

Solubility in System $Zn_2P_2O_7-(NH_4)_2P_2O_7-H_4P_2O_7-H_2O$ at 25°C

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Results of measurements at 25°C of the solubility of $Zn_2P_2O_7$ in different concentrations of ammonium pyrophosphates with constant ratios $H_4P_2O_7$ to $(NH_4)_2P_2O_7$ showed that zinc is only slightly soluble in these solutions at pH 5.25 and below, but that its solubility increases regularly with increase in concentration of ammonium pyrophosphate and with rising pH above pH 5.25. This effect is attributed to the formation of soluble zinc pyrophosphate and ammine zinc complexes, both of which increase in amount as the pH is raised.

Interest in the use of ammonium polyphosphate fertilizers as carriers for micronutrients (5, 9) prompted a study of the system $Zn_2P_2O_7-(NH_4)_2P_2O_7-H_4P_2O_7-H_2O$ at 25°C. The study was restricted to the region of major importance in fertilizer technology, that in which the mole ratio $H_4P_2O_7$ to $(NH_4)_2P_2O_7$ ranges from 0-1, and the P_2O_5 concentration ranges from about 1% to saturation.

EXPERIMENTAL

Samples were prepared by saturating ammonium pyrophosphate solutions with $Zn_2P_2O_7 \cdot 5H_2O$ or $Zn_2P_2O_7 \cdot 2H_2O$. The ammonium phosphate solutions were intended to have the weight ratios $H_4P_2O_7$ to $(NH_4)_2P_2O_7$ 0.0, 0.103, 0.241, 0.434, and 0.723. Equilibrations were made at each ratio with ammonium pyrophosphate solutions whose concentrations ranged from 1% to saturation. Because of the incongruent dissolution of the zinc pyrophosphates, the amount of solid phase at equilibrium was kept as small as practical to minimize changes in the ratio $H_4P_2O_7$ to $(NH_4)_2P_2O_7$ in the liquid phase. All the final ratios, however, were slightly different from the initial ratios, and the change in some ratios was considerable because of supersaturation making it difficult to keep the amount of solid phase at a minimum.

The pyrophosphate solutions were prepared from mixtures of crystalline $(NH_4)_2P_2O_7$, $(NH_4)_3HP_2O_7 \cdot H_2O$, and $(NH_4)_2H_2P_2O_7$. The samples, in rubber-stoppered glass bottles, were equilibrated with constant agitation for 1 to 2 weeks at $25.00 \pm 0.05^\circ C$. The pH then was measured with a commercial pH meter, and the solids were filtered off. The solid phases were identified by X-ray diffraction and by petrographic examination (4, 8) and were shown by chemical analysis to have the proper composition. The solutions were analyzed for zinc, nitrogen, and phosphorus. Zinc was determined by atomic absorption spectrophotometry (1), nitrogen was determined by distillation from NaOH solution, and phosphorus was determined by the official AOAC gravimetric quinolinium method (2).

Ammonium pyrophosphates were first crystallized as $(NH_4)_3HP_2O_7 \cdot H_2O$ from a solution of crude (about 83%) ammonium pyrophosphate (6). When the $(NH_4)_3HP_2O_7 \cdot H_2O$ was thrice recrystallized at 0°C from its aqueous solution that had been saturated at room temperature, paper chromatography (7) showed it to be 99.2% pyrophosphate; the remainder was composed of about equal parts of ortho- and tripolyphosphates.

$(NH_4)_2H_2P_2O_7$ was prepared by adjusting the pH of a 20% solution of $(NH_4)_3HP_2O_7 \cdot H_2O$ to 3.8 with the hydrogen form of Dowex 120 ion exchange resin and adding methanol to precipitate the diammonium salt.

$(NH_4)_2P_2O_7$ was prepared by neutralizing a 20% solution of

$(NH_4)_3HP_2O_7 \cdot H_2O$ with a slight excess of ammonia and then adding methanol to precipitate the tetraammonium salt.

