Cesium – Molybdenum – Oxygen

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Introduction

Cs and Mo are important large yield fission products formed in a nuclear fuel during burn up. Molybdenum is a fission product whose chemical state in the oxide fuel changes from metal to oxide with increasing oxygen potential of the fuel. Cesium molybdate (Cs_2MoO_4) is considered to be one of the typical fission product compound in the fuel-cladding gap at high burnup. That is why thermodynamic properties of Cs_2MoO_4 were extensively studied. The review of phase diagram, crystallographic data and thermodynamic data is presented in [1990Cor].

Phase diagram of the Cs_2MoO_4-MoO_3 system was studied by [1951Spi] using thermal analysis. Later the phase diagram of this system was studied by [1969Sal] and [1973Hoe]. [1969Sal] examined the Cs_2MoO_4-MoO_3 system by solid state reactions. The products were analyzed by XRD and DTA. There are some inconsistencies between the diagrams obtained by [1951Spi], [1969Sal] and [1973Hoe]. The most reliable is diagram from [1973Hoe]. The obtained compounds were characterized by XRD, IR and Raman spectroscopy. Later the results of [1973Hoe] were confirmed by [1990Baz] using XRD, DTA, IR-spectroscopy. The structure of the compounds $Cs_2Mo_2O_7$, $Cs_2Mo_3O_{10}$, $Cs_2Mo_4O_{13}$, $Cs_2Mo_5O_{16}$ and $Cs_2Mo_7O_{22}$ was studied by XRD and lattice parameters were determined [1970Koo, 1973Gon, 1975Gat, 1995Mar, 1997Ish, 1999Enj]. The phase diagram of the Cs_2O-Cs_2MoO_4 system is not known. The phase with the hexagonal structure $Cs_6Mo_2O_9$ was found by [1977Wec] and its lattice parameters were calculated. Another kind of compounds, where Mo atoms have charge +6 and +5, were obtained: $Cs_{0.14}MoO_3$, $Cs_{0.25}MoO_3$, $Cs_{0.3}MoO_3$, $Cs_{0.33}MoO_3$ and $CsMo_{4-x}O_{12}$ (x = 0.13). The structure of those compounds (bronzes) was studied by [1970Mum, 1970Rei, 1984Sch, 1987Abr, 1987Tsa, 1998Eda].

Thermodynamic data are available for Cs_2MoO_4 and $Cs_2Mo_2O_7$. The Cs_2MoO_4 phase was studied by vapor pressure measurement [1975Joh, 1989Tan, 1992Cor, 1993Yam, 1997Kaz] and calorimetrically [1974Osb, 1974Fre, 1975Den, 1982Koh, 1988Kon]. The $Cs_2Mo_2O_7$ phase was studied by differential scanning calorimetry (DSC) in [1994Koh] and by aqueous solution calorimetry in [1975OHa]. Potential diagrams were calculated by [1978Tak] and [2005Wal] using thermodynamic data available for compounds.

Thermal conductivity of Cs_2MoO_4 was measured in [1996Ish, 1996Min, 1997Ish, 1997Min]; thermal expansion was determined in [1996Min, 1997Min]. The electric properties of $Cs_2Mo_2O_7$, $Cs_2Mo_3O_{10}$, $Cs_2Mo_4O_{13}$, $Cs_2Mo_5O_{16}$ and $Cs_2Mo_7O_{22}$ were measured by [1990Baz]. Bronzes were found to be semiconductors. Their electric properties were studied in [1981Str, 1984Sch, 1987Abr].

The experimental studies in the Cs-Mo-O system are summarized in Table 1.

Binary Systems

Phase diagram for the binary system Mo-O is accepted from [1980Bre, Mas2]. The phase diagram for the Cs-O is accepted from [1979Kni]. Crystallographic data for phases are from [V-C2] (Table 2). The data on phase equilibria in the Cs-O system are scarce and contradictory. The latest phase diagram is from [1979Kni], where it was claimed that phase diagram data between Cs_7O and Cs_3O presented by [Mas2] were not correct. It should be mentioned that formulas Cs_7O_2 from [1979Kni] and $Cs_{11}O_3$ [V-C2, Mas2] present the same phase. According to [1979Kni] this phase melts at –10.5°C contrary to 53°C given by [V-C2, Mas2]. According to [Mas2] Cs_3O has a homogeneity range, while [1979Kni] show this phase as stoichiometric. The Cs_2O_3 phase [V-C2] was not found in [1979Kni]. Probably this phase is metastable. In [V-C2] two polymorphic modifications of CsO_2 phase are presented. The phase diagram of the Cs-Mo system was not studied experimentally. The calculated diagram for the Cs-Mo system is accepted from [Mas2]. The Cs-O phase diagram from [1979Kni] is presented in Fig. 1.

Solid Phases

Several solid phases of constant composition were found in the Cs_2MoO_4-MoO_3 system by [1973Hoe]. The crystallographic study of Cs_2MoO_4 was performed by [1970Koo, 1973Gon, 1997Min], $Cs_2Mo_3O_{10}$ [1999Enj], $Cs_2Mo_4O_{13}$ [1995Mar], $Cs_2Mo_5O_{16}$ and $Cs_2Mo_7O_{22}$ [1975Gat]. Several studies [1973Hoe, 1974Fre, 1988Kon, 1996Min, 1997Min] demonstrated that orthorhombic Cs_2MoO_4 transforms to a hexagonal phase at 568°C. However, crystallographic data for this phase are not available. The lattice parameters of $Cs_2Mo_2O_7$ are available from [1973Hoe]. [1977Wec, 1981Sou] reported the hexagonal phase $Cs_6Mo_2O_9$ in the Cs_2O-Cs_2MoO_4 system. Polymorphism in this compound was not found [1981Sou]. The parameters of $Cs_6Mo_2O_9$ were determined by XRD in [1977Wec].
Another kind of compounds found in the Cs-Mo-O system are bronzes. The peculiarity of bronzes is that their structure contains both Mo^{+6} and Mo^{+5} [1987Abr]. The method to prepare bronzes is electrolysis from the Cs_2MoO_4-MoO_3 melts [1970Mum, 1970Rei, 1981Str]. The review of crystallographic data for bronzes was presented by [1998Eda].

