							
Series I		428.20	8.8185	573.56	9.1072	763.81	9.33572	930.49	9.5306	730.82	9.4392
308.15	8.3278	444.21	8.8258	590.28	9.1553	781.83	9.36459	949.50	9.5582	748.38	9.4464
320.37	8.3639	460.29	8.8462	607.07	9.1974	800.00	9.35256	968.70	9.6376	766.07	9.4319
332.59	8.4950	476.46	8.9304	623.94	9.2203	818.31	9.34534	988.04	9.7206	783.88	9.4837
348.56	8.5864	492.03	11.331[a]	640.88	9.2864	836.74	9.34053	Series III			
364.49	8.6441	507.56	8.9545	657.90	9.3465	855.29	9.38022	661.61	9.3129		
380.44	8.6682	523.99	9.0002	675.02	9.33933	873.96	9.46081	678.76	9.3213		
396.34	8.7704	540.47	9.0459	Series II		892.71	9.50411	696.01	9.3658		
412.24	8.7801	556.96	9.1096	745.93	9.29844	911.56	9.52095	713.37	9.3393		

[a] Includes enthalpy of fusion of selenium present; $n = \Delta H/\Delta_{fus}H_m = 292.2 \text{ J}/6159 \text{ J} \cdot \text{mol}^{-1} = 0.04743$ mol of free Se.
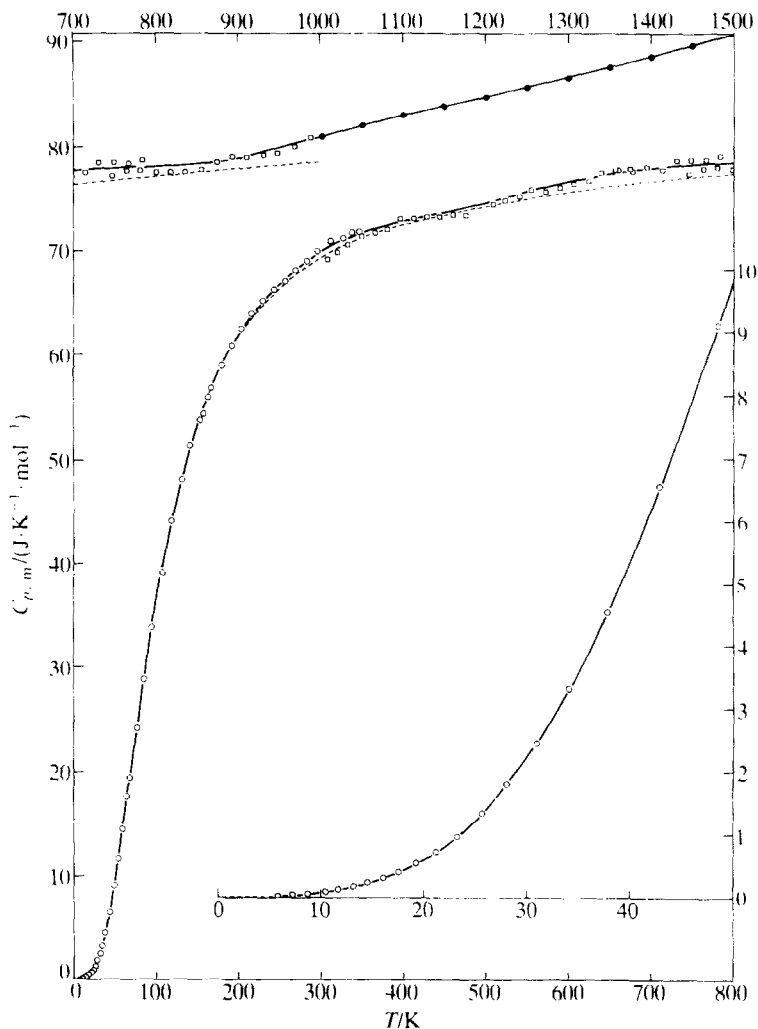
FIGURE 1. Molar heat capacities of RuSe$_2$. ◯, From University of Michigan; □, from University of Oslo; ●, calculated from drop-calorimetry, University of Oslo; ————, least-squares line; — — — — , calculated $C_{p,m}$.