$Zn_2P_2O_7 \cdot 5H_2O$ was prepared by slowly adding a 20% excess of $H_4P_2O_7$ to a 2.6% slurry of ZnO and allowing the slurry to equilibrate overnight. The acid was prepared by passing a solution of $Na_4P_2O_7$ through a column of the hydrogen form of

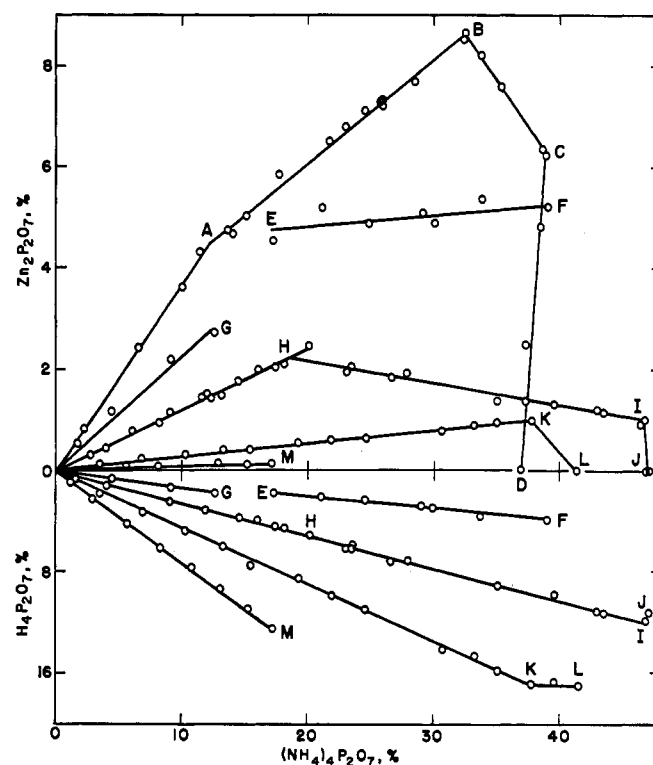


Figure 1. The system $Zn_2P_2O_7-(NH_4)_2P_2O_7-H_4P_2O_7-H_2O$ at 25°C, projected on the $Zn_2P_2O_7-(NH_4)_2P_2O_7-H_2O$ and $H_4P_2O_7-(NH_4)_2P_2O_7-H_2O$ faces. Letters on segments are those in Table I

Segment	Weight ratio $H_4P_2O_7$ to $(NH_4)_2P_2O_7$	Solid phase
OA	0.004	$Zn_3(NH_4)_2(P_2O_7)_2 \cdot 2H_2O$
AB	0.004	$Zn(NH_4)_2P_2O_7 \cdot H_2O$
BC	0.014	$Zn(NH_4)_2(P_2O_7)_2 \cdot 6H_2O$
CD	0.012	$(NH_4)_2P_2O_7$
EF	0.10	$Zn(NH_4)_2P_2O_7 \cdot H_2O$
OG	0.12	$Zn_3(NH_4)_2(P_2O_7)_2 \cdot 2H_2O$
OH	0.24	$Zn_3(NH_4)_2(P_2O_7)_2 \cdot 2H_2O$
HI	0.26	$Zn(NH_4)_2P_2O_7 \cdot H_2O$
IJ	0.25	$(NH_4)_3HP_2O_7 \cdot H_2O$
OK	0.45	$Zn_3(NH_4)_2(P_2O_7)_2 \cdot 2H_2O$
KL	0.43	$(NH_4)_3HP_2O_7$
OM	0.73	$Zn_3(NH_4)_2(P_2O_7)_2 \cdot 2H_2O + Zn(NH_4)_2(P_2O_7)_2 \cdot 2H_2O$

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Table I. System $\text{Zn}_2\text{P}_2\text{O}_7\text{--}(\text{NH}_4)_4\text{P}_2\text{O}_7\text{--H}_4\text{P}_2\text{O}_7\text{--H}_2\text{O}$ at 25°C

