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ANALYSIS OF VAPORIZATION OF
LIQUID URANIUM, METAL, AND CARBON
SYSTEMS AT 9000° AND 10,000° R

by L. Kaufman and E. T. Peters

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ANALYSIS OF VAPORIZATION OF LIQUID URANIUM, METAL,

AND CARBON SYSTEMS AT 9000° AND 10,000^O R

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FOREWORD

Research related to advanced nuclear rocket propulsion

is described herein. This work was performed under NASA

Contract Number NAS 3-8036 with Mr. Maynard F. Taylor,

Nuclear Reactor Division, NASA Lewis Research Center as

Technical Manager.

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1. INTRODUCTION AND SUMMARY

An analysis has been performed to identify candidate liquid uranium bearing materials systems which could function as heat exchangers for hydrogen gas at 100 atm. pressure and temperatures between 8000-10,000°R. In the first report of this analysis, vaporization characteristics of liquid Zr-C-U and Nb-C-U alloys were calculated in order to define compositional limits where injection of heavy atoms into the hydrogen via vaporization would be minimized. These computations indicated that at 9000°R the Nb-C-U case was superior to the Zr-C-U case; the former offered a range of compositions over which the average molecular weights (in the gas) were no more than 50% larger than that of hydrogen. At 10,000°R, however, the best compositions in the Nb-C-U system indicated average gas molecular weights which were two and a half times that of hydrogen. In the present analysis, the system W-C-U was also considered (the isotope W^{184} having an acceptable capure cross section). This system yielded lower gas molecular weights than either the zirconium or niobium cases discussed in the earlier report. At 10,000°R, for example, liquid alloy compositions can be chosen which correspond to gaseous molecular weights only seventy per cent larger than hydrogen.

The interaction between hydrogen and the various liquid components has been considered by examining the free energies of formation of common gaseous hydrocarbons and metal hydrides. In the temperature range of interest, acetylene is the only compound which has a negative free energy of formation under standard conditions. Utilization of this free energy of formation data permits computation of an upper limit for carbon activity in the liquid alloy, below which formation of acetylene should not occur. Calculation of these limits has been performed

for each of the systems in question at 9000 and 10,000°R. Specification of these compositional limits provides an additional systems constraint.

In order to evaluate the time stability of these systems with respect to compositional changes resulting from vaporization, computations of Langmuir evaporation rates were performed. Ternary congruency conditions were not predicted in any of the systems considered. The calculations indicate that zirconium and niobium would be lost preferentially in the Nb-C-U and Zr-C-U cases while carbon would be lost preferentially in the W-C-U case. Mass loss rates through hydrogen transport and through vaporization were compared for flow rates of one hundred feet/sec through a ten foot long-4 inch diameter pipe. In all of the systems under consideration at 9000 and 10,000°R, the mass loss rate via hydrogen transport is computed to be about 1000 times less than the vaporization rate.

The principle limitation of the engine system is the reported triple point of graphite at about 100 atmospheres and 7200°R. Although a substantial discrepency exists between the current vapor pressure-temperature curve for graphite and the experimental liquid/solid equilibrium line, it seems unlikely that the latter is seriously in error. As a consequence, unless a means is devised for insulating the liquid alloy from a solid graphite back-up tube, substained operation above 7200°R will not be feasible.

2. THERMODYNAMIC ANALYSIS OF W-C-U SYSTEM

Calculation of the vapor pressures over various liquid alloys of W-C-U and of the average molecular weight of gaseous W-C-U-H mixtures has been carried out according to the scheme used earlier ($\underline{1}^*$).

The imposed constraints for a reference ternary system U-X_1-X_2 are:

a) The system, when heated to temperatures between 8,000 - 10,000°R in contact with 100 atm. of hydrogen gas, will exhibit a partial pressure of uranium less than or equal to 0.016 atm.

b) None of the components considered for inclusion (i.e., X_1 and X_2) shall have a nuclear capture cross section greater than 5 barns.

c) The selection of X_1 and X_2 will be subject to the requirement that the average molecular weight of $U + X_1 + X_2$ plus hydrogen at temperatures between 8,000°R and 10,000°R shall not exceed that of pure hydrogen by a factor which is more than 1.5.

d) The atomic fraction of uranium in the alloy will be constrained to lie between 0.001 and 0.02.

In all cases, it is assumed that the liquid phase can be approximated by a regular solution. In addition, it is assumed that vapors of U, X_1, X_2 and H do not interact, with one exception, C_2H_2, which will be discussed later.

The necessary thermodynamic formulation for a ternary system has been given earlier (see Eqs. (5) and (6), Ref. 1). The interaction parameters (L factors) required for these equations were calculated by appropriate equilibration of liquid and solid phases at a fixed composition. (See Appendix A.)

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* Underscored numbers in parentheses indicate References given at the end of this report.

From the average of interaction parameters calculated for the β, β', and σ solid phases,

$$L_{W-C} \approx -18,100 \text{ cal/mol.} \tag{1a}$$

The W-U system forms a miscibility gap. Appropriate calculation yields

$$L_{W-U} \approx +10,100 \text{ cal/mol.} \tag{1b}$$

and

$$L_{U-C} \approx -36,000 \text{ cal/mol.} \underline{(2)} \tag{1c}$$

With use of Eq. (5), Ref. 1, the equilibrium partial pressures for the W-C-U ternary system are:[*]

$$\log (p_W/p_W{}^o) \approx \log (1-x) -18,100x^2/4.575T \tag{2a}$$

$$\log a_C \approx \log x -18,100 (1-x)^2/4.575T^{[**]} \tag{2b}$$

$$\log (p_U/p_U{}^o) \approx \log y + (1/4.575T) \{-18,100\ x^2$$

$$-28,000x (1-y) + 10,100 (1-y)^2 \} \tag{2c}$$

where x = atomic fraction of carbon, y = atomic fraction of uranium, T is in ^oK, and log is to base 10.

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[*] According to the initial conditions, the atomic fraction of uranium is constrained to lie between 0.001 and 0.02, i.e., y_{max} = 0.02. The y terms in Eqs. (5a) and (5b), Ref. 1, become very small and can be ignored.

[**] The total partial pressure of carbon (p_C(total)) is taken as the vapor pressure of the monomer C plus the pressures of the polymers C_2, C_3, C_4, and C_5. For the general reaction nC (s) $\rightleftharpoons C_n$ (v), one determines the partial pressure of the n polymer from the expression

$$p_{C_n} = a_C^n\ p_{C_n}^o$$

The pressures of the polymers over pure carbon are listed in Appendix A, Ref. 1.