Quasibinary Systems

The Cs_2MoO_4-MoO_3 system was studied experimentally in [1951Spi, 1969Sal, 1973Hoe]. The compounds with the general formula $Cs_2Mo_xO_{3x+1}$ were found in this system. The compounds $Cs_2Mo_3O_{10}$ and $Cs_2Mo_4O_{13}$ were found by [1951Spi]. Two other compounds with $x = 6$ and 8 indicated by [1951Spi] were not confirmed by latter investigations. The $Cs_2Mo_2O_7$ compound was found by [1969Sal]. The solid solutions $Cs_2Mo_9O_{28}$ indicated by [1969Sal] were not confirmed by latter studies. It should be noted that phase diagram presented by [1969Sal] contradicts the phase rule in the range of melting of $Cs_2Mo_9O_{28}$. In this work the phase diagram of [1973Hoe] is accepted. It should be also noted that in spite of some differences in melting relations the liquidus line of [1973Hoe] is in reasonable agreement with the previous studies of [1951Spi, 1969Sal]. [1990Baz] synthesized all solid phases found by [1973Hoe]. Their crystallographic parameters and IR spectra were obtained and electric properties were studied. The phase diagram from the study of [1973Hoe] is presented in Fig. 2. A phase transition in $Cs_2Mo_2O_7$ indicated by a very small DTA maximum is shown by a dashed line, because there was no major structural reorganization confirmed by XRD [1973Hoe] and this transformation was not mentioned in latter studies.

Isothermal Sections

Isothermal section at temperatures valid between 160 and 425°C was calculated by [1981Lin] based on estimates of thermodynamic properties for τ_1-τ_7. It is shown in Fig. 3. Bronzes were not taken into account.

Potential Diagrams

Potential phase diagrams are calculated by [1978Tak, 1981Lin, [2005Wal]. Only one ternary compound Cs_2MoO_4 was taken into account by [2005Wal]. Two compounds Cs_2MoO_4 and $Cs_2Mo_2O_7$ were considered by [1978Tak]. However, at the temperature of the calculation (727°C) the dimolybdate phase is not stable. [1981Lin] took into account all phases found in the Cs_2O-MoO_3 system. Figures 4 and 5 present potential diagrams from [1978Tak] and [2005Wal], respectively. Potential diagrams from [1981Lin] are presented in Figs. 6, 7. Potential diagrams presented here should not be considered as equilibrium diagrams, because not all ternary phases were taken into account.

Thermodynamics

The standard enthalpy of Cs_2MoO_4 was derived from aqueous solution calorimetry measurements by [1973OHa]. Based on low-temperature C_p data obtained by adiabatic calorimetry standard entropy of Cs_2MoO_4 at 25°C was derived by [1974Osb]. The C_p of Cs_2MoO_4 at 77-500°C was measured by differential scanning calorimetry by [1982Koh] and the enthalpy increment at 142-427°C was measured by drop calorimetry [1988Kon]. [1974Fre] studied enthalpy increment by drop calorimetry method in the temperature range of 283-918°C. The enthalpy increment was also measured for the Cs_2MoO_4 in the liquid

state using drop calorimetry at 980-1227°C by [1975Den]. The DSC measurements preformed by [1988Kon] indicated transformation from orthorhombic to hexagonal structure at 568°C and melting at 956°C. The enthalpy of α-β phase transformation was determined to be 4.6 kJ·mol^{-1} from the DSC measurements. This value is in a good agreement with data of [1974Fre]. The enthalpy of fusion was measured by drop calorimetry in [1975Den]. The thermodynamic properties for Cs_2MoO_4 are accepted from [1988Kon] who analyzed all available thermodynamic data for this compound and combined the most reliable data with his own measurements. The C_p data of [1974Fre] was discarded because they do not fit the low-temperature data of [1974Osb].
The thermodynamic properties of the $Cs_2Mo_2O_7$ phase were studied in [1975OHa, 1994Koh]. The enthalpy of formation of this compound was obtained from aqueous solution calorimetry measurements [1975OHa]. The heat capacity of $Cs_2Mo_2O_7$ was measured by DSC in the temperature range 37-427°C by [1994Koh]. There is only estimate of standard entropy for $Cs_2Mo_2O_7$ as 340 J·(mol·K)$^{-1}$ made by [1975OHa], because experimental data are not available so far. The thermodynamic functions for $Cs_2Mo_2O_7$ are accepted from [1994Koh] who combined his own measurements and estimates with data of [1975OHa]. The thermodynamic data for the compounds Cs_2MoO_4 and $Cs_2Mo_2O_7$ are presented in Tables 3 and 4. Estimates of thermodynamic properties from [1981Lin] are not presented here, because they are not based on any physical considerations.
The vapor pressure of Cs_2MoO_4 (gas) was studied by Knudsen effusion mass spectrometry over solid and liquid phases of Cs_2MoO_4 in [1993Yam]. It was proved [1975Joh, 1993Yam, 1997Kaz] that Cs_2MoO_4 evaporates congruently in the form of the Cs_2MoO_4 molecules. The results of [1993Yam] are in a reasonable agreement with previous vapor pressure data [1975Joh, 1989Tan, 1992Cor]. The new determinations of vapor pressure over solid Cs_2MoO_4 by high-temperature mass-spectrometry [1997Kaz] are in a very good agreement with the data of [1993Yam] presented in Table 5. The enthalpy of vaporization calculated by the third-law at 25°C is presented in Table 3.