Segment ^a	Nominal wt ratio $\text{H}_4\text{P}_2\text{O}_7$ to $(\text{NH}_4)_4\text{P}_2\text{O}_7$	Liquid phase					Solid phase ^b
		Composition, wt %			Wt ratio $\text{H}_4\text{P}_2\text{O}_7$ to $(\text{NH}_4)_4\text{P}_2\text{O}_7$	pH	
		$(\text{NH}_4)_4\text{P}_2\text{O}_7$	$\text{Zn}_2\text{P}_2\text{O}_7$	$\text{H}_4\text{P}_2\text{O}_7$			
OA	0.004	2.33	0.843	0.005	0.002	7.77	Q
		6.68	2.43	0.043	0.006	7.34	Q
		10.2	3.61	0.073	0.007	7.50	Q
		11.6	4.27	0.027	0.002	7.40	Q
AB	0.004	13.7	4.72	0.029	0.002	7.33	R
		14.1	4.68	0.026	0.002	...	R
		15.2	5.02	0.020	0.001	7.24	R
		17.9	5.84	0.018	0.001	7.30	R
		21.9	6.52	0.041	0.002	7.45	R
		23.1	6.80	0.033	0.001	7.40	R
		24.6	7.12	0.000	0.000	7.53	R
		25.9	7.28	0.033	0.001	7.46	R
		26.0	7.19	0.031	0.001	7.47	R
		26.0	7.34	0.054	0.002	7.40	R
		28.6	7.72	0.441	0.015	7.41	R
		32.5	8.52	0.499	0.015	7.45	R
		32.3	8.69	0.459	0.014	7.41	R + S
		BC	0.014	33.9	8.22	0.643	0.019
35.5	7.62			0.632	0.018	7.65	S
38.7	6.35			0.118	0.003	7.70	S
CD	0.012	37.1	0.00	0.710	0.019	8.13	W
		37.5	2.49	0.796	0.020	8.05	W
		37.7	1.37	0.372	0.010	8.15	W
		37.9	3.46	0.522	0.013	7.97	W
		38.6	4.83	0.479	0.012	7.87	W
		39.0	6.27	0.000	0.000	7.70	W
EF	0.10	17.4	4.53	1.68	0.097	6.36	R
		21.2	5.20	2.08	0.098	6.36	R
		24.7	4.87	2.14	0.087	6.48	R
		29.2	5.11	2.84	0.097	6.55	R
		30.1	4.87	2.89	0.094	6.70	R
		33.9	5.39	3.62	0.107	6.57	R
		39.2	5.24	3.93	0.100	6.74	R
OG	0.12	0.703	0.116	0.114	0.162	6.91	Q
		2.00	0.466	0.213	0.106	6.74	Q
		4.74	1.12	0.542	0.114	6.48	Q
		9.27	2.14	1.08	0.117	6.36	Q
		12.7	2.70	1.55	0.121	6.37	Q
OH	0.24	0.703	0.036	0.118	0.168	6.33	Q
		0.834	0.058	0.190	0.228	6.13	Q
		1.68	0.140	0.445	0.264	6.23	Q
		2.90	0.300	0.775	0.267	6.13	Q
		4.22	0.419	1.06	0.251	5.97	Q
		6.15	0.730	1.52	0.247	5.96	Q
		8.30	0.878	2.06	0.248	5.84	Q
		9.09	1.09	2.16	0.238	5.86	Q
		11.8	1.44	2.85	0.242	5.81	Q
		12.0	1.46	2.86	0.239	5.76	Q
		12.3	1.37	2.78	0.226	5.75	Q
		14.6	1.74	3.52	0.241	5.77	Q
		16.1	1.97	3.80	0.236	5.75	Q
17.5	2.00	4.22	0.241	5.75	Q		
18.2	2.08	4.38	0.241	5.68	Q		
20.2	2.45	4.94	0.245	5.71	Q		
HI	0.26	23.2	1.93	6.07	0.262	5.64	R
		23.5	2.02	6.01	0.256	5.72	R
		23.8	2.06	5.84	0.245	5.70	R
		26.8	1.84	7.13	0.266	5.77	R
		28.0	1.91	7.02	0.250	5.60	R
		35.1	1.40	8.91	0.254	5.67	R
		39.7	1.35	9.84	0.247	5.67	R
		43.1	1.24	11.1	0.258	5.64	R
		43.6	1.15	11.2	0.257	5.84	R
		46.9	1.03	11.9	0.254	5.02	R + X
IJ	0.25	46.6	0.908	11.8	0.253	5.94	X
		46.8	0.992	11.6	0.248	5.78	X
		47.0	0.00	11.6	0.247	5.97	X
		47.2	0.011	11.2	0.238	5.88	X