with the drop-calorimetry results, the calculated enthalpy increments from the high-temperature heat capacities in the range 298 to 1000 K, together with the enthalpy increments from the drop calorimetry, were fitted to the polynomial:

$$\Delta_{298.15\,K}^{T}H_m^\circ(T) = A(T/K) + B(T/K)^2 + C(K/T) + D(T/K)^{5/2} + E, \qquad (1)$$

by the method of least squares, with the restrictions in the calculation that $C_{p,m}(298.15\ K) = 69.87\ J \cdot K^{-1} \cdot mol^{-1}$ and $\Delta_{298.15\,K}^{T}H_m^\circ(T) = 0$ at $T = 298.15$ K. The heat capacities derived from this polynomial in the temperature interval 1000 to 1500 K were combined with the experimental heat capacities over the range 713 to

TABLE 6. Enthalpy increments relative to 298.15 K obtained by drop-calorimetry. $M = 258.99 \text{ g} \cdot \text{mol}^{-1}$; $T' = 298.15$ K

$\dfrac{T}{K}$	$\dfrac{\Delta_{T'}^{T} H_m^{\circ}(T)}{R \cdot K}$	Δ^a	$\dfrac{T}{K}$	$\dfrac{\Delta_{T'}^{T} H_m^{\circ}(T)}{R \cdot K}$	Δ^a	$\dfrac{T}{K}$	$\dfrac{\Delta_{T'}^{T} H_m^{\circ}(T)}{R \cdot K}$	Δ^a	$\dfrac{T}{K}$	$\dfrac{\Delta_{T'}^{T} H_m^{\circ}(T)}{R \cdot K}$	Δ^a
882.1	5354.1	0.22	1076.8	7299.4	1.05	1178.6	8200.1	0.44	1379.8	10391	0.75
882.2	5358.8	0.29	1077.8	7240.7	0.10	1180.0	8206.2	0.53	1380.5	10334	0.61
979.3	6265.7	0.12	1077.8	7189.3	0.61	1280.9	9278.4	0.48	1381.1	10391	0.12
979.4	6264.3	0.16	1078.1	7189.1	0.65	1281.1	9324.9	0.22	1381.1	10317	0.10
979.4	6258.0	0.26	1178.3	8230.9	0.02	1281.1	9289.4	0.10	1483.7	11410	0.21
979.6	6243.5	0.52	1178.6	8205.3	0.37	1281.7	9307.0	0.00			

^{a} Percentage relative deviation from equation (1).

TABLE 7. Comparison of results accomplished by adiabatic and drop-calorimetry in the region 900 to 1000 K; $T' = 298.15$ K

Calorimeter	$\dfrac{T}{K}$	$\dfrac{\Delta_{T'}^{T} H_m^{\circ}(T)}{R \cdot K}$	Calorimeter	$\dfrac{T}{K}$	$\dfrac{\Delta_{T'}^{T} H_m^{\circ}(T)}{R \cdot K}$	Calorimeter	$\dfrac{T}{K}$	$\dfrac{\Delta_{T'}^{T} H_m^{\circ}(T)}{R \cdot K}$
Drop	900	5.512	Drop	950	5.991	Drop	1000	6.473
Adiabatic	900	5.474	Adiabatic	950	5.950	Adiabatic	1000	6.434

988 K and again fitted to a polynomial by the method of least squares to give the final values of the thermodynamic functions in the highest temperature range.

The thermodynamic functions from 5 to 1500 K are presented in table 8. By means of propagation-of-error calculations, based on variances and covariances from the least-squares treatment of the polynomials, the standard deviations for the derived functions are given in table 9. These values comprise the standard deviations of the fit of the polynomials for the full and empty ampoule experiments. The polynomials were fitted to $C_{p,m}$ values over restricted temperature intervals. To avoid discontinuities in the function values, large overlap regions had to be applied. The standard deviations in the temperature interval 60 to 298 K therefore have higher values than expected from the experimental results.

Table 10 presents the Se_2 partial pressures of $RuSe_2$ with and without excess selenium. The decomposition pressures of the compound can be formulated according to the reaction:

$$RuSe_2(s) = Ru(s) + Se_2(g),$$

which was applied in the third- and second-law treatment of the pressures.