Notes on Materials Properties and Applications

As it was mentioned in the *Introduction* chapter, Cs and Mo are important fission products and their behavior at various oxygen partial pressure is important to understand migration phenomena and interaction between fuel and clad. [1972Nei] studied stainless-steel - clad mixed-oxide fuel elements after irradiation to burnup of 11 at.%. The separation of the fuel and cladding at high burnup is related to the deposition of Cs-Mo-O at the interface. At low O/M (oxygen-to-metal ratio) in which Mo did not migrate to the interface, the fuel and cladding remain in contact. The axial migration of cesium in the low O/M ratio element resulted in apparently nondetrimental reaction with the UO_2 blanket and insulator pellet.
Thermal expansion and thermal conductivity of Cs_2MoO_4 are necessary to analyze and predict the fuel-clad mechanical interaction and fuel temperature. Thermal diffusivity of Cs_2MoO_4 was experimentally measured by laser flash method and the thermal conductivity was calculated in [1996Ish, 1997Ish, 1997Min]. The temperature dependence of the lattice parameters of Cs_2MoO_4 was measured using high-temperature XRD from 25 to 500°C in [1996Min, 1997Min]. Thermal expansions were obtained nearly isotropic. The geometric mean of thermal expansion of orthorhombic Cs_2MoO_4 was compared with the thermal expansion of UO_2 in [1996Min]. The thermal diffusivity of Cs_2MoO_4 was found to present discontinuity because of the transformation to the hexagonal structure [1996Min, 1997Min]. The thermal conductivity of UO_2 is much larger than that of Cs_2MoO_4, while thermal expansion is considerably larger for Cs_2MoO_4 [1996Min]. Thermomigration of Cs was experimentally studied in oxide fuel systems *i.e.* Cs-O-U and Cs-Mo-O by [1973Ada]. Cesium molybdate, Cs_2MoO_4, appears to be the only ternary Cs-Mo-O compound that can form in oxide fuels (O/M ≤ 2). It is stable at oxygen potentials above the equilibrium $\mu O_2(Mo/MoO_2)$, but it does not form in liquid Cs at 800°C. Thermal gradient tests show that Cs_2MoO_4 is slightly less stable than Cs-O-U compounds in the presence of excess fuel at 700 to 1000°C, but it is considerably more volatile. The Cs_2MoO_4 (gas) molecule may be sufficiently stable to provide additional transport path for Cs, Mo and O in oxide fuel at high burnup.
The temperature dependence of resistivity of compounds in the Cs_2MoO_4-MoO_3 system and their electron transport numbers were studied by [1990Baz]. At high temperature the single crystals of Cs_2MoO_4 and

$Cs_2Mo_3O_{10}$ possess essentially electronic conductance. It was shown that the resistivity increases with increasing MoO_3 content, but there is no correlation between activation energy of ionic conductance and the MoO_3 content. The activation energy of ionic conductance is related to crystal structure of the compounds.
The molybdenum oxide bronzes attract attention, because many of them are semiconductors. The electric and magnetic properties of the $Cs_{0.33}MoO_3$ and $Cs_{0.19}MoO_{2.85}$ bronzes were measured by [1984Sch]. The $Cs_{0.33}MoO_3$ (red bronze) is a diamagnetic semiconductor at all temperatures. The $Cs_{0.19}MoO_{2.85}$ (blue bronze) is also semiconductor, but an anomaly in the magnetic susceptibility at 200 K suggesting a phase transition was observed. The resistivity of $CsMo_{4-x}O_{12}$ (the same phase as $Cs_{0.19}MoO_{2.85}$) was also measured by [1987Abr] and anisotropy was found. The electric resistivity of Cs_xMoO_3 ($x = 0.31$ red bronze) was measured by [1981Str].

Miscellaneous

The structure of Cs_2MoO_4 molecule in gas phase was studied by electron-diffraction in [1973Uga]. Principal parameters (internuclear distances and vibration amplitudes) were derived. Adsorption of cesium and co-adsorption of cesium and oxygen on Mo surface at room temperature was studied by electron spectroscopy [1984Riw] and by electron-loss and photoemission spectroscopy using synchrotron radiation by [1984Sou, 1985Sou]. The IR absorption spectra of Cs_2MoO_4 in nitrogen matrix were obtained at 12 K by [1981Spo]. Matrix-isolated anion vibrational frequencies were obtained from IR spectra.
The crystal lattice energy and enthalpy of formation of Cs_2MoO_4 and many other solid compounds were calculated by empirical method based on effective charges of atoms in molecules and ions (calculated by adjusting some special potentials of atoms) by [1984Kaz]. However, the predicted value for the enthalpy of formation of Cs_2MoO_4 are 30 kJ·mol^{-1} more negative than experimentally measured by [1973OHa].
Solid state reactions between UO_2MoO_4 and Cs_2MoO_4 up to 750°C were investigated by [1995Mis]. Two phases of $Cs_2UO_2(MoO_4)_2$ and single phase compound $Cs_2(UO_2)_2(MoO_4)_3$ were isolated and characterized by thermal analysis, XRD, chemical and IR method. The reactions in the U-Cs-Mo-I-O were experimentally studied as a function of oxygen potential using CO-CO_2 gas equilibration method by [1996Uga]. The chemical constitution and the morphology were examined mainly for reaction products containing volatile element Cs. Thermodynamic calculations were performed to verify the experimental results. Predominance of Cs_2MoO_4 over Cs_2UO_4 was proved at oxygen potentials between –380 and –420 kJ·mol^{-1}. Calculations suggested that Cs_2UO_4 should coexist with Cs_2MoO_4 at such potentials unless the excess of Mo over Cs is guaranteed. The relative stability of Cs_2MoO_4 to Cs_2UO_4 would be altered at oxygen potential of –530 kJ·mol^{-1}. Calculations of Cs-I-Mo-O and Cs-I-O-U potential diagrams were performed by [2005Wal]. The results are presented on the basis of three dimension potential diagrams, calculated at 350°C. It was shown that the iodine partial pressure could be controlled by formation of Cs_2UO_4 from CsI in the fuel. If formation of Cs_2MoO_4 would take place the iodine partial pressure is expected to increase.