(Continued on next page)

Table I. (Continued)

Segment ^a	Nominal wt ratio H ₄ P ₂ O ₇ to (NH ₄) ₄ P ₂ O ₇	Liquid phase						Solid phase ^b	
		Composition, wt %			pH	Wt ratio H ₄ P ₂ O ₇ to (NH ₄) ₄ P ₂ O ₇			
		(NH ₄) ₄ P ₂ O ₇	Zn ₂ P ₂ O ₇	H ₄ P ₂ O ₇					
OK	0.45	0.703	0.006	0.329	0.468	5.67	Q		
		1.44	0.023	0.649	0.451	5.50	Q		
		3.60	0.075	1.65	0.458	5.48	Q		
		6.98	0.168	3.15	0.452	5.28	Q		
		10.4	0.262	4.58	0.440	5.19	Q		
		13.4	0.356	5.93	0.443	5.12	Q		
		15.5	0.393	7.41	0.478	5.02	Q		
		19.4	0.515	8.43	0.435	5.00	Q		
		22.0	0.599	9.84	0.447	4.93	Q		
		24.7	0.655	11.0	0.447	4.91	Q		
		30.8	0.805	14.2	0.462	4.74	Q		
		33.3	0.899	14.6	0.438	4.69	Q		
		35.1	0.992	15.8	0.449	4.68	Q		
		KL	0.43	37.9	0.992	16.9	0.447	4.65	Y
				39.7	0.543	16.8	0.423	4.65	Y
41.6	0.000			17.1	0.411	4.72	Y		
OM	0.73	0.571	0.014	0.456	0.798	3.37	Q		
		1.190	0.005	0.864	0.725	3.82	Q		
		2.90	0.026	2.20	0.758	3.44	Q		
		5.71	0.022	4.11	0.719	3.50	Q		
		8.30	0.045	6.01	0.725	3.47	Q + T		
		10.8	0.058	7.70	0.713	3.60	Q + T		
		13.0	0.084	9.29	0.712	3.57	Q + T		
		15.3	0.072	11.0	0.717	3.47	Q + T		
		17.3	0.107	12.4	0.717	3.56	T		

^a Segments of isotherms in Figure 1. ^b Determined microscopically. Q = Zn₃(NH₄)₂(P₂O₇)₂·2H₂O; R = Zn(NH₄)₂P₂O₇·H₂O; S = Zn(NH₄)₆(P₂O₇)₂·6H₂O; T = Zn(NH₄)₂(P₂O₇)₂·2H₂O; W = (NH₄)₄P₂O₇; X = (NH₄)₃HP₂O₇·H₂O; Y = (NH₄)₂H₂P₂O₇.

Dowex 120 ion exchange resin, and the effluent was dripped into the ZnO slurry to minimize hydrolysis. Any orthophosphate formed by hydrolysis was kept in solution by the excess acid. Zn₂P₂O₇·2H₂O was prepared by simultaneously adding stoichiometric amounts of dilute (NH₄)₄P₂O₇ solution and dilute ZnSO₄ solution into a vigorously stirred reaction vessel. Zn₂P₂O₇·2H₂O was thus precipitated from a solution very dilute with respect to zinc and pyrophosphate ions as easily filtered crystals of high purity.

RESULTS AND DISCUSSION

The compositions and pH of the equilibrated solutions and the identification of the corresponding solid phases are shown in Table I. Solutions with ratios H₄P₂O₇ to (NH₄)₄P₂O₇ that differed from the means by more than two standard deviations were omitted. The concentration of H₄P₂O₇ was obtained by difference, so that the ratio H₄P₂O₇ to (NH₄)₄P₂O₇ contains all the analytical errors. As a result, the inclusion of data from only solutions with constant ratios H₄P₂O₇ to (NH₄)₄P₂O₇ served both to eliminate data with large analytical errors and to provide a means for defining the solubility model.

