Gas Complexation in the NaI–ErI$_3$ System

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The vapour phase above an equimolar NaI–ErI$_3$ mixture has been studied by Knudsen cell mass spectrometry. The presence of the complex molecule NaErI$_4$ in the equilibrium vapor has been established. There is also evidence for the existence of the complex dimer Na$_2$Er$_2$I$_8$ in small amounts. The main complexation reaction is given by reaction (4) with $\Delta H = -244 \pm 12$ kJ mol^{-1} and $\Delta S = -163 \pm 12$ J mol^{-1} K^{-1}

$$\text{NaI(g)} + \text{ErI}_3(\text{g}) \rightleftharpoons \text{NaErI}_4(\text{g}) \qquad (4)$$

at 890 K. For the complex dimerization reaction (5) the corresponding enthalpy

$$2\text{NaErI}_4(\text{g}) \rightleftharpoons \text{Na}_2\text{Er}_2\text{I}_8(\text{g}) \qquad (5)$$

and entropy changes are $\Delta H = -200 \pm 20$ kJ mol^{-1} and $\Delta S = -187 \pm 17$ J mol^{-1} K^{-1} at 890 K. The volatility enhancement of ErI$_3$ due to the complexation has been calculated to be approximately 21 at 900 K and 50 at 825 K.

In the field of high-temperature vapour chemistry the formation of gas complex molecules between metal halides with a common anion have been extensively studied for the last three decades. Several review articles summarize the complexes observed and the corresponding thermo-chemical data.[1–9] Among them several lanthanide halide – alkali halide systems have been investigated, with special emphasis on the chlorides. The lanthanide fluoride – alkali fluoride systems studied are relatively few, and no lanthanide bromide – alkali bromide system to our knowledge has been investigated. Within the lanthanide halide – alkali halide systems scandium and yttrium halide systems have been included.

Special interest in investigating the iodides, besides the fundamental one, arose because of the use of lanthanide iodides as additives in high-intensity discharge lamps.[10] In the lanthanide iodide – alkali iodide systems studied[10–17] the volatility of the lanthanide iodide increases because of the complexation. When this reaction takes place in the lamp envelope, the concentration of LnI$_3$ increases in the arc, resulting in better colour rendition.

In the present study the NaI–ErI$_3$ system has been investigated by high-temperature mass spectrometry.

Experimental

ErI$_3$ was prepared by the iodination of erbium metal,[18] which was purchased from Cerac Micropure (purity 99.9%). Iodine was purchased from Merck (purity 99.9%). ErI$_3$ was purified by vapour transport. NaI was purchased from Merck (purity 99.9%) and was dehydrated by heating in a vacuum for about 1 h at 100 °C. The chemicals were handled in a nitrogen dry-box with moisture content lower than 1 ppm.

The mass spectrometry measurements were performed using an Extranuclear Laboratories quadrupole mass spectrometer, with a cross-beam ion source, equipped with a Knudsen effusion assembly. Two Edwards oil-diffusion pumps were used to evacuate the furnace and the quadrupole compartment to a high vacuum, better than 10^{-5} Torr. The use of a shutter allowed us to distinguish between the background particles and those originating from the Knudsen cell. The Knudsen cell was made of nickel. It was 20 mm long and the orifice area was 0.25 mm^2. The temperature was measured by a Pt/Pt – 10% Rh thermocouple, touching the crucible surface loosely. The electron energy was 50 eV.

In order to ensure that the lid of the crucible was kept slightly warmer than the bottom for all experimental temperatures, experiments with pure NaI were performed, displacing the crucible holder vertically in the mass-spectrometer furnace. At the final position, the sublimation enthalpy at 825 K was -198 ± 8 kJ mol^{-1}, which is in good agreement with literature data[19] giving a value of -193 kJ mol^{-1}.

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Results and discussion

The mass spectra of the equilibrium vapour above the NaI–ErI₃ mixture gave direct evidence that gas comples molecules are formed. The ions detected are: Na^+, NaI^+, Na_2I^+, Er^+, ErI^+, ErI_2^+, ErI_3^+, $NaErI^+$, $NaErI_2^+$, $NaErI_3^+$, $NaErI_4^+$ and $Na_2ErI_4^+$.