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Table 1: Investigations of the Cs-Mo-O Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1951Spi]	Thermal analysis	450-925°C, Cs_2MoO_4-MoO_3
[1967Cai, 1969Sal]	Solid state reactions, XRD, DTA	300-940°C, Cs_2MoO_4-MoO_3
[1970Mum]	XRD, electrochemistry	530°C, 0.3 Cs_2MoO_4-0.7 MoO_3, lattice parameters for $Cs_{0.25}MoO_3$
[1970Rei]	XRD, electrochemistry	530°C, 0.3 Cs_2MoO_4-0.7 MoO_3, lattice parameters for $Cs_{0.33}MoO_3$
[1973Gon]	Single crystal X-ray	Cs_2MoO_4 lattice parameters
[1973Hoe]	XRD, thermal analysis (DTA-TGA), IR, Raman spectroscopy	300-940, Cs_2MoO_4-MoO_3
[1973OHa]	Aqueous solution calorimetry (enthalpy of formation)	25°C, Cs_2MoO_4
[1973Uga]	Electron-diffraction	1050°C, Cs_2MoO_4 in gas
[1974Fre]	Drop calorimetry	283-918°C, Cs_2MoO_4
[1974Osb]	Adiabatic calorimetry (heat capacity, entropy)	5-350°C, Cs_2MoO_4
[1975Den]	Drop calorimetry	969-1227°C, Cs_2MoO_4
[1975Gat]	XRD	$Cs_2Mo_5O_{16}$, $Cs_2Mo_7O_{22}$ lattice parameters
[1975Joh]	Mass spectrometric study of vapor pressure over solid and liquid phase	797-897°C, Cs_2MoO_4 solid
[1975OHa]	Aqueous solution calorimetry (enthalpy of formation)	25°C, $Cs_2Mo_2O_7$
[1977Wec]	Solid state reaction at 350°C, XRD at 20°C	$Cs_6Mo_2O_9$ lattice parameters
[1978Tak]	Calculation of potential diagrams based on thermodynamic data	727°C $\mu(O_2)$ *vs* μ(Cs)
[1981Lin]	Calculation of potential diagrams based on thermodynamic data	100-700°C, $\mu(O_2)$ *vs T*
[1981Str]	XRD, electrical resistivity	$Cs_{0.31}MoO_3$ crystal growth by electrolysis from Cs_2MoO_4-MoO_3 melts with 70-77 mol% MoO_3 at 540°C
[1982Koh]	DSC (heat capacity)	27-527°C, Cs_2MoO_4
[1984Sch]	XRD	$Cs_{0.33}MoO_3$, lattice parameters
[1987Abr]	XRD	$CsMo_{4-x}O_{12}$ (x = 0.13) lattice parameters
[1987Tsa]	Single crystal XRD	$Cs_{0.33}MoO_3$, lattice parameters

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1988Kon]	Drop calorimetry (enthalpy increment) DSC (phase transition)	142-427°C, Cs_2MoO_4 523-1227°C, Cs_2MoO_4
[1989Tan]	Vaporization over liquid by transpiration technique, chemical and XRD analysis	957-1037°C, Cs_2MoO_4 liquid
[1990Baz]	XRD, DTA, IR-spectroscopy	450-500°C, Cs_2MoO_4-MoO_3
[1992Cor]	Vapor pressure over solid phase by entrainment method	844-917°C Cs_2MoO_4 solid
[1993Dep]	Synthesis from CsCl, WO_2 and MoO_3, XRD	560°C, vacuum 10^{-4} mbar, $Cs_{0.14}MoO_3$, lattice parameters
[1993Yam]	Vaporization by Knudsen effusion mass spectrometry	862-947°C, Cs_2MoO_4 solid 957-972°C Cs_2MoO_4 liquid
[1994Koh]	DSC (heat capacity)	37-427°C $Cs_2Mo_2O_7$
[1995Mar]	Solid state reaction, XRD, pycnometry	$Cs_2Mo_4O_{13}$ synthesis at 627°C, lattice parameters
[1997Kaz]	Vapor pressure measurements by high-temperature mass-spectrometry	753-875°C Cs_2MoO_4 solid
[1997Min]	XRD, DTA	25-500°C, Cs_2MoO_4, lattice parameters, phase transformation
[1998Eda]	XRD	$Cs_{0.3}MoO_3$, lattice parameters
[1999Enj]	Solid state reaction, XRD	$Cs_2Mo_3O_{10}$, lattice parameters
[2005Wal]	Calculation of potential diagrams based on thermodynamic data	Cs-Mo-O 127- 427°C, $\mu(O_2)$ *vs T*