The solubility diagram constructed from the data of Table I and shown in Figure 1 consists of orthogonal plots of the concentrations of Zn₂P₂O₇ and H₄P₂O₇ vs. concentration of (NH₄)₄P₂O₇ at different constant ratios H₄P₂O₇ to (NH₄)₄P₂O₇. The figure represents projections from the surface of the three-dimensional solubility model along lines of constant ratio H₄P₂O₇ to (NH₄)₄P₂O₇ onto the two faces Zn₂P₂O₇-(NH₄)₄P₂O₇-H₂O and H₄P₂O₇-(NH₄)₄P₂O₇-H₂O.

Intersections of the practically straight portions of the curves in Figure 1 represent points at which two solid phases are in equilibrium with a saturated solution. These points lie on curves generated by the intersection of the different surfaces of the three-dimensional isotherm of the four-component system and thus are univariant points. The data are too meager to

locate lines of surface intersections, with the possible exception at weight ratio H₄P₂O₇ to (NH₄)₄P₂O₇ of 0.716 where two solid phases are present from about 5 to 15% (NH₄)₄P₂O₇. Since it is improbable, however, that any two surfaces will intersect along any particular line of constant ratio H₄P₂O₇ to (NH₄)₄P₂O₇, the presence of the two solid phases may indicate failure to attain equilibrium.

The solutions in Table I with ratios H₄P₂O₇ to (NH₄)₄P₂O₇ of 0.10 and 0.12 were intended to have the same ratio, 0.103, but experimental difficulties caused by supersaturation resulted in different ratios. Hydrolysis of the pyrophosphate in the concentrated region of the most acidic solutions was extensive—up to 10% in 2 weeks—and data for solutions containing more than 18% (NH₄)₄P₂O₇ were omitted.

When the ratio H₄P₂O₇ to (NH₄)₄P₂O₇ is zero the isotherm of the resulting three-component system can be shown on a two-dimensional plot. The uppermost curves in Figure 1 have ratios near zero and so can be considered as the isotherm for the system Zn₂P₂O₇-(NH₄)₄P₂O₇-H₂O. Intersections of the different straight segments of this isotherm then represent invariant points.

From Figure 1 it is seen that the solubility of Zn₂P₂O₇ varies practically linearly with the concentration of (NH₄)₄P₂O₇ at each ratio H₄P₂O₇ to (NH₄)₄P₂O₇ over the range of solution compositions in equilibrium with each solid phase. Since linearity of solubility curves is somewhat unusual, the statistical significance of the linear relationships was determined. The linear regression equation

$$Z = AN + B \quad (1)$$

where

$$\begin{aligned} Z &= \text{concentration, wt } \%, \text{ of Zn}_2\text{P}_2\text{O}_7 \\ N &= \text{concentration, wt } \%, \text{ of (NH}_4\text{)}_4\text{P}_2\text{O}_7 \\ A \text{ and } B &= \text{constants} \end{aligned}$$

was fitted to the data for each linear section by the method of least squares. The results are shown in Table II. With one

Table II. Effect of Concentration of $(\text{NH}_4)_4\text{P}_2\text{O}_7$ on Solubility of $\text{Zn}_2\text{P}_2\text{O}_7$

Solid phase	Segment ^a	Nominal wt ratio $\text{H}_4\text{P}_2\text{O}_7$ to $(\text{NH}_4)_4\text{P}_2\text{O}_7$	Range of concn of $(\text{NH}_4)_4\text{P}_2\text{O}_7$, wt %	Regression parameter ^b		Correlation coefficient	Standard error of estimate ^c
				A	B		
$\text{Zn}_3(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	OA	0.004	2.3-11.6	0.363	0.00	0.999	0.077
	OG	0.12	0.7-12.7	0.217	0.00	0.997	0.095
	OH	0.24	0.7-20.2	0.120	0.00	0.992	0.11
	OK	0.45	0.7-35.1	0.028	0.00	0.999	0.019
$\text{Zn}_3(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O} + \text{Zn}(\text{NH}_4)_2\text{H}_4(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$	OM	0.72	0.5-15.3	0.006	0.00	0.962	0.010
$\text{Zn}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$	AB	0.004	13.7-32.3	0.206	1.95	0.996	0.12
	EF	0.10	17.4-39.2	0.026	4.30	0.671	0.24
	HI	0.26	23.2-46.9	-0.042	2.98	-0.986	0.07
$\text{Zn}(\text{NH}_4)_6(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$ $(\text{NH}_4)_4\text{P}_2\text{O}_7$	BC	0.014	32.3-38.7	-0.370	20.7	-0.998	0.072
	CD	0.012	37.1-39.0	3.12	-1.16	0.957	0.74