In addition to the foregoing, it is necessary to consider the possible interactions of hydrogen with the components, U, Zr, Nb, W and C to form stable hydrides. In the case of the abovementioned metals, little stability is observed at elevated temperatures. However, carbon does form quite a number of hydrocarbons which are stable as gases and could provide an additional means of mass loss. Recently, Jefferies and McKerrel (3) have reviewed the free energies of formation of hydrocarbons and provide the following convenient table of results:

Hydrocarbon	Reaction	Free Energy of Formation cal/mole
Methane	$1/2C + H_2 = 1/2CH_4$	$-\ 9,620 + 12.75T\ (^\circ K)$
Ethane	$2/3C + H_2 = 1/3C_2H_6$	$-\ 7,760 + 16.60T$
Propane	$3/4C + H_2 = 1/4C_3H_8$	$-\ 7,140 + 18.67T$
n-Butane	$4/5C + H_2 = 1/5C_4H_{10}$	$-\ 6,900 + 19.89T$
Ethylene	$C + H_2 = 1/2C_2H_4$	$+\ 5,260 + 9.01T$
Propylene	$C + H_2 = 1/3C_3H_6$	$+\ \ \ \ 590 + 13.95T$
1-Butane	$C + H_2 = 1/4C_4H_8$	$-\ \ \ \ 820 + 16.67T$
Acetylene	$2C + H_2 = \ \ \ \ C_2H_2$	$+\ 53,710 - 12.97T$
Propyne	$3/2C2H_2 = 1/2C_3H_4$	$+\ 21,340 + 5.77T$
1-Butyne	$4/3C + H_2 = 1/3C_4H_6$	$+\ 12,350 + 12.06T$

Reference to this summary for temperatures in the range of current interest (3500 to 5500°K) indicates that acetylene gas presents the only gaseous hydrocarbon with sufficient stability to remove carbon from solutions in the liquid alloys. All of the other hydrocarbons exhibit positive free energies of formation at the temperatures in question.

Jeffries and McKerrel (3) report the free energy of formation of acetylene, C_2H_2, to be:

$$\Delta F_{C_2H_2} = 53,710 - 12.97 \, T(^{o}K)$$

According to the JANAF Tables, 31 March 1961:

$$\Delta F^{f}_{C_2H_2} \, (9,000^{o}R) = -8,715 \text{ cal/mole}$$

$$\Delta F^{f}_{C_2H_2} \, (10,000^{o}R) = -15,436 \text{ cal/mole}$$

For the reaction

$$2 \, C \text{ (liquid solution)} + H_2 \text{ (100 atm.)} \rightarrow C_2H_2 \text{ (1 atm.)}$$
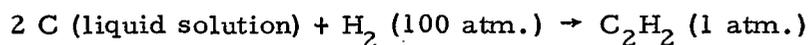
one has

$$\Delta F_{C_2H_2} = -RT \ln (P_{C_2H_2}/a_C^2 P_{H_2}) \doteq RT \ln 100 \, a_C^2$$

and, with rearrangement

$$\log a_C \, (C_2H_2) = \left(\frac{\Delta F^{f}_{C_2H_2} - 4.6 \, RT}{4.6 \, RT}\right) \qquad (3)$$

Eq. (2b) will therefore apply without restriction for values of $x \lesssim x^{*}$ where

$$\log a_C \text{ (liquid solution)} \lesssim \log a_C(C_2H_2) \qquad (4)$$

Values of $\log p^{o}$ vs. T have been given for carbon and uranium in Ref. 1. The values for tungsten are given in Table 1. The partial pressures of W and C were calculated as a function of x at 9,000 and 10,000^{o}R according to Eqs. (2a) and (2b). The results are presented in Table 2 and Figures 1 and 2. The partial pressure of uranium and the average

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molecular weight of the gaseous mixtures W-C-U-H as functions of x for y = 0.001, 0.01 and 0.02 are given in Tables 3 and 4 and are plotted in Figures 3 and 4. The critical values of x which satisfy Eq. (4), i. e., x^* (together with those for the Zr-C-U-H and Nb-C-U-H systems) are given in Table 5 and are indicated on Figures 1-4. These figures are therefore valid for values of x = 0 to x^*.

The average molecular weight of the gaseous mixture is less than 1.5 M_H (Constraint c) for all compositions where x < 0.6 at 9,000°R, but is greater than 1.5 M_H for all compositions at 10,000°R. The W-C-U system appears more favorable than either the Nb-C-U or Zr-C-U systems previously studied, primarily as a result of the lower vapor pressure of tungsten.

TABLE 1

THE VAPOR PRESSURE OF TUNGSTEN
AS A FUNCTION OF TEMPERATURE*

T-^{o}K	T-^{o}R	log p_W^o
3,000	5,400	-6.97
3,200	5,760	-6.04
3,400	6,120	-5.22
3,600	6,480	-4.49
3,800	6,840	-3.86
4,000	7,200	-3.30
4,100	7,380	-3.04
4,200	7,560	-2.79
4,300	7,740	-2.56
4,400	7,920	-2.33
4,500	8,100	-2.18
4,600	8,280	-1.91
4,700	8,460	-1.72
4,800	8,640	-1.53
4,900	8,820	-1.35
5,000	9,000	-1.17
5,100	9,180	-1.00
5,200	9,360	-0.85
5,300	9,540	-0.69
5,400	9,720	-0.54
5,500	9,900	-0.40
5,555	10,000	-0.32
5,600	10,080	-0.26
5,700	10,260	-0.13

*   JANAF Tables, December 31, 1961.