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cs) < 28.39	*cI*2 $Im\bar{3}m$ W	a = 614.1	at 25°C [Mas2]
(Mo) < 2623	*cI*2 $Im\bar{3}m$ W	a = 314.7	[V-C2]
CsO < 590	*oI*8 *Immm* CsO	a = 432.2 b = 751.7 c = 643	[V-C2]
αCsO_2(r) < 200	*tI*6 *I*4/*mmm* CaC_2	a = 446.2 c = 732.6	[V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
βCsO_2(h) 200 - 450	*cF*8 *Fm*$\bar{3}$*m* NaCl	*a* = 662	[V-C2]
CsO_3 < 70	*mP*16 *P*2_1/*c* RbO_3	*a* = 670.9 *b* = 624.4 *c* = 899.7	[V-C2]
Cs_2O < 495	*hR*9 *R*$\bar{3}$*m* WN_2	*a* = 425.6 *c* = 1899.2	[2005Gem]
Cs_2O_3 < 502	*cI*28 *I*$\bar{4}$3*d* Th_3P_4	*a* = 986	[V-C2], probably metastable
Cs_7O < 3	*hP*24 *P*$\bar{6}$*m*2 Cs_7O	*a* = 1639.3 *c* = 919.3	[V-C2]
$Cs_{11}O_3$ also Cs_7O_2 < -10.5	*mP*56 *P*2_1/*c* $Cs_{11}O_3$	*a* = 1761 *b* = 921.8 *c* = 2404.7 β = 100.14°	[V-C2]
Cs_4O < 53	*oP** *Pna*2_1	*a* = 1682.3 *b* = 2052.5 *c* = 1237.2	[V-C2]
Cs_3O < 164	-	-	[1979Kni]
MoO_3 < 804 (subl.)	*oP*16 *Pbnm* MoO_3	*a* = 396.28 *b* = 1385.5 *c* = 369.64	[1980Bre]
MoO_2 < 2300 (dec.)	*mP*12 *P*2_1/*c* VO_2	*a* = 561.08 *b* = 485.62 *c* = 562.85 β = 120.953°	[1980Bre]
Mo_4O_{11} < 818	*oP*60 *Pnma* Mo_4O_{11}	*a* = 2449.0 *b* = 545.7 *c* = 675.2	[1980Bre]
Mo_8O_{23}	*mP*62 *P*2/*a* Mo_8O_{23}	*a* = 1688 *b* = 450.2 *c* = 1339 β = 106.19°	[1980Bre]
Mo_9O_{26}	*mP*70 *P*2/*c* Mo_9O_{26}	*a* = 1674 *b* = 401.9 *c* = 1453 β = 95.45°	[1980Bre]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$Mo_{17}O_{47}$	*oP*128 *Pba*2 $Mo_{17}O_{47}$	*a* = 2161.5 *b* = 1963.2 *c* = 395.15	[1980Bre]
*τ_1, αCs_2MoO_4 (l) < 568	*oP*28 *Pcmn* βK_2SO_4	 *a* = 1159 *b* = 656 *c* = 850 *a* = 1183 *b* = 673 *c* = 865	[1970Koo, 1973Gon, 1997Min] at 25°C at 500°C [1997Min]
* τ_1', βCs_2MoO_4 (h) 957 - 568	*h**	*a* = 719 *c* = 926	[1990Cor, 1997Min]
* τ_2, $Cs_2Mo_2O_7$	*o**	*a* = 1554 *b* = 721.6 *c* = 1561	[1973Hoe]
* τ_3, $Cs_2Mo_3O_{10}$	*mC*64 *C*2/*c*	*a* = 1446.5 *b* = 839.97 *c* = 946.14 β = 97.74°	[1999Enj]
* τ_4, $Cs_2Mo_4O_{13}$	*mC*228 *C*2/*c*	*a* = 4592 *b* = 1041.8 *c* = 792.3 β = 92.94°	[1995Mar]
* τ_5, $Cs_2Mo_5O_{16}$	*mC*72 *C*2/*c*	*a* = 2144 *b* = 555.9 *c* = 1433.8 β = 122.74°	[1975Gat]
* τ_6, $Cs_2Mo_7O_{22}$	*mC*124 *C*2/*c*	*a* = 2154 *b* = 553.7 *c* = 1891 β = 122.71°	[1975Gat]
* τ_7, $Cs_6Mo_2O_9$	*h**	*a* = 1310 *c* = 851	[1977Wec]
* τ_8, $Cs_{0.14}MoO_3$	*hP** $P6_3/m$	*a* = 1062 *c* = 372.2	[1993Dep], dark blue
* τ_9, $Cs_{0.25}MoO_3$	*mP** $P2_1/m$	*a* = 642.5 *b* = 754.3 *c* = 816.9 β = 96.3°	red [1970Mum]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_{10}, $Cs_{0.19}MoO_{2.85}$ or $CsMo_{4-x}O_{12}$	*mC** *C*2/*m*	*a* = 1906.3 *b* = 558.27 *c* = 1211.47 β = 118.94°	blackish-blue [1984Sch] *x* = 0.132 [1987Abr]
* τ_{11}, $Cs_{0.33}MoO_3$	*mC** *C*2/*m*	*a* = 1586.2 *b* = 772.8 *c* = 640.8 β = 94.37°	red [1987Tsa], [1970Rei]
* τ_{12}, $Cs_{0.3}MoO_3$	*m**	*a* = 1936.2 *b* = 756.7 *c* = 1050.6 β = 121.07°	blue [1998Eda]

Table 3: Thermodynamic Data of Reaction or Transformation

Reaction or Transformation	Temperature [°C]	Quantity, per mol of atoms [kJ, mol, K]	Comments
1/7{2(Cs) + (Mo) + $2O_2$(gas) ⇌ Cs_2MoO_4(α)}	25	Δ*H* = –216.37	recommended by [1988Kon]
1/7{Cs_2MoO_4(α) ⇌ Cs_2MoO_4(β)}	568	Δ*H* = 0.657	[1988Kon]
1/7{Cs_2MoO_4(β) ⇌ Cs_2MoO_4(L)}	956	Δ*H* = 4.543	recommended by [1988Kon]
1/7{Cs_2MoO_4(β) ⇌ Cs_2MoO_4(L)}	25	Δ*H* = 42.2	[1993Yam]
1/11{2(Cs) + 2(Mo) + 7/2O_2(gas) ⇌ $Cs_2Mo_2O_7$(s)}	25	Δ*H* = –209.31	recommended by [1994Koh]