In the third-law calculation of the standard molar enthalpy of formation for $RuSe_2$, the expression based on the reference temperature 298.15 K was used:[†]

$$\Delta_f H_m^{\circ}(RuSe_2, 298.15 \text{ K}) = \Delta_f H_m^{\circ}(Se_2, \text{g}, 298.15 \text{ K})$$
$$+ RT \ln\{p(Se_2, \text{g})/p^{\circ}\} - T[\{\Phi_m^{\circ}(T, 298.15 \text{ K})\}(Ru)$$
$$+ \{\Phi_m^{\circ}(T, 298.15 \text{ K})\}(Se_2, \text{g}) - \{\Phi_m^{\circ}(T, 298.15 \text{ K})\}(RuSe_2)].$$

[†] $p^{\circ} = 101325$ Pa.

TABLE 8. Thermodynamic functions for RuSe$_2$; $M = 258.99$ g·mol^{-1}; $T' = 298.15$ K

$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{\Delta_0^T H_m^\circ(T)}{R \cdot K}$	$\dfrac{\Delta_0^T S_m^\circ(T)}{R}$	$\dfrac{\Phi_m^\circ(T,0)}{R}$	$\dfrac{T}{K}$	$\dfrac{C_{p,m}}{R}$	$\dfrac{\Delta_0^T H_m^\circ(T)}{R \cdot K}$	$\dfrac{\Delta_0^T S_m^\circ(T)}{R}$	$\dfrac{\Phi_m^\circ(T,0)}{R}$	$\dfrac{\Phi_m^\circ(T,T')}{R}$
5	0.00180	0.0023	0.00060	0.00014	298.15	8.404	1566.2	9.6321	4.3788	9.6321
10	0.0111	0.0313	0.00427	0.00113	300	8.413	1581.7	9.6840	4.4113	9.6316
15	0.0315	0.1312	0.01209	0.00334	350	8.612	2007.9	10.9974	5.2605	9.7350
20	0.0735	0.3819	0.0262	0.00713	400	8.738	2441.8	12.1550	6.0514	9.9670
25	0.1496	0.9230	0.0500	0.01315	450	8.850	2881.4	13.1917	6.7883	10.269
30	0.2694	1.9513	0.0872	0.02219	500	8.964	3326.8	14.1299	7.4763	10.609
40	0.6479	6.3882	0.2123	0.05257	550	9.080	3777.9	14.9898	8.1207	10.968
50	1.1861	15.442	0.4121	0.1032	600	9.189	4234.6	15.7836	8.7267	11.337
60	1.8360	30.487	0.6846	0.1764	650	9.280	4696.5	16.5233	9.2983	11.708
70	2.5246	52.285	1.0192	0.2723	700	9.347	5162.3	17.2137	9.8394	12.077
80	3.1934	80.902	1.4004	0.3891	750	9.385	5630.7	17.8596	10.353	12.441
90	3.8187	116.00	1.8131	0.5242	800	9.403	6100.5	18.4670	10.841	12.798
100	4.3895	157.09	2.2454	0.6745	850	9.416	6571.0	19.0371	11.307	13.150
110	4.9019	203.60	2.6883	0.8374	900	9.492	7043.5	19.5771	11.751	13.491
120	5.3558	254.93	3.1347	1.0102	950	9.594	7520.7	20.0931	12.177	13.826
130	5.7542	310.53	3.5795	1.1908	1000	9.713	8003.2	20.5886	12.586	14.152
140	6.1019	369.84	4.0190	1.3771	1050	9.842	8492.1	21.0649	12.978	14.469
150	6.4055	432.42	4.4505	1.5677	1100	9.972	8987.5	21.5256	13.355	14.779
160	6.6713	497.83	4.8726	1.7611	1150	10.096	9489.2	21.9718	13.721	15.082
170	6.9053	565.74	5.2843	1.9563	1200	10.211	9997.0	22.4036	14.073	15.378
180	7.1124	635.86	5.6849	2.1523	1250	10.316	10510.2	22.8233	14.415	15.668
190	7.2957	707.91	6.0745	2.3486	1300	10.412	11028.5	23.2299	14.746	15.951
200	7.4575	781.70	6.4529	2.5444	1350	10.505	11551.5	23.6244	15.068	16.227
220	7.7240	933.62	7.1767	2.9329	1400	10.603	12079.2	24.0080	15.381	16.499
240	7.9326	1090.3	7.8580	3.3153	1450	10.722	12612.2	24.3881	15.684	16.764
260	8.1147	1250.7	8.5003	3.6897	1500	10.879	13152.0	24.7489	15.980	17.025
280	8.2839	1414.8	9.1079	4.0552						

For Ru(s) the heat-capacity equation derived by Kelley[33] $C_{p,m}/(J \cdot K^{-1} \cdot mol^{-1}) = 21.966 + 6.276 \times 10^{-3}(T/K)$ has been assumed valid up to 1480 K since there is no allotropy[34] in the metal. For the entropy at 298.15 K the value $S_m^\circ(Ru) = (28.53 \pm 0.21)$ J·K^{-1}·mol^{-1} was taken from Clusius and Piesbergen.[34] In the analysis of the third-law results a procedure for detecting outlying[35-38] observations was applied with a significance level of 5 per cent.