TABLE 2

CALCULATION PARAMETERS FOR THE PARTIAL PRESSURES OF TUNGSTEN AND CARBON OVER W-C ALLOYS AT 9000 AND 10,000°R

a) 9000°R

x	x^2	$\log(1-x)$	$\log(p_W/p_W^o)$	(p_W/p_W^o)	p_W	$\log p_W$
0.01	10^{-4}	-0.0044	-0.0045	0.9897	0.0669	-1.175
0.10	0.01	-0.0458	-0.0538	0.8835	0.0597	-1.224
0.20	0.04	-0.0969	-0.1286	0.7437	0.0503	-1.298
0.30	0.09	-0.1549	-0.2261	0.5932	0.0402	-1.396
0.40	0.16	-0.2219	-0.3485	0.4482	0.0303	-1.519
0.50	0.25	-0.3010	-0.4988	0.3171	0.0214	-1.670
0.60	0.36	-0.3979	-0.6828	0.2076	0.0140	-1.854
0.70	0.49	-0.5229	-0.9106	0.1229	0.0083	-2.081
0.80	0.64	-0.6990	-1.2634	0.0558	0.0038	-2.481
0.90	0.81	-1.0000	-1.6409	0.0228	0.0015	-2.824
0.99	0.98	-2.0000	-2.7754	0.0017	0.0001	-4.000

b) 10,000°R

x	$\log(p_W/p_W^o)$	(p_W/p_W^o)	p_W	$\log p_W$
0.01	-0.0045	0.9897	0.4741	-0.325
0.10	-0.0529	0.8854	0.4241	-0.378
0.20	-0.1254	0.7492	0.3589	-0.445
0.30	-0.2190	0.6040	0.2893	-0.539
0.40	-0.3358	0.4615	0.2210	-0.656
0.50	-0.4790	0.3319	0.1590	-0.799
0.60	-0.6543	0.2217	0.1062	-0.974
0.70	-0.8719	0.1343	0.0643	-1.192
0.80	-1.1557	0.0699	0.0335	-1.476
0.90	-1.5769	0.0265	0.0127	-1.897
0.99	-2.6980	0.0020	0.0096	-3.018

TABLE 2 (Cont'd.)

CALCULATION PARAMETERS FOR THE PARTIAL PRESSURES OF TUNGSTEN AND CARBON OVER W-C ALLOYS AT 9000 AND 10,000°R

c) $9000°R$

x	a_c	p_C	p_{C_2}	p_{C_3}	p_{C_4}	p_{C_5}	$p_C(T)$	$\log p_C(T)$
0.01	0.0017	0.0080					0.008	-2.097
0.10	0.0228	0.1072	0.0067	0.0003			0.114	-0.943
0.20	0.0558	0.2623	0.0401	0.0043			0.307	-0.513
0.30	0.1229	0.5776	0.1946	0.0467	0.0008	0.0002	0.820	-0.086
0.40	0.2076	0.9757	0.5556	0.2246	0.0066	0.0020	1.765	+0.247
0.50	0.3171	1.4904	1.2961	0.8002	0.0359	0.0169	3.640	0.561
0.60	0.4482	2.1065	2.5893	2.2598	0.1432	0.0949	7.194	0.857
0.70	0.5942	2.7927	4.5511	5.2657	0.4425	0.3884	13.440	1.128
0.80	0.7437	3.4954	7.1293	10.3243	1.0860	1.1949	23.230	1.366
0.90	0.8835	4.1525	10.0615	17.3097	2.1630	2.8261	36.513	1.562
0.99	0.9897	4.6516	12.6259	24.3324	3.4060	4.9852	50.005	1.699