Table 4: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Property, per mole of atoms [J, mol, K]	Comments
αCs_2MoO_4	25	*S* = 35.48	[1974Osb]
αCs_2MoO_4	25 - 568	$C_p = 16.6291 + 0.01546 \cdot T$	[1988Kon]
βCs_2MoO_4	568 - 956	$C_p = 17.471 + 0.013864 \cdot T$	[1988Kon]
Cs_2MoO_4(L)	> 956	C_p = 30.022	[1988Kon]
$Cs_2Mo_2O_7$	37 - 427	$C_p = 24.211 + 0.06521T - 5.137 \cdot 10^5 \cdot T^{-2}$	[1994Koh]
$Cs_2Mo_2O_7$	25	*S* = 30.82	[1975OHa], estimated

Table 5: Vapor Pressure Measurements

Phase(s)	Temperature [°C]	Pressure [Pa], T [K]	Comments
βCs_2MoO_4	862 - 957	$\log_{10}(p/\text{Pa}) = 11.02 - 1.36 \cdot 10^4 \cdot T^{-1}$	[1993Yam]
Cs_2MoO_4(L)	957 - 982	$\log_{10}(p/\text{Pa}) = 9.80 - 1.21 \cdot 10^4 \cdot T^{-1}$	[1993Yam]

Table 6: Investigations of the Cs-Mo-O Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1981Str]	Resistivity	electric properties of $Cs_{0.31}MoO_3$ (red)
[1984Sch]	Resistivity, Faraday method	electric properties, magnetic susceptibility $Cs_{0.19}MoO_{2.85}$ and $Cs_{0.33}MoO_3$
[1987Abr]	Resistivity	electric properties of $CsMo_{4-x}O_{12}$(x = 0.13)
[1990Baz]	Resistivity in direct and alternating current	electric properties of $Cs_2Mo_nO_{3n+1}$ (n = 1-5, 7)
[1996Min] [1997Min]	XRD, laser flash	thermal expansion and thermal diffusivity of Cs_2MoO_4
[1996Ish] [1997Ish]	laser flash	thermal diffusivity of Cs_2MoO_4
[1998Eda]	Magnetometer	susceptibility, para-diamagnetic transition at 180 K