The temperature dependence of the corresponding ion intensities has been studied and the result is plotted as ln (IT) against $1/T$ in Fig. 1. The relative abundances of the above ions at 900 K are given in Table 1. The ionization efficiency curves have been measured, and the relevant appearance potentials are given in Table 1. The electron energy scale has been calibrated through the appearance potential of NaI. In Fig. 2 the ionization efficiency curves of the ions $NaErI^+$, $NaErI_2^+$, $NaErI_3^+$ and $NaErI_4^+$ are presented.

Following the general rules for interpreting the experimental mass spectrometry results[20] the molecular precursors of the ions have to be assigned, and the total ion intensity for each molecular precursor has to be converted into partial pressures. To convert the ion currents into the corresponding partial pressures, we applied a calibration procedure as described below.

Calibration procedure. Mass spectra over pure ErI₃ have been obtained (Fig. 3). The total ion intensity of the fragments of ErI₃ is related to the pressure of ErI₃ at the same
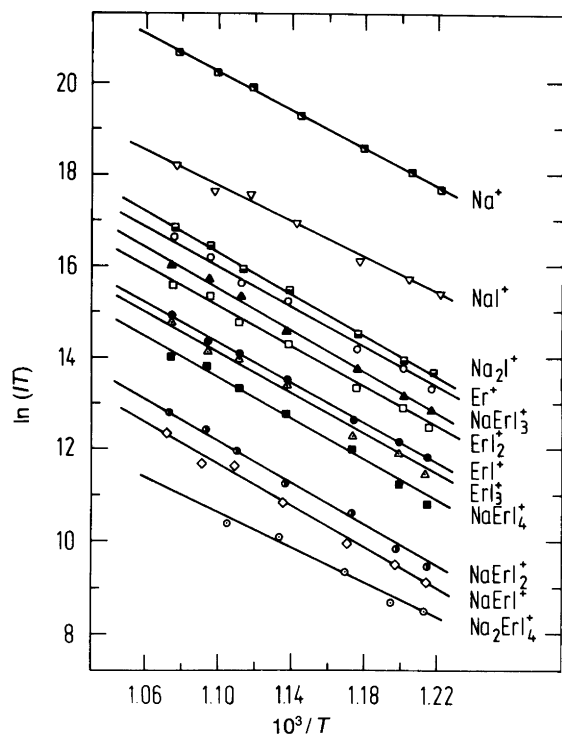
Table 1. Ions, relative abundance and appearance potentials observed from mass spectra of vapour above a NaI–ErI₃ mixture at 890 K.

Ion	Relative abundance	Appearance potential/eV
Na^+	6600.00	8.4
NaI^+	461.00	7.6
Na_2I^+	105.00	8.1
Er^+	100.00	16.0
ErI^+	19.39	13.2
ErI_2^+	42.82	10.0
ErI_3^+	15.66	8.9
$NaErI^+$	0.66	13.9
$NaErI_2^+$	1.76	12.2
$NaErI_3^+$	46.11	8.0
$NaErI_4^+$	7.17	7.4
$Na_2ErI_4^+$	0.13	

temperature, determined by Knudsen effusion.[21] The product $(I_{total}T)$ is proportional to the pressure of ErI₃ [eqn. (1)]. The pressure in the temperature range

$$P = \alpha(I_{total}T) \tag{1}$$

898–1016 K is given by eqn. (2).[21] Using eight different

$$\log(P/1 \text{ atm}) = -15\,122(T/K)^{-1} + 10.901 \tag{2}$$

temperatures in the range where this equation is valid, we calculated the proportionality constant α to be $(1.72 \pm 0.08) \times 10^{-12}$. This factor was calculated for ions in the mass range 166–547 amu (Er^+, ErI^+, ErI_2^+ and ErI_3^+). The sublimation enthalpy of pure ErI₃ was calculated to be -253 ± 12 kJ mol⁻¹, which is very close to literature data[22] giving a value of -254 ± 10 kJ mol⁻¹ at 895 K. The same procedure was applied to the determination of a proportionality factor, β, in the lower mass range. Mass spectra
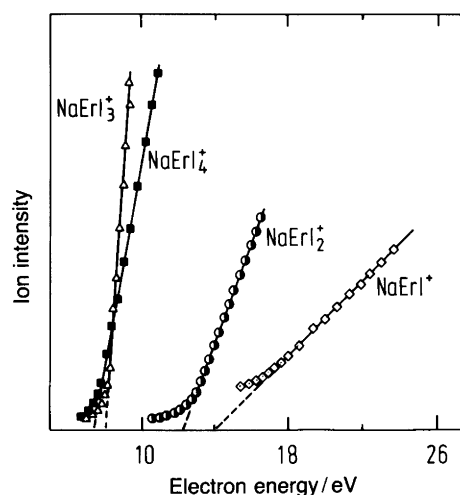