^a Segments of isotherms in Figure 1 and Table I. ^b As in Equation 1. ^c In units of concentration, wt %, of $\text{Zn}_2\text{P}_2\text{O}_7$ in solution.

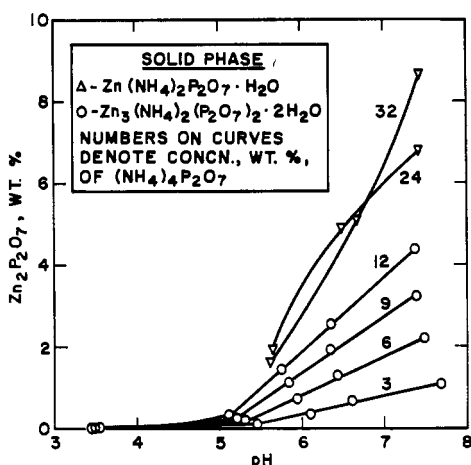


Figure 2. Effect of pH on solubility of $\text{Zn}_2\text{P}_2\text{O}_7$ in $(\text{NH}_4)_4\text{P}_2\text{O}_7$ solutions

exception, the correlation coefficients ranged from about 0.96 to 0.999 and their significance ranged from 99% to more than 99.9%, indicating that the linear relationships were real. The exception had a regression coefficient of 0.671 which is high enough to denote a linear trend, but the coefficient was based on only a few scattered data.

The unit of the standard error of the estimate is, for each straight segment, the amount, in weight percent, of $\text{Zn}_2\text{P}_2\text{O}_7$ dissolved, and its variability reflects either the experimental variability or the marked change in the solubility of $\text{Zn}_2\text{P}_2\text{O}_7$ with a small change in concentration of $(\text{NH}_4)_4\text{P}_2\text{O}_7$, as in the last entry in Table II.

In Figure 2 is shown the effect of pH on the solubility of $\text{Zn}_2\text{P}_2\text{O}_7$ at different $(\text{NH}_4)_4\text{P}_2\text{O}_7$ concentrations of solutions in which $\text{Zn}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ and $\text{Zn}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ are the saturating solid phases. $\text{Zn}_2\text{P}_2\text{O}_7$ is sparingly soluble at pH 3.5 [about the pH of $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$ solutions] even in concentrated pyrophosphate solutions, and its solubility increases

only slightly with rising pH up to about pH 5.25. Above pH 5.25, however, there is a marked and almost linear increase in the solubility of $\text{Zn}_2\text{P}_2\text{O}_7$ with rising pH.

Although $\text{Zn}_2\text{P}_2\text{O}_7$ is quite insoluble in water, it readily dissolves in pyrophosphate solutions in amounts that increase with increasing concentration of pyrophosphate, an effect attributed to the ability of polyphosphates to form soluble complexes with almost all cations (10). The effect of rising pH is to increase the solubility of $\text{Zn}_2\text{P}_2\text{O}_7$, which indicates that the most stable complexes are those of Zn^{2+} ions with $\text{P}_2\text{O}_7^{4-}$ or $\text{HP}_2\text{O}_7^{3-}$ ions because the concentration of these ions increases with rise in pH.

It should be noted also that many water-insoluble zinc salts are soluble in aqueous ammonia because of the formation of ammine zinc complexes (3). These complexes may exist in the pyrophosphate solutions with high pH in the present study as a result of the hydrolysis of the ammonium ion, and hence would also contribute to the solubility of zinc.

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