d) $10,000°R$

x	a_c	p_C	p_{C_2}	p_{C_3}	p_{C_4}	p_{C_5}	$p_C(T)$	$\log p_C(T)$
0.01	0.0020	0.051					0.051	-1.292
0.10	0.0265	0.681	0.061				0.742	-0.130
0.20	0.0699	1.796	0.426	0.049	0.001		2.272	0.356
0.30	0.1343	3.452	1.571	0.351	0.011	0.002	5.387	0.731
0.40	0.2217	5.698	4.281	1.581	0.082	0.027	11.669	1.067
0.50	0.3319	8.530	9.595	5.301	0.411	0.202	24.039	1.381
0.60	0.4615	11.861	18.551	14.252	1.538	1.049	47.251	1.674
0.70	0.6040	15.523	31.776	31.951	4.512	4.023	87.785	1.943
0.80	0.7492	19.254	48.889	60.977	10.681	11.826	151.627	2.180
0.90	0.8854	22.755	68.280	100.643	20.833	27.260	239.771	2.380
0.99	0.9897	25.435	85.315	140.566	32.525	47.572	331.413	2.520
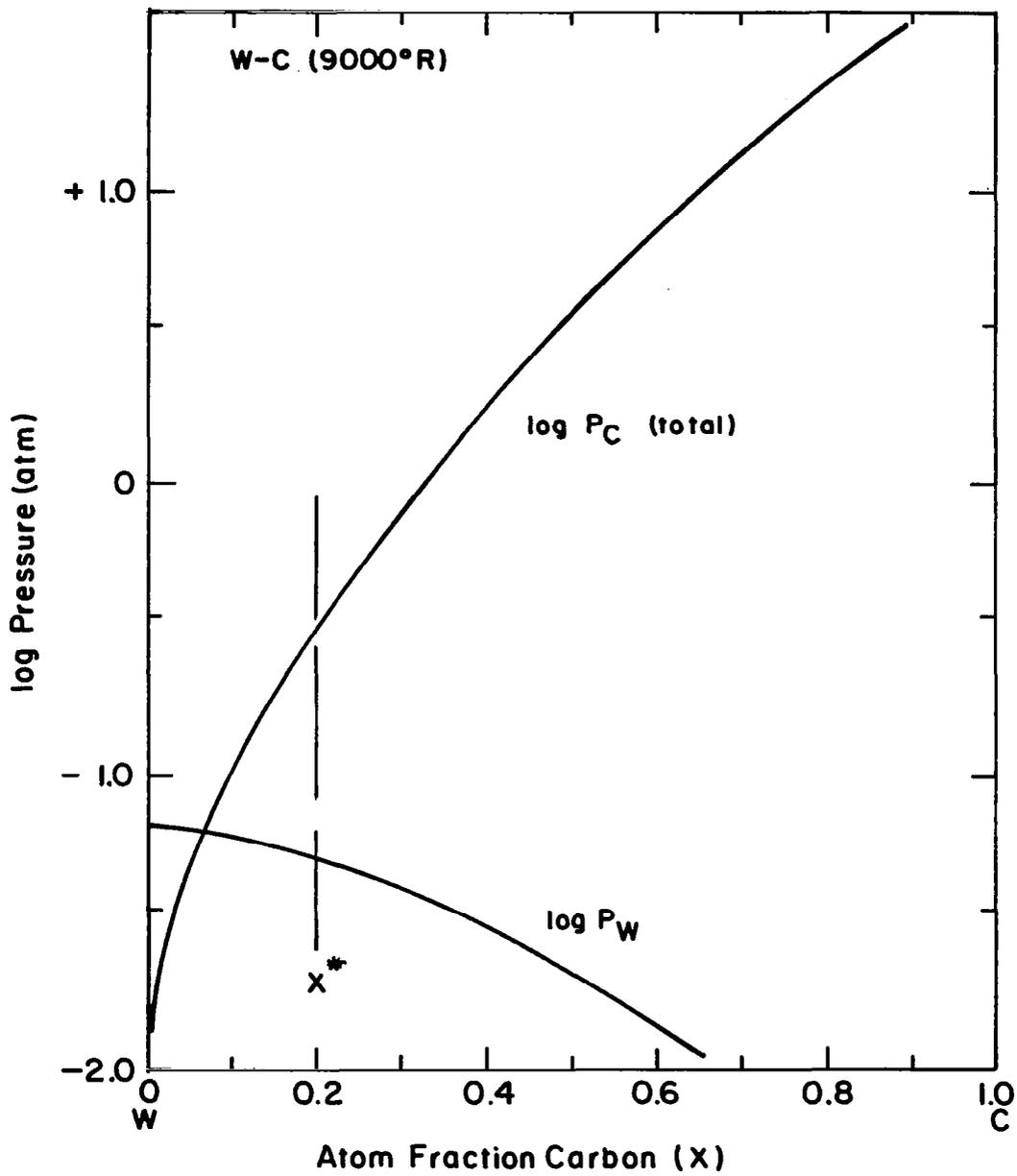
Figure 1.   The Partial Pressures of Tungsten and Carbon at $9,000^{\circ}R$ as a Function of Alloy Composition.
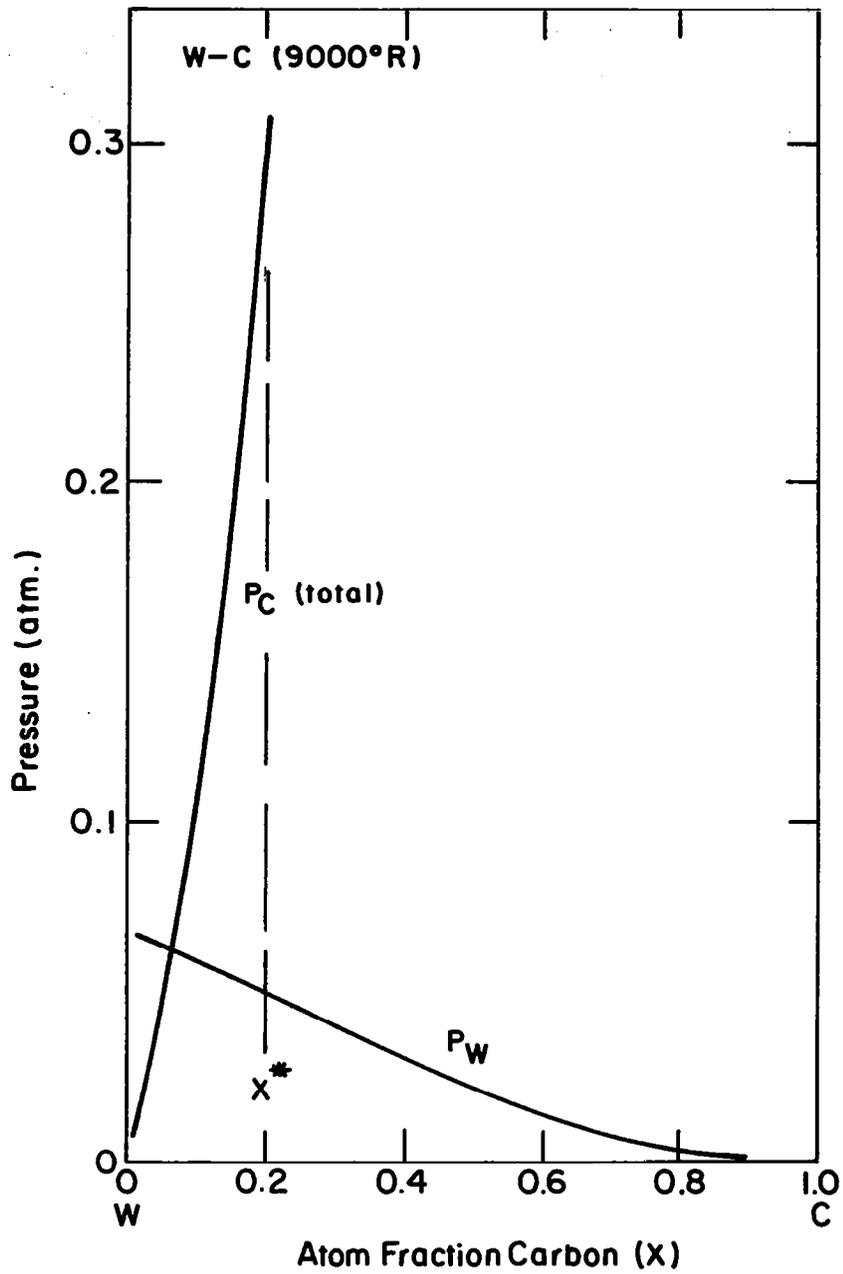
Figure 1.   (Continued)
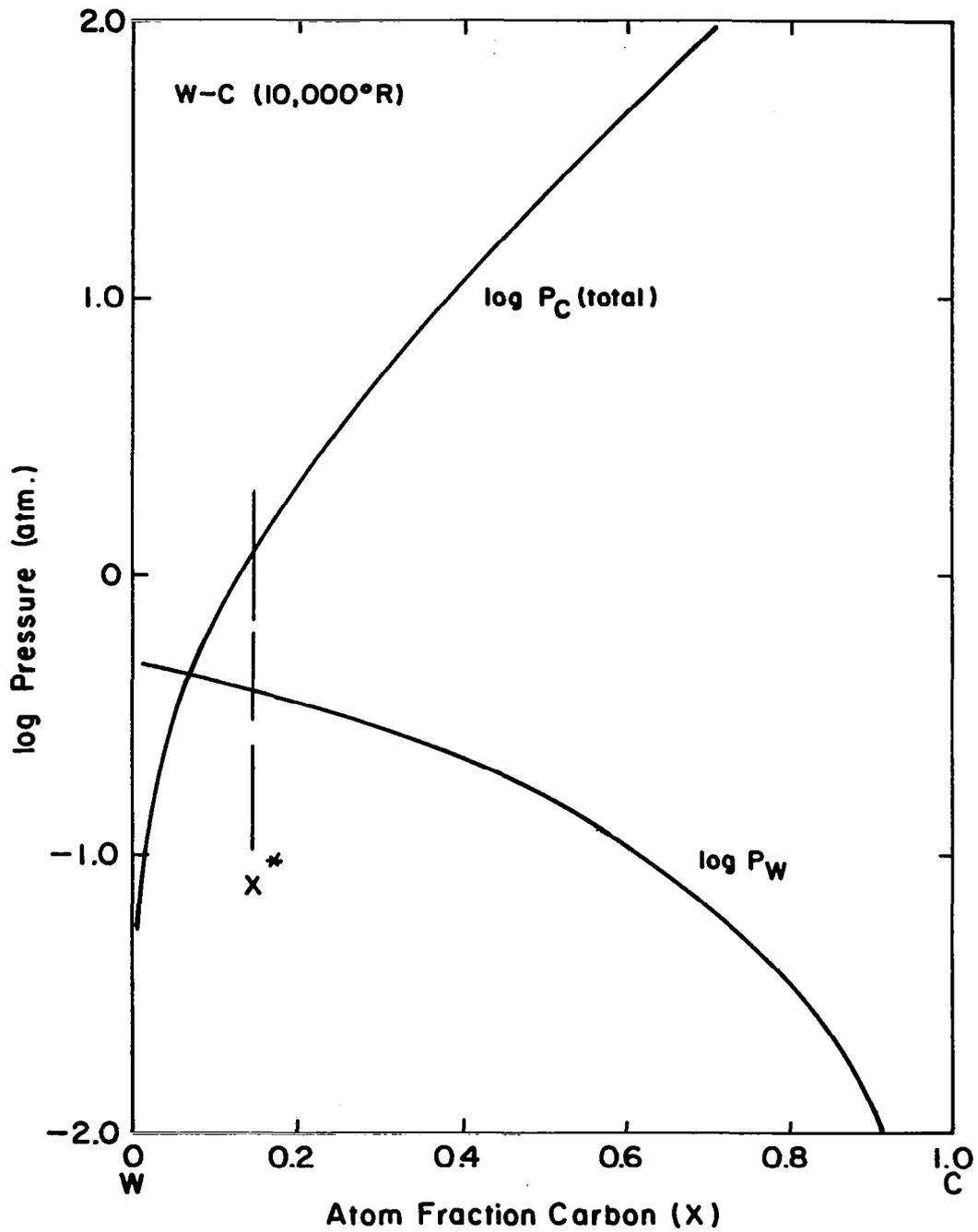
Figure 2.   The Partial Pressures of Tungsten and Carbon at 10,000°R as a Function of Alloy Composition.