Fig. 1. Plot of ln (IT) vs. $1/T$ for the ions above the NaI–ErI₃ mixture.

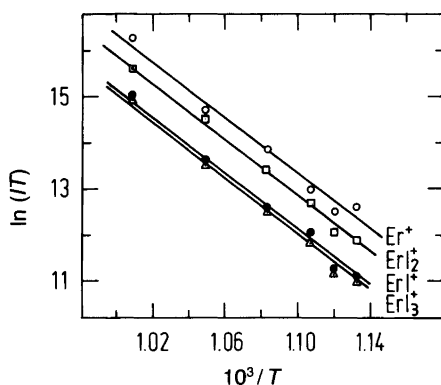*Fig. 2.* Ionization efficiency curves for the ions $NaErI^+$, $NaErI_2^+$, $NaErI_3^+$ and $NaErI_4^+$.

Fig. 3. Plot of ln (IT) vs. $1/T$ for the ions above pure ErI₃.

over pure NaI were obtained, and the total intensity was related to eqn. (3), derived from literature data,[23] giving
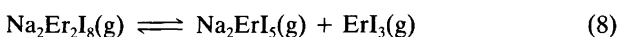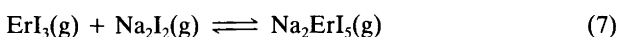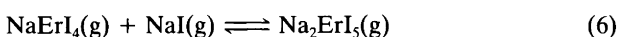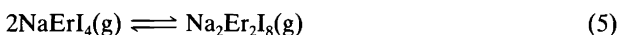
$$\beta = (1.00 \pm 0.2) \times 10^{-13}.$$

$$\log(P/1 \text{ atm}) = -8964(T/\text{K})^{-1} + 5.734 \tag{3}$$

The uncertainty of the coefficient β is due to the rapid contamination of the ion source from Na, so that the signal of the ion Na⁺ was stronger than it should have been.

Molecular precursors. The NaErI_n^+ ions, i.e. NaErI^+, NaErI_2^+, NaErI_3^+ and NaErI_4^+, contain one Na and one Er cation. These ions are believed to originate from the complex molecule NaErI₄, formed by the gas-phase reaction (4). The ion with the highest IT value is NaErI_3^+,

$$\text{NaI(g)} + \text{ErI}_3\text{(g)} \rightleftharpoons \text{NaErI}_4\text{(g)} \tag{4}$$

which is the same type of fragment of the complex molecule in all the similar systems studied (see Table 3 later). In the present system the second intense ion detected was NaErI_4^+, with intensity ratio 1/14 to the intensity of NaErI_3^+, over the whole temperature range studied (Fig. 1). In similar systems this ion has either not been detected[11] or shows a much lower intensity.[24] The slopes of the plots of ln (IT) against T^{-1} shown in Fig. 1 for the ions with Na/Er = 1 are essentially parallel, supporting the argument that NaErI₄ is the molecular precursor of the above ions. The ion $\text{Na}_2\text{ErI}_4^+$ (Ref. 12) may have two molecular precursors, namely the complex dimer Na₂Er₂I₈, formed by reaction (5), or the molecule Na₂ErI₅, which can be formed by one, or more, equilibria (6)–(8).

$$2\text{NaErI}_4\text{(g)} \rightleftharpoons \text{Na}_2\text{Er}_2\text{I}_8\text{(g)} \tag{5}$$

$$\text{NaErI}_4\text{(g)} + \text{NaI(g)} \rightleftharpoons \text{Na}_2\text{ErI}_5\text{(g)} \tag{6}$$

$$\text{ErI}_3\text{(g)} + \text{Na}_2\text{I}_2\text{(g)} \rightleftharpoons \text{Na}_2\text{ErI}_5\text{(g)} \tag{7}$$

$$\text{Na}_2\text{Er}_2\text{I}_8\text{(g)} \rightleftharpoons \text{Na}_2\text{ErI}_5\text{(g)} + \text{ErI}_3\text{(g)} \tag{8}$$