TABLE 9. The standard deviations in the thermodynamic function values for RuSe$_2$

T/K [a]	5 to 67	48 to 348	255 to 988	713 to 1500
Number of terms in $C_{p,m}$ polynomial	10	18	6	6
T/K [b]	5 to 60	60 to 298	298 to 1000	1000 to 1500
$C_{p,m}/R$	0.00066	0.0426	0.0467	0.166
$\Delta_0^{\langle T \rangle} H_m^\circ(T)/(R \cdot K)$	0.0088	3.406	9.55	41.5
$\Delta_0^{\langle T \rangle} S_m^\circ(T)/R$	0.0130	0.0284	0.0342	0.077
$\Phi_m^\circ(T,0)/R$	0.00112	0.0165	0.0182	0.0409

[a] The temperature intervals correspond to the $C_{p,m}$ values applied in the polynomials.
[b] The temperature intervals correspond to the $C_{p,m}$ values calculated from the polynomials and given in table 8.

TABLE 10. Partial Se₂(g) pressure of RuSe₂ with and without excess selenium

Column pair 1

T/K	$p(\mathrm{Se_2})/\mathrm{kPa}$
Series 4: RuSe$_{2.709}$	
794.7	1.665
806.0	2.107
817.0	2.609
827.6	3.244
838.2	4.001
848.7	4.894
858.2	5.834
868.4	6.961
878.7	8.360
888.7	9.928
907.6	13.66
926.3	17.32
944.4	21.15
878.5	8.407
858.2	5.748
838.4	3.958
817.0	2.657
795.2	1.636
773.7	1.025
751.2	0.5931
728.7	0.3326
708.4	0.1976
Series 5: RuSe$_{2.424}$	
705.5	0.1522
728.4	0.3104
750.5	0.5652
764.7	0.8098
773.2	0.9936

Column pair 2

T/K	$p(\mathrm{Se_2})/\mathrm{kPa}$
707.8	0.1734
738.1	0.3896
764.7	0.7887
806.0	2.089
827.6	3.267
848.7	4.870
867.9	6.893
888.7	9.857
907.4	13.28
926.2	17.78
944.9	23.38
944.9	23.22
878.4	8.388
837.9	3.926
795.2	1.670
751.3	0.5608
708.9	0.1639
Series 6: RuSe$_{2.016}$	
1271.4	0.1658
1296.8	0.3008
1322.2	0.5414
1348.7	0.9663
1372.1	1.690
1398.5	2.719
1422.1	3.953

Column pair 3

T/K	$p(\mathrm{Se_2})/\mathrm{kPa}$
1447.9	5.207
Series 7: RuSe$_{2.003}$	
1347.6	0.9795
1373.8	1.675
1386.2	2.117
1397.7	2.582
Series 8: RuSe$_{1.993}$	
1272.7[a]	0.2721
1297.7	0.3611
1321.8	0.6251
1347.5	1.009
1372.5	1.726
1385.2	2.197
1398.0	2.747
1410.3	3.488
1422.2	4.276
1435.1	5.345
1447.7	6.588
1460.5	8.057
1473.2	9.910
Series 9: RuSe$_{1.987}$	
1270.8[a]	0.3153
1297.1	0.4134
1309.5	0.4997
1320.0	0.6394
1335.2	0.8180
1347.8	1.048

Column pair 4

T/K	$p(\mathrm{Se_2})/\mathrm{kPa}$
1359.7	1.373
1372.5	1.734
1378.6	1.943
1384.8	2.159
1391.3	2.422
1397.7	2.731
1404.1	3.044
1410.2	3.402
1416.2	3.817
1422.6	4.234
1428.8	4.691
1435.1	5.253
1441.1	5.802
1446.1	6.485
1454.1	7.181
1460.3	7.957
1467.0	8.825
1473.2	9.770
Series 10: RuSe$_{1.963}$	
1321.3[a]	0.3728
1333.8[a]	0.3871
1346.4[a]	0.7960
1358.6[a]	1.089
1371.0[a]	1.337
1377.5[a]	1.465
1384.6[a]	1.868
1389.5	2.153