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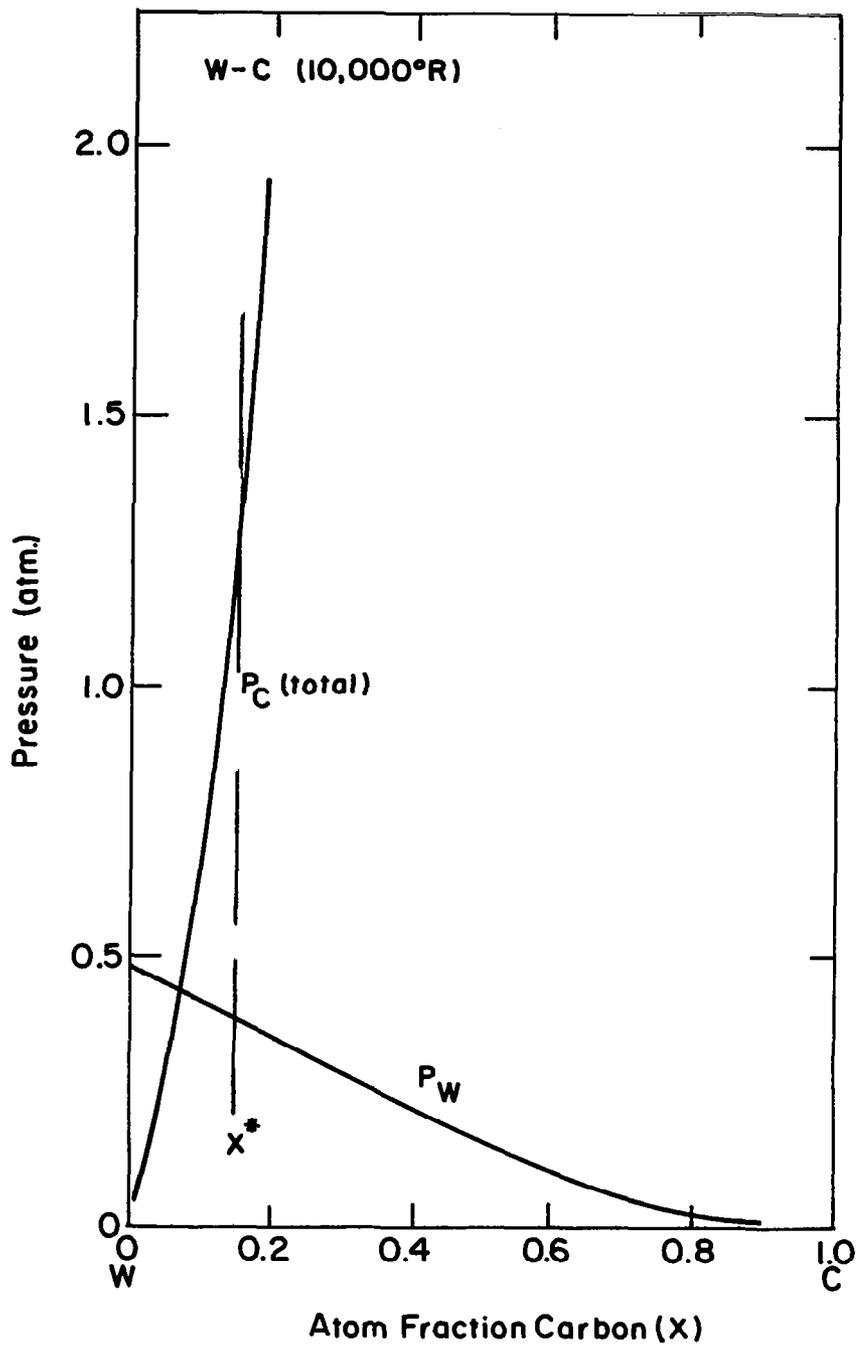
Figure 2.   (Continued)