Equilibrium (8) cannot be studied from the experimental data, since both Na₂Er₂I₈ and Na₂ErI₅ should denote their presence by the same fragment, $\text{Na}_2\text{ErI}_4^+$. To see if equilibrium (7) was occurring, we performed a qualitative experiment in which a crucible containing the $X_{\text{ErI}_3}/X_{\text{NaI}} = 1/1$ melt was left in the furnace at 890 K for 7 h and measurements were performed after 1, 3 and 7 h. Since NaI is more volatile than ErI₃, the melt composition becomes richer in ErI₃ with increasing time. However, measurements indicated that the intensities of all the ions decreased. The effect was especially pronounced for the intensities of Na_2I^+. These observations make equilibrium (7) less likely to occur. In contrast to equilibrium (6), equilibrium (5) does not require the consumption of additional NaI, and since the intensity of the $\text{Na}_2\text{ErI}_4^+$ fragment was not affected much by the time that the sample was maintained at 890 K, equilibrium (5) is probably the reaction which is producing the molecular precursor of the $\text{Na}_2\text{ErI}_4^+$ ion.

The following scheme represents one reaction path for the formation of $\text{Na}_2\text{ErI}_4^+$ from the probable complex dimer. Two Na–I bonds of the complex dimer break, and the bigger fragment stabilizes itself by forming new internal Na–I bonds.

$$\tag{9}$$
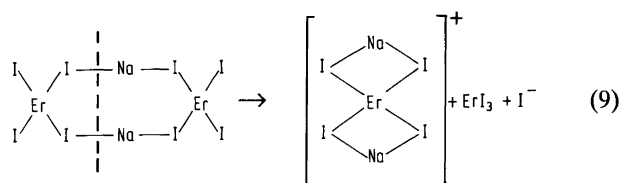
ErI_4^+ has not been detected, and it probably dissociates immediately to ErI₃ and I.

The ions containing only Na or Er cations can originate from both the pure species and from the complexes. Making the reasonable assumption that the fragmentation of Na₂Er₂I₈ contributes negligibly to the intensities of the previous ions, in view of the very low $\text{Na}_2\text{ErI}_4^+$ intensity, they can originate either from pure NaI or ErI₃, respectively, or from NaErI₄.

Data evaluation

In order to make quantitative calculations, a computer model has been developed. The model is based on the fact that for the particular composition there is solid ErI₃ present for the whole temperature range studied, 830–950 K.[25] Consequently the partial pressure of ErI₃ above the mixture will be the vapour pressure of pure ErI₃, eqn. (10),

$$P_{\text{ErI}_3} = \alpha \sum_{i=1}^{4} I_i^\circ T \tag{10}$$

where I_i° is the total ion intensity above pure ErI₃ and i refers to the ions $\text{Er}^+(i=1)$, $\text{ErI}^+(i=2)$, $\text{ErI}_2^+(i=3)$ and $\text{ErI}_3^+(i=4)$. The partial pressure of the complex can be

Table 2. Partial pressures above the NaI–ErI₃ mixture and equilibrium constants of reactions (4) and (5) versus temperature.

T /K	P_{ErI_3} /10^{-7} atm	P_{NaI} /10^{-5} atm	P_{NaErI_4} /10^{-5} atm	$P_{Na_2Er_2I_8}$ /10^{-8} atm	K_4 /10^3	K_5
830	0.96	0.52	0.34	0.80	6962	659
850	2.27	0.92	0.63	1.34	3041	329
870	5.16	1.59	1.13	2.20	1376	170
890	11.32	2.70	1.96	3.53	642	91
910	23.99	4.47	3.31	5.54	308	50
930	49.26	7.27	5.44	8.53	151	28
950	98.17	11.60	8.72	12.90	76	17

Table 3. Enthalpies and entropies of gas complexation reactions of alkali iodides with lanthanide iodides.