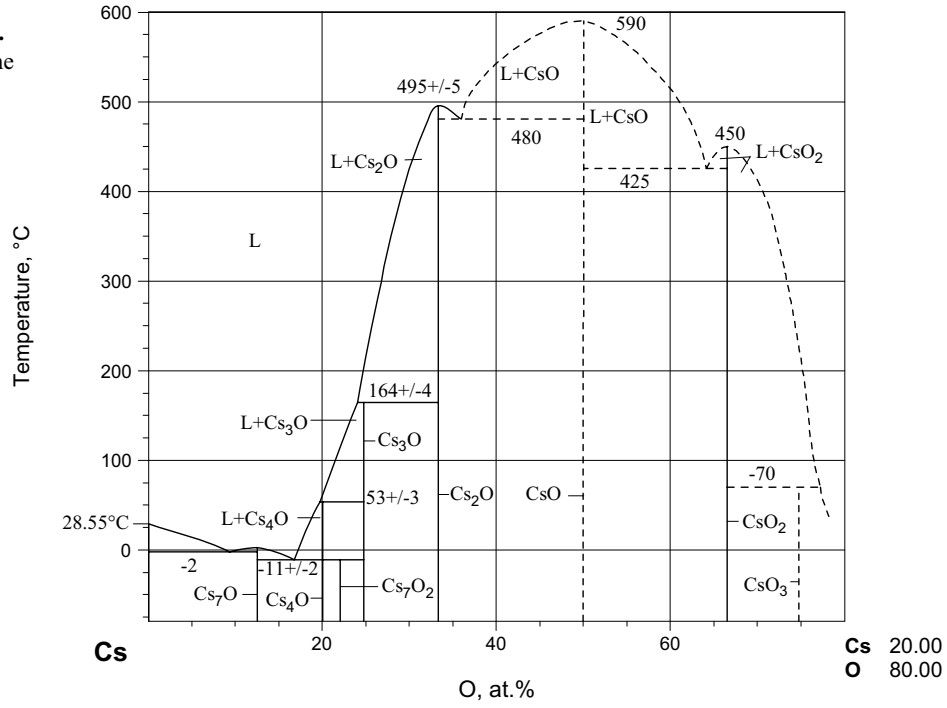

Fig. 1: Cs-Mo-O. Phase diagram of the Cs-O system

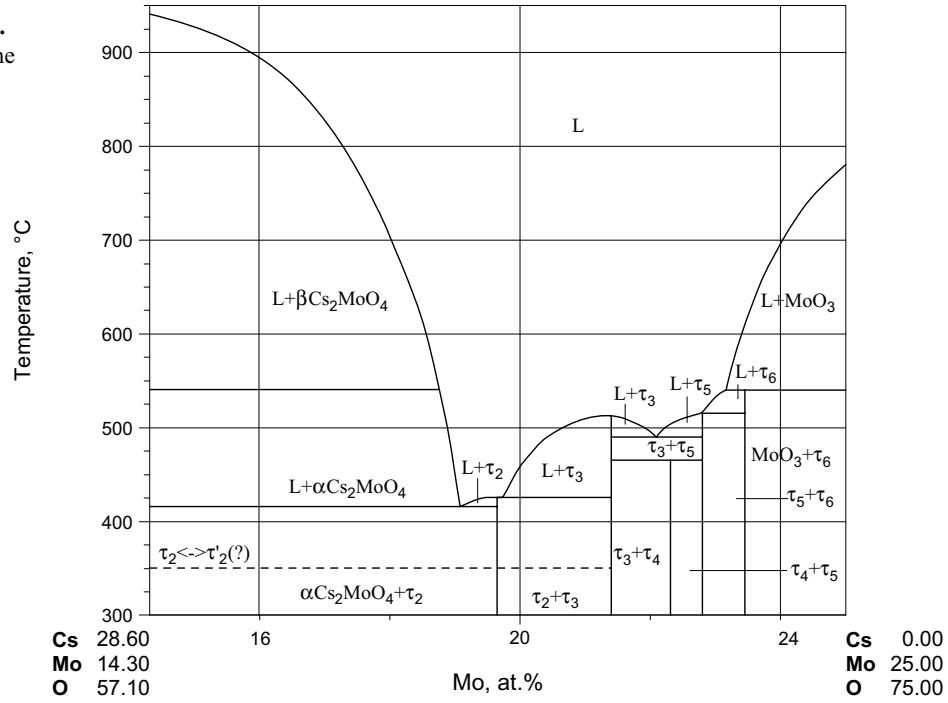

Fig. 2: Cs-Mo-O. Phase diagram of the Cs_2MoO_4-MoO_3 quasibinary system

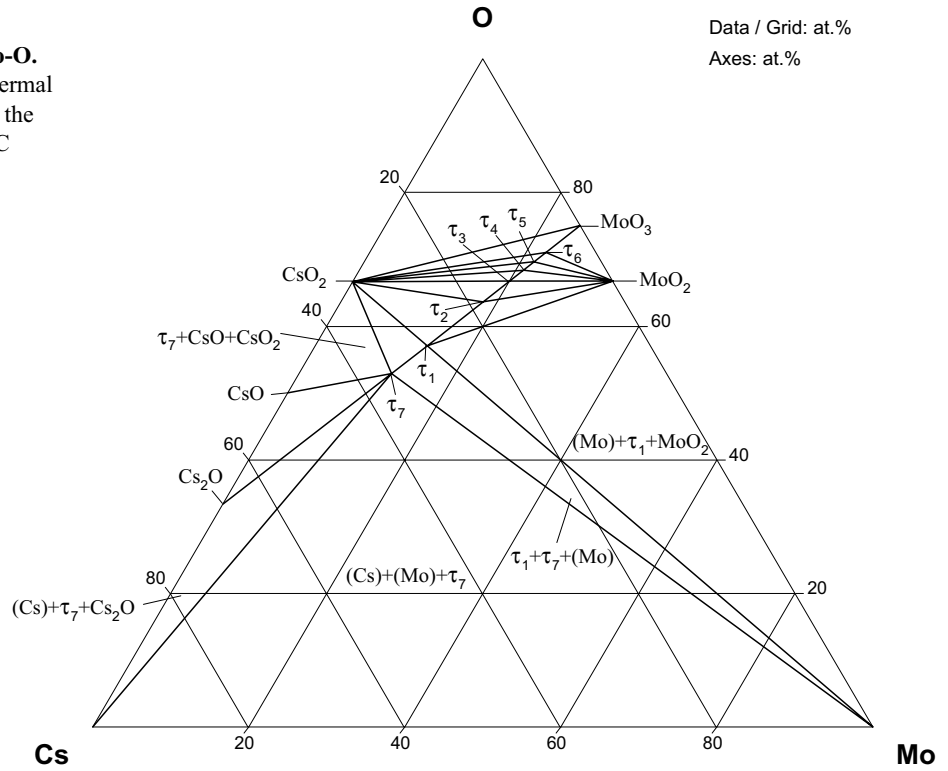

Fig. 3: Cs-Mo-O. Calculated isothermal section; valid in the range 160-425°C

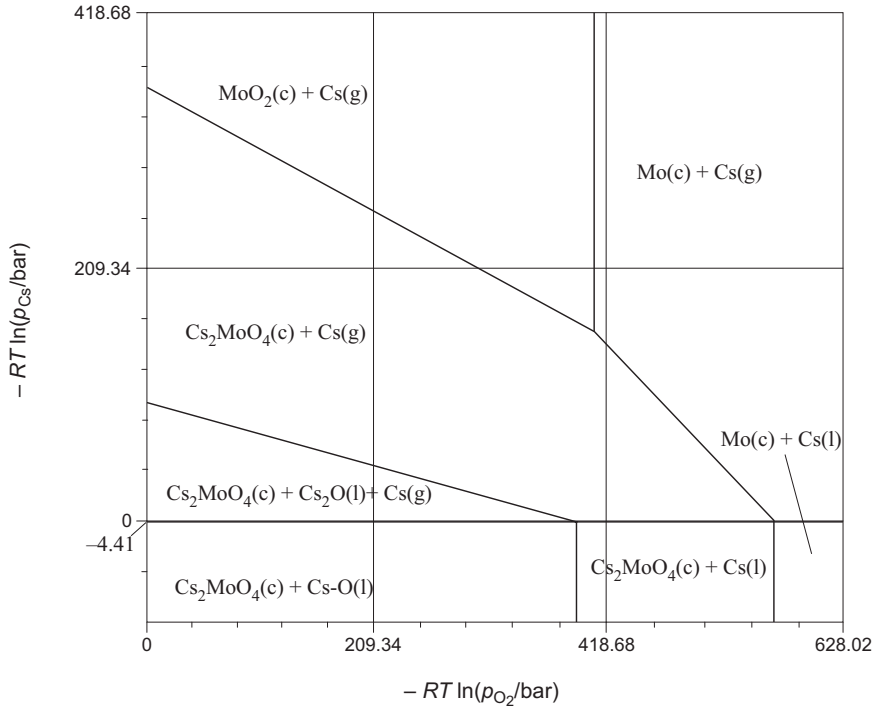

Fig. 4: Cs-Mo-O. Potential diagram at 727°C