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TABLE 3

THE PARTIAL PRESSURE OF URANIUM OVER W-C-U ALLOYS AND THE AVERAGE MOLECULAR WEIGHTS OF W-C-U-H GASEOUS MIXTURES AT 9000° R

	x	$\bar{F}^L_{E-U}$	$\log(p_U/p_U^o)$	$(p_U/p_U^o) \times 10^3$	p_U [8]	$\tilde{M}$
$y = 0.001$	0.01	+0.424	-2.574	2.667	0.0125	1.6870
	0.10	+0.311	-2.689	2.046	0.0096	1.6780
	0.20	+0.161	-2.859	1.384	0.0065	1.6736
	0.30	+0.004	-2.996	1.009	0.0047	1.7038
	0.40	-0.174	-3.174	0.669	0.0031	1.7781
	0.50	-0.367	-3.367	0.430	0.0020	1.9450
	0.60	-0.576	-3.576	0.265	0.0012	
$y = 0.01$	0.01	+0.421	-1.579	26.36	0.1233	1.9450
	0.10	+0.304	-1.696	20.14	0.0942	1.8749
	0.20	+0.159	-1.841	14.42	0.0674	1.8151
	0.30	-0.002	-2.002	9.953	0.0466	1.8006
	0.40	-0.179	-2.179	6.623	0.0310	1.8420
	0.50	-0.371	-2.371	4.256	0.0199	1.9853
	0.60	-0.579	-2.579	2.636	0.0123	
$y = 0.02$	0.01	+0.412	-1.287	51.64	0.2415	2.2196
	0.10	+0.292	-1.407	39.18	0.1832	2.0816
	0.20	+0.152	-1.547	28.38	0.1374	1.9775
	0.30	-0.007	-1.706	19.68	0.0920	1.9055
	0.40	-0.183	-1.882	1.311	0.0613	1.9113
	0.50	-0.374	-2.073	8.453	0.0395	2.0293
	0.60	-0.581	-2.280	5.250	0.0246	

TABLE 4

THE PARTIAL PRESSURE OF URANIUM OVER W-C-U ALLOYS
AND THE AVERAGE MOLECULAR WEIGHTS OF W-C-U-H
GASEOUS MIXTURES AT 10,000°R