System	T /K	ΔH /kJ mol^{-1}	ΔS /J mol^{-1} K^{-1}	Method[a]	Ref.
CsI–CeI₃	950	−280	−134	MS	11
LiI–NdI₃	1175	−210±2	−115±3	AS	12
CsI_NdI₃	1250	−238±16	−117±12	AS	13
NaI–DyI₃	900	−197±10	−119	MS	14
CsI–DyI₃	900	−181±12	−157	MS	14
NaI–ScI₃	721	−223±2	−154±3	MS	17
NaI–ErI₃	890	−244±12	−163±12	MS	This work

[a]MS, mass spectrometry; AS, absorption spectroscopy.

derived from the intensities of all the Er-containing ions, subtracting those originating from pure ErI₃, eqn. (11),

$$P_{NaErI_4} = \alpha \left(\sum_{i=1}^{4} (I_i^m T - I_i^\circ T) \right) + \alpha \sum_{i=5}^{8} I_i^m T \qquad (11)$$

where I^m is the intensity of ions above the mixture, and when $i > 4$, i refers to the ions with Na/Er = 1, i.e. NaErI$^+$ (i=5), NaErI₂$^+$ (i=6), NaErI₃$^+$ (i=7) and NaErI₄$^+$ (i=8). The partial pressure of the complex dimer, Na₂Er₂I₈, is given by eqn. (12). The partial pressure of NaI is derived

$$P_{Na_2Er_2I_8} = \alpha I_{Na_2ErI_4}^m + T \qquad (12)$$

from the measured intensities of the ions containing only the Na cation, subtracting those which originate from the complexes. The latter can be expressed in Er-containing species intensities, since the ratio of Na/Er atoms in the complex molecule is 1/1, from eqn. (13), in which $i = 10$–12 refers to ions containing only the Na cation.
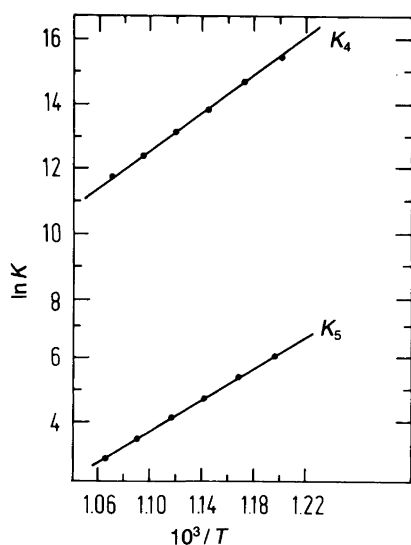

Fig. 4. Equilibrium constants for reactions (4) and (5) based on the present mass-spectrometric data.

$$P_{NaI} = \beta \sum_{i=10}^{12} I_i^m T - \alpha \left(\sum_{i=1}^{4} (I_i^m T - I_i^\circ T) \right) \qquad (13)$$

The equilibrium constants K_4 and K_5 for reactions (4) and (5) are given by eqns. (14) and (15). The partial

$$K_4 = P_{NaErI_4} / P_{NaI} P_{ErI_3} \qquad (14)$$

$$K_5 = P_{Na_2Er_2I_8} / P_{NaErI_4}^2 \qquad (15)$$

pressures and the resultant chemical reaction constants are presented in Table 2, and the temperature dependence of K_4 and K_5 is plotted in Fig. 4, in a diagram of ln K vs. 1/T. The enthalpy and entropy values derived at 890 K are: $\Delta H_4 = -244 \pm 12$ kJ mol^{-1}, $\Delta S_4 = -163 \pm 12$ J mol^{-1} K^{-1}, and $\Delta H_5 = -200 \pm 20$ kJ mol^{-1}, $\Delta S_5 = -187 \pm 17$ J mol^{-1} K^{-1}, respectively.