Column pair 5

T/K	$p(\mathrm{Se_2})/\mathrm{kPa}$
1396.0	2.463
1402.0	2.811
1408.1[a]	2.816
1414.6[a]	3.256
1420.7	3.675
1426.9	4.117
1433.5	4.714
1439.6	5.289
1446.2	5.780
1452.5	6.564
1457.4	7.495
1458.5	7.795
1464.5	8.204
1470.5	8.978
Series 11: RuSe$_{1.953}$	
1332.3[a]	0.5898
1344.9[a]	0.8806
1357.7	1.190
1370.1	1.530
1376.4	1.736
1382.5	1.927
1388.7	2.198
1395.2	2.525
1401.5	2.809
1407.5	3.183
1413.7	3.547
1420.2	3.969

Column pair 6

T/K	$p(\mathrm{Se_2})/\mathrm{kPa}$
1426.3	4.418
1433.5	4.938
1438.7	5.517
1445.2	6.076
1451.2	6.746
1457.3	7.534
1463.5	8.311
1470.0	9.197
Series 12: RuSe$_{1.892}$	
1320.9[a]	0.4174
1331.1[a]	0.5586
1345.3[a]	0.9055
1357.5	1.167
1369.9	1.568
1375.9	1.827
1382.1	2.007
1388.6	2.265
1394.5	2.546
1400.8	2.870
1407.4	3.179
1413.8	3.581
1419.7	3.865
1426.1	4.406
1432.3	4.956
1438.3	5.515
1445.5	6.147
1457.7	6.822

Column pair 7

T/K	$p(\mathrm{Se_2})/\mathrm{kPa}$
1458.3	7.536
1464.7	8.340
1470.4	9.302
Series 13: RuSe$_{1.810}$	
1319.8[a]	0.4618
1332.8[a]	0.6081
1344.9[a]	0.8247
1357.6[a]	1.125
1369.2	1.530
1375.6	1.786
1381.9	1.988
1388.2	2.211
1394.8	2.528
1400.7	2.818
1406.8	3.133
1413.1	3.536
1419.1	3.944
1425.9	4.369
1431.8	4.902
1438.1	5.480
1444.7	6.074
1450.7	6.735
1456.6	7.469
1463.1	8.287
1469.4	9.189
1479.6	10.19

[a] Rejected during the third- and second-law analysis.

Of the 122 pressure measurements in the two-phase region series 8 to 13, 20 were rejected during the analysis which then gave as a result $-(162.07\pm0.72)\,\text{kJ}\cdot\text{mol}^{-1}$ for the standard molar enthalpy of formation at 298.15 K.

In the second-law treatment the same 20 pressures were deleted. The Σ-plot procedure gave $-(161.76\pm1.13)\,\text{kJ}\cdot\text{mol}^{-1}$ for the standard molar enthalpy of formation and $(80.0\pm1.1)\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the standard molar entropy at 298.15 K. The uncertainties given are standard deviations of single measurements.

HOMOGENEITY RANGE

The vapour-pressure measurements for samples with excess selenium show a break at 776 K, see figure 2, where the logarithm of the total selenium pressure for Series V is plotted against reciprocal temperature. The break or bend in the curve is most probably related to the maximum extension of the $RuSe_2$-phase on the selenium-rich side. Loss of mass of selenium from a sample with gross composition $RuSe_{2.50}$ in vacuum indicates the Se-rich phase limit to be $RuSe_{2.04}$ or $Ru_{0.98}Se_2$. The excess selenium presumably creates an increasing number of Ru-vacancies in the $RuSe_2$ structure until this temperature is reached. Evidence for this is the negative partial molar entropy of solution of liquid selenium in liquid selenium—saturated with $RuSe_2$—up to 776 K. Table 11 presents the vapour pressure and activity of liquid selenium under such conditions. The activities have been smoothed, and the calculation of the partial molar properties then performed over small temperature increments, see table 12.
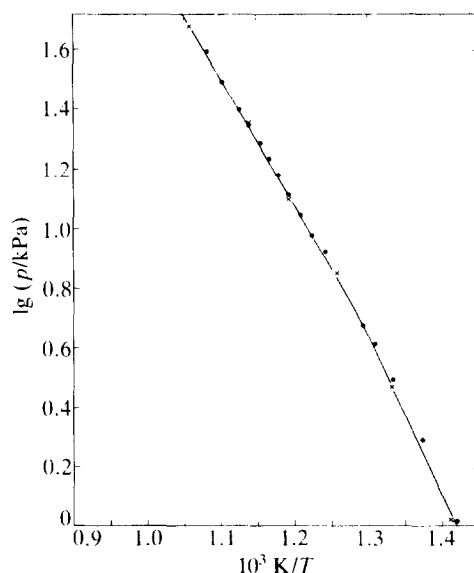