	x	$\bar{F}^L_{E-U}$	$\log(p_U/p_U^o)$	$(p_U/p_U^o) \times 10^3$	p_U^o	$\tilde{M}$
$y = 0.001$	0.01	+0.382	-2.618	2.410	0.0449	2.3009
	0.10	+0.280	-2.720	1.905	0.0355	2.2558
	0.20	+0.115	-2.885	1.303	0.0243	2.2604
	0.30	+0.004	-2.996	1.009	0.0188	2.4159
	0.40	-0.157	-3.157	0.697	0.0130	2.8317
	0.50	-0.330	-3.330	0.468	0.0087	3.6474
	0.60	-0.518	-3.518	0.303	0.0056	4.8953
$y = 0.01$	0.01	+0.378	-1.622	23.88	0.4446	3.2220
	0.10	+0.273	-1.727	18.75	0.3491	2.9748
	0.20	+0.143	-1.857	13.90	0.2588	2.7908
	0.30	-0.002	-2.002	9.954	0.1853	2.7817
	0.40	-0.161	-2.161	6.902	0.1285	3.0711
	0.50	-0.334	-2.334	4.634	0.0863	3.7919
	0.60	-0.521	-2.521	3.013	0.0561	4.9742
$y = 0.02$	0.01	+0.371	-1.328	46.99	0.8750	4.2058
	0.10	+0.262	-1.437	36.56	0.6807	3.7302
	0.20	+0.138	-1.561	27.35	0.5093	3.3548
	0.30	-0.006	-1.705	19.72	0.3672	3.1801
	0.40	-0.164	-1.863	13.71	0.2553	3.3333
	0.50	-0.336	-2.035	9.226	0.1718	3.9508
	0.60	-0.523	-2.222	5.998	0.1117	5.0533
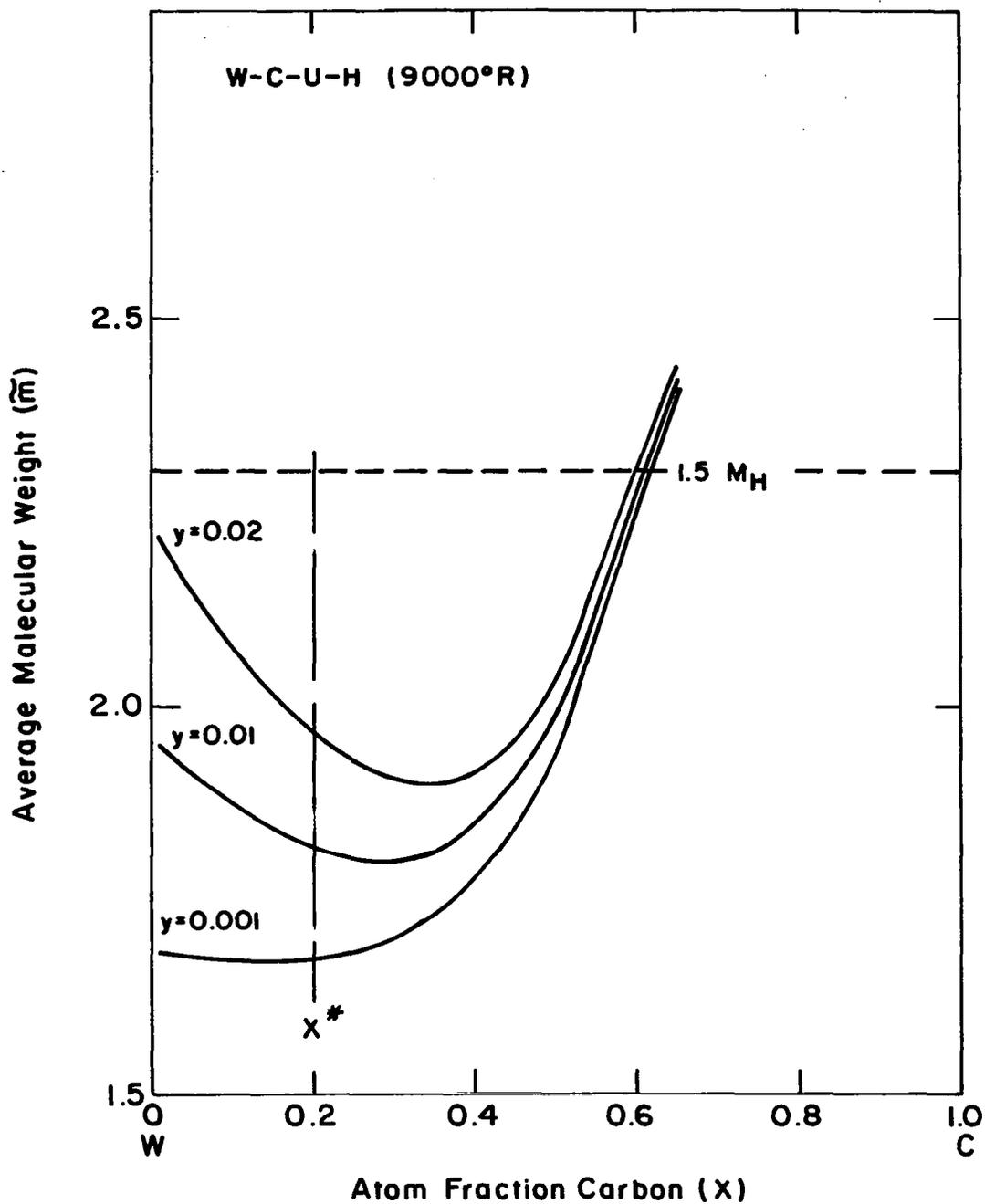
Figure 3.   Average Molecular Weight of Gaseous W-C-U-H Mixtures at 9000°R.
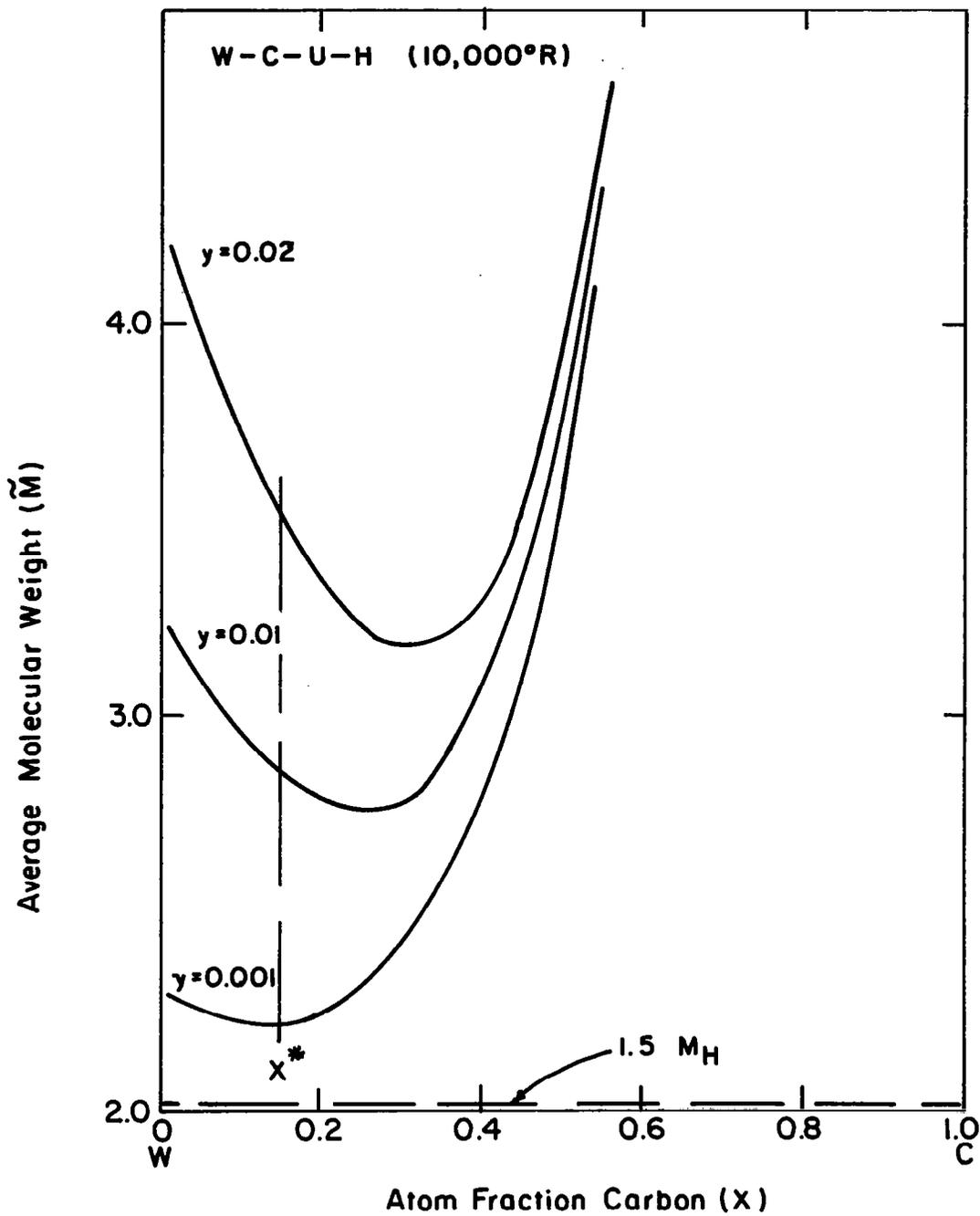
Figure 4. Average Molecular Weight of Gaseous W-C-U-H Mixtures at 10,000°R.