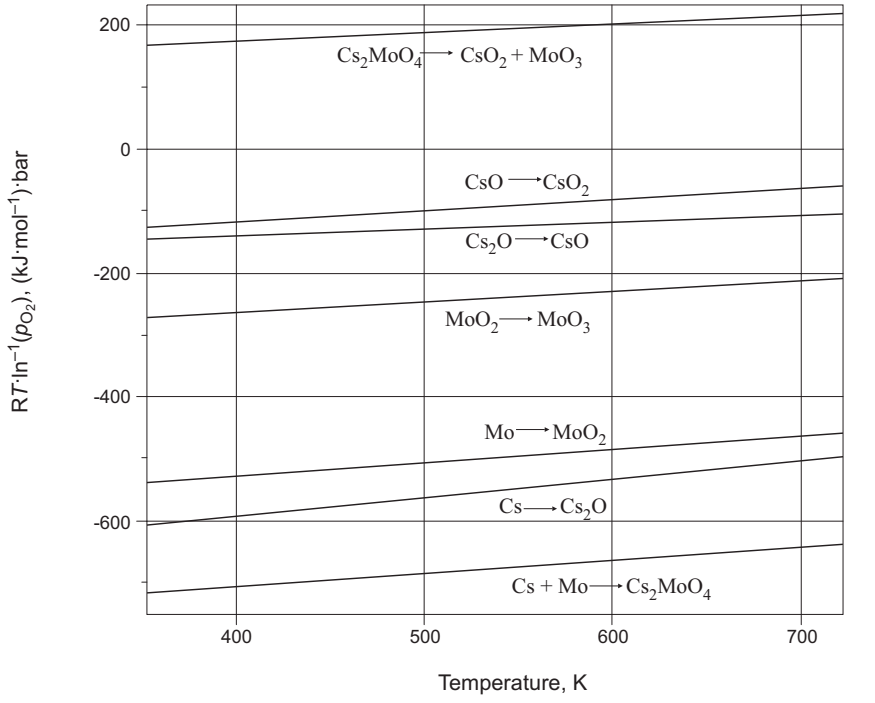

Fig. 5: Cs-Mo-O. Oxygen potential diagram

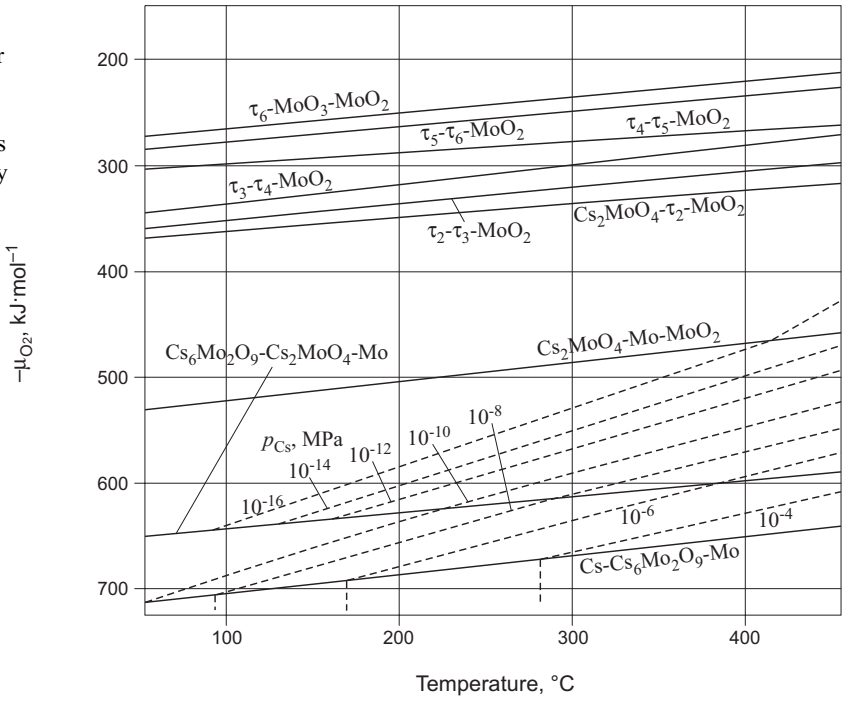

Fig. 6: Cs-Mo-O. Potential diagram for compositions between Cs and MgO_3. Isobars for Cs pressure are shown by dashed line

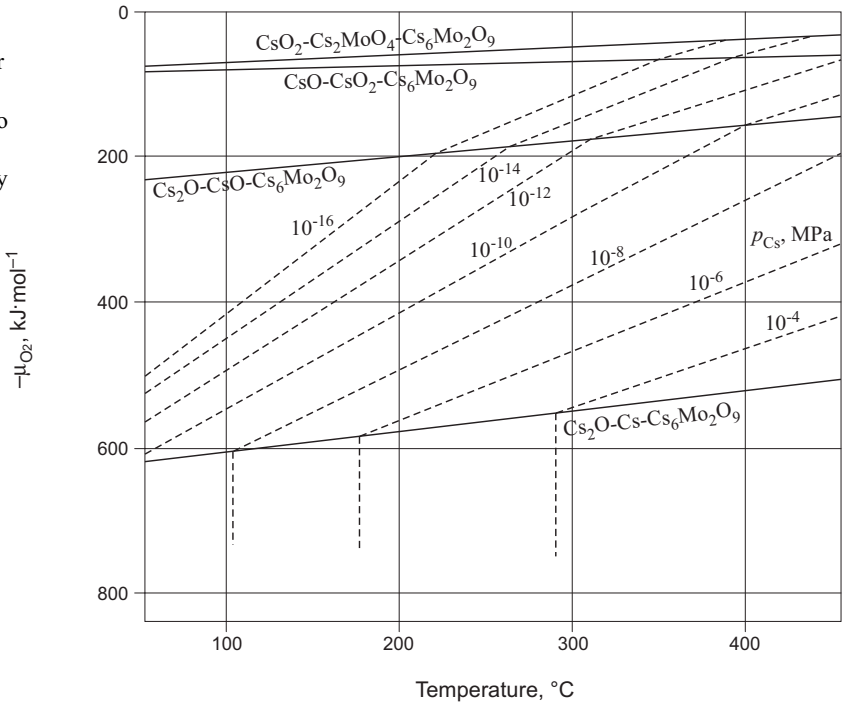

Fig. 7: Cs-Mo-O. Potential diagram for compositions between Cs and O/Mo < 9:2. Isobars for Cs pressure are shown by dashed line