FIGURE 2. Logarithm of total selenium pressure p as a function of temperature. $RuSe_2$ with excess selenium, gross composition $RuSe_{2.424}$. ●, Increasing pressure, ×, decreasing pressure.

TABLE 11. Vapour pressure p and activity of liquid selenium saturated with $RuSe_2$ (gross composition $RuSe_{2.424}$, series 5). $a(Se, l) = \{p(Se_2)/p^*(Se_2)\}^{1/2}$ with $p^*(Se_2)$ from saturated pure-selenium pressure

T/K	p/kPa	$a(Se, l)$	T/K	p/kPa	$a(Se, l)$	T/K	p/kPa	$a(Se, l)$	T/K	p/kPa	$a(Se, l)$
705.5	1.098	0.9506	773.2	5.019	0.9704	837.9 [a]	13.23	0.9317	878.6	23.53	0.9157
708.9 [a]	1.106	0.9377	794.7	7.574	0.9725	838.2	13.71	0.9386	888.7	26.38	0.9069
728.4	2.074	0.9750	795.2 [a]	7.486	0.9683	848.7	15.86	0.9325	907.4	32.76	0.8927
750.5	3.300	0.9759	806.0	8.817	0.9620	858.2	18.04	0.9272	926.2	41.12	0.8833
751.3 [a]	3.125	0.9620	817.0	9.981	0.9473	868.4	20.40	0.9192	944.9	50.92	0.8726
764.7	4.377	0.9736	827.6	11.76	0.9438	878.4 [a]	23.80	0.9189	944.9 [a]	50.29	0.8696

[a] Decreasing temperatures.

TABLE 12. Partial molar quantities of solution of Se(l) in Se(l) saturated with $RuSe_2$

T/K	$\Delta G_m^\circ/RT$	$\Delta H_m^\circ/RT$	$\Delta S_m^\circ/R$	T/K	$\Delta G_m^\circ/RT$	$\Delta H_m^\circ/RT$	$\Delta S_m^\circ/R$	T/K	$\Delta G_m^\circ/RT$	$\Delta H_m^\circ/RT$	$\Delta S_m^\circ/R$
705.6	−37.3			750.8	−24.7					389.7	0.524
		−234.2	−0.279			−233.9	−0.278	797.0	−28.5		
716.9	−34.2			762.1	−21.5					406.5	0.545
		−233.9	−0.278			−234.2	−0.279	807.5	−34.2		
728.2	−28.5			773.4	−18.4					423.4	0.566
		−233.8	−0.278	776.0	−17.6			818.0	−40.1		
739.5	−27.8							373.5	0.504	441.4	0.588
		−233.8	−0.278	786.5	−22.9			828.5	−46.3		

Above 776 K the partial molar entropy of solution becomes positive, which indicates that liquid selenium now goes into the solution which thus accommodates increasing amounts of solid ruthenium or $RuSe_2$.

The homogeneity range of the $RuSe_2$-phase also makes itself evident in the isobaric expansivity $\alpha = V^{-1}(\partial V/\partial T)_p$. Unit-cell volumes V_u were calculated from the lattice constants of $RuSe_2$ at different temperatures, see table 13, and fitted by the method of least squares to a third-order polynomial in T:

$$V_u = a + b(T/K) + c(T/K)^2 + d(T/K)^3.$$

TABLE 13. Lattice constant a and isobaric expansivity α for $RuSe_2$

T/K	a/pm	$10^4\alpha/K^{-1}$	T/K	a/pm	$10^4\alpha/K^{-1}$	T/K	a/pm	$10^4\alpha/K^{-1}$
93±10	592.6 ±0.1	0.10 ±0.37	268±10	593.4 ±0.1	0.22 ±0.37	773± 3	595.65±0.03	0.223±0.027
118±10	593.1 ±0.1	0.11 ±0.37	293±10	593.4 ±0.1	0.24 ±0.37	823± 3	595.87±0.02	0.224±0.027
143±10	592.9 ±0.1	0.13 ±0.37	298± 3	593.39±0.02	0.266±0.027	873± 3	596.07±0.04	0.226±0.027
168±10	592.8 ±0.1	0.15 ±0.37	373± 3	593.83±0.04	0.253±0.027	973± 3	596.53±0.04	0.233±0.027
193±10	592.9 ±0.1	0.16 ±0.37	473± 3	594.25±0.07	0.239±0.027	1073± 3	597.01±0.03	0.244±0.027
218±10	593.1 ±0.1	0.18 ±0.37	573± 3	594.79±0.02	0.229±0.027	1173± 3	597.56±0.04	0.259±0.027
243±10	593.3 ±0.1	0.20 ±0.37	673± 3	595.16±0.03	0.224±0.027	1273± 3	598.03±0.03	0.278±0.027

Lattice constant a at 298.15 K: (593.5±0.1) pm (reference 4); (593.3±0.2) pm converted from "kX" units (reference 37); (593.39±0.02) pm (this work).
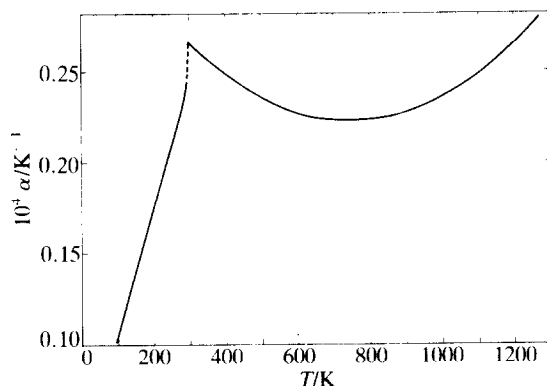
FIGURE 3. Isobaric expansivity $\alpha = V^{-1}(\partial V/\partial T)_p$ for RuSe$_2$ as a function of temperature.

By differentiation of the polynomial with respect to temperature and dividing by volume, the expansivity was calculated at the temperatures of measurement, see table 13 and figure 3. The two sets of values do not merge smoothly, especially because the temperature control of the low-temperature camera was not completely satisfactory.

The expansivity shows two inflections, one in the temperature range 250 to 300 K, and the other around 770 K. The former reflects the beginning deviation of the RuSe$_2$-phase from exact stoichiometry, and the latter the solubility limit of selenium in the RuSe$_2$-phase. At temperatures above 770 K the expansivity shows the usual increase, characteristic of a homogeneous sample, and no definite sign of retrograde solubility.

To evaluate the excess heat capacity due to the solution of selenium up to 770 K, a reference heat capacity was needed. It was obtained from extrapolation of the lower-temperature heat capacity in the harmonic approximation and including a dilatation contribution. The latter was obtained through the Nernst-Lindemann equation.[39]

$$C_{\mathrm{m}}(\mathrm{d}) = C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = A C_{p,\mathrm{m}}^2 T,$$

where $A = (V_{\mathrm{u}}\alpha^2 L)/(n_{\mathrm{u}} C_{p,\mathrm{m}}^2 \kappa) = 7.18 \times 10^{-7}$ J$^{-1}\cdot$mol, V_{u} the unit-cell volume, L the Avogadro constant, n_{u} the number of formula units in the unit cell, and κ the isothermal compressibility. The value of the constant A was derived at $T = 298$ K taking the unknown κ as equal to that of isostructural FeS$_2$, $\kappa = 6.37 \times 10^{-12}$ Pa^{-1}.[40] Subtraction of the dilatation contribution in combination with the Debye heat-capacity model lead to a maximum $\Theta_{\mathrm{D}} = 411$ K at 120 K. This Debye temperature was used for calculating the harmonic $C_{V,\mathrm{m}}$ in the higher-temperature region, and the resulting $C_{p,\mathrm{m}}$ in the range 200 to 1000 K is shown in figure 1. It falls only slightly below the experimental curve in the 400 to 500 and the 800 to 900 K ranges, and shows a more marked deviation in between, which we ascribe to the solution process. The resulting enthalpy increment for the solution of Se(l) in RuSe$_2$ over the range 500 to 800 K is (270 ± 115) J$\cdot$mol^{-1}.

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