In Table 3 literature data from reactions similar to reaction (4) are given. The calculated enthalpy and entropy values for reaction (4) are in good agreement with the recently studied system NaI–ScI₃,[17] with $\Delta H = -223 \pm 1.6$ kJ mol^{-1} and $\Delta S = -154 \pm 2.6$ J mol^{-1} K^{-1} at 721 K. The enthalpy and entropy change of reaction (4) can be approached theoretically by the pressure-independent reaction (16). The enthalpy and entropy

$$(NaI)_2(g) + (ErI_3)_2(g) \rightleftharpoons 2 NaErI_4(g) \qquad (16)$$
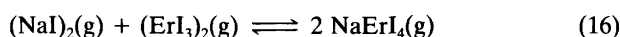
changes of this reaction are not known, but the values of the corresponding reaction with (ScI₃)₂ can be used as a qualitative approach: $\Delta H_{16} = -86.7 \pm 5.7$ kJ mol^{-1} and $\Delta S_{16} = -31.4 \pm 6.1$ J mol^{-1} K^{-1} at 736 K.[17] The thermodynamic data for the dimerization of ScI₃ are $\Delta H_1 = -189 \pm 15$ kJ mol^{-1} and $\Delta S_1 = -154.8$ J mol^{-1} K^{-1},[26] while for the dimerization of NaI they are $\Delta H_2 = -162 \pm 9$ kJ mol^{-1} and $\Delta S_2 = -112.2$ J mol^{-1} K^{-1},[27] at elevated temperatures (750–800 K). The estimated thermodynamic quantities for reaction (4) are given by eqns. (17) and (18), showing the consistency of the data.

$$\Delta H_4 = (\Delta H_{16} + \Delta H_1 + \Delta H_2)/2 = 219 \pm 29 \text{ kJ mol}^{-1} \qquad (17)$$

Table 4. Thermodynamic data for some gas complex dimerization reactions of the type $2MeMX_4(g) = Me_2M_2X_8(g)$.

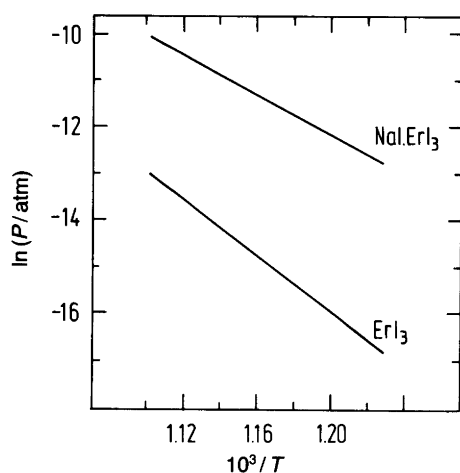| System	T /K	ΔH /kJ mol^{-1}	ΔS /J mol^{-1} K^{-1}	Method[a]	Ref.
LiAlF$_4$	946	-203 ± 14	-140	MS	4
NaAlF$_4$	910	-189 ± 10	-142	MS	4
KAlF$_4$	838	-161 ± 12	-132	MS	4
LiAlCl$_4$	508	-157 ± 2	-180 ± 3	E,MS	28
NaAlCl$_4$	573	-154 ± 2	-170 ± 4	E,MS	28
KAlCl$_4$	633	-126 ± 3	-125 ± 4	E,MS	28
LiScCl$_4$	739	-156	-126	MS	29
NaErI$_4$	890	-200 ± 20	-187 ± 17	MS	This work

[a] E, effusion; MS, mass spectrometry.

Fig. 5. Vapour-pressure enhancement for ErI$_3$ in the presence of NaI.

$$\Delta S_4 = (\Delta S_{16} + \Delta S_1 + \Delta S_2)/2 = 149 \pm 7.5 \text{ J mol}^{-1}\text{ K}^{-1} \quad (18)$$

For reactions similar to reaction (5), the literature data are inadequate to allow reasonable comparisons.[4,28,29] The apparent tendency of the entropy change to decrease towards the iodide, shown in Table 4, should be checked in the future, after a study of complex dimerization reactions in other iodide systems.

In Fig. 5 the pressure of the Er-containing species above the NaI–ErI$_3$ mixture, as well as the pressure above pure ErI$_3$, are presented. The volatility enhancement due to the complexation has been calculated to be 21 at 900 K and 50 at 825 K. This result is in good agreement with data from the systems LiI–NdI$_3$ and CsI–NdI$_3$, showing a vapour-pressure enhancement of 7.5 and 5.7 at 1100 K, respectively.[12,13] In a more recent study of the CsI–NdI$_3$ system[30] the reported vapour-pressure enhancement at 1100 K is 8.9. There is also good agreement with the system TlI–NdI$_3$,[31] with enhancement factor 22, at 1000 K.

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