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TABLE 5

CRITICAL VALUES OF x WHERE

$\text{LOG } a_C \text{ (LIQUID SOLUTION)} = \text{LOG } a_C \text{ } (C_2H_2)$

W-C-U-H	$9,000^\circ R$	$10,000^\circ R$
$x^*(\underline{3})$	0.195	0.145
$x^*(\text{JANAF})$	0.210	0.160
x^* ave.	0.202	0.152
Zr-C-U-H		
$x^*(\underline{3})$	0.315	
$x^*(\text{JANAF})$	0.330	
x^* ave.	0.322	
Nb-C-U-H		
$x^*(\underline{3})$	0.320	0.270
$x^*(\text{JANAF})$	0.335	0.285
x^* ave.	0.327	0.277

3. CALCULATION OF CONGRUENCIES FOR METAL - CARBON - URANIUM TERNARY SYSTEMS

The rate of evaporation (vaporization) from a liquid into vacuum is given by:

$$G = 44.4 \, p T^{-1/2} M^{-1/2} \tag{3}$$

where G = rate of evaporation in moles/cm^2/sec

p = vapor pressure

T = temperature in $^{\circ}$K

M = molecular weight

For a binary system AB, congruent vaporization is achieved at a composition x where the expression

$$\frac{G_A}{G_B} = \frac{x_A}{x_B} = \frac{x_A}{(1-x_A)} \tag{4}$$

is satisfied.[*]   If, in a ternary system ABC, the expression

$$\frac{G_A}{G_C} = \frac{x'_A}{x_C}$$

is also satisfied, ternary congruency is obtained for the case where $x'_A = x_A$.

The various parameters required for solution of Eq. (3) and calculated G values for the components of Zr-C-U at 9,000°R and of Nb-C-U and W-C-U at both 9,000°R and 10,000°R are tabulated in Table 6. The calculated rates of evaporation G_C, G_{Me}, and G_U (for atom fraction of uranium held constant at 0.001, 0.01, or 0.02) are plotted as a function of the atom fraction of carbon, x, in Figures 5-9.

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[*] where x = atom fraction.

TABLE 6

CALCULATION PARAMETERS FOR
DETERMINING RATE OF EVAPORATION

Z	$M^{-1/2}$	$T^{-0}R$	$T^{-1/2}(^{\circ}K)$
C	0.28854	9,000	0.01414
Zr	0.10470	10,000	0.01342
Nb	0.10375		
W(184)	0.07372		
U(235)	0.06523		

Rate of Evaporation - G

where $G_A = a\,p_A$ and $a = 44.4\,T^{-1/2}\,M^{-1/2}$

	$9000^{\circ}R$		$10,000^{\circ}R$	
A	a	A	a
C	0.18115	C	0.17192
Zr	0.06573	Zr	0.06182
Nb	0.06513	Nb	0.043925
W	0.04628	U	0.03887
U	0.04095		
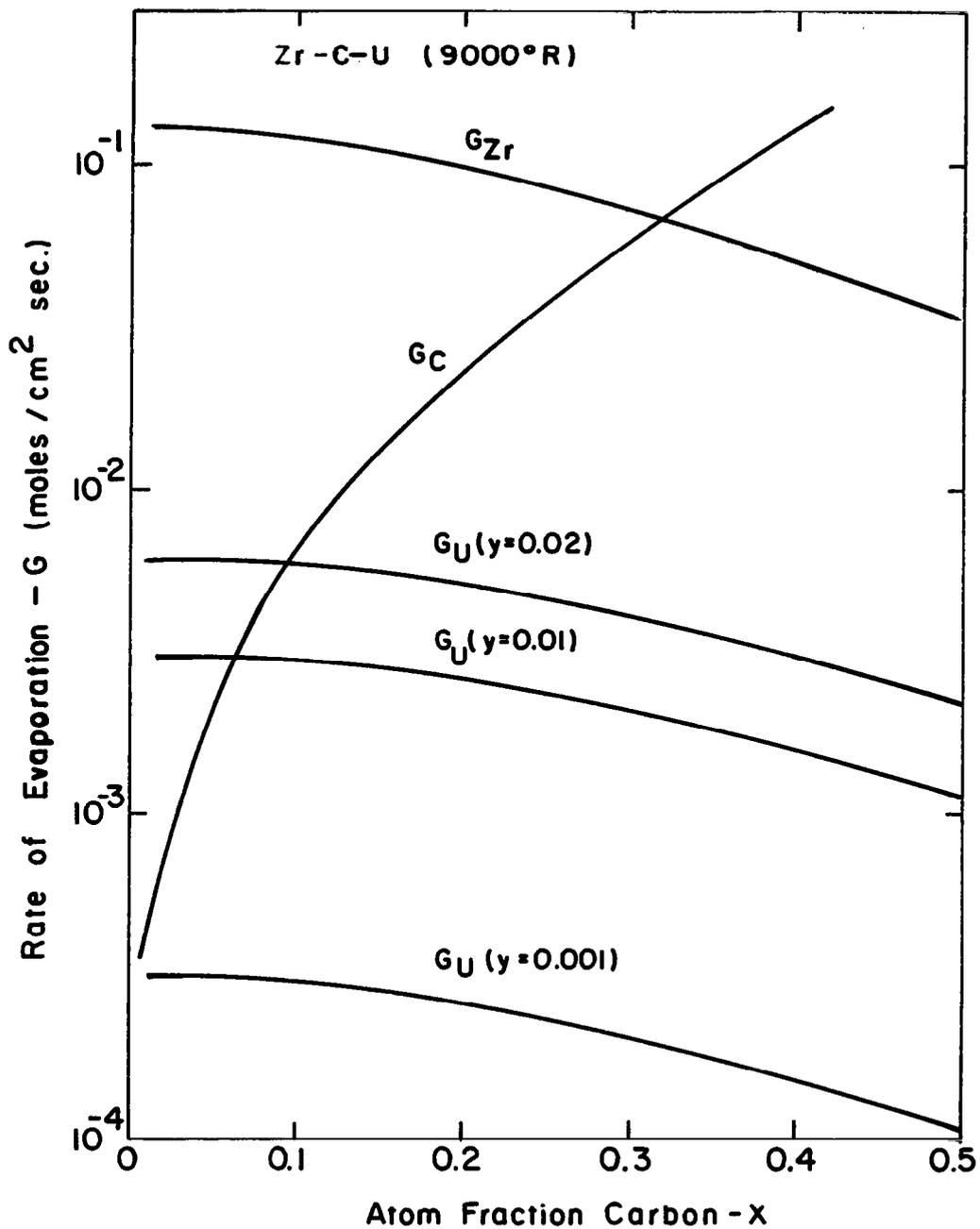
Figure 5. Rates of Evaporation of Zr, C and U in Zr-C-U Alloys at 9000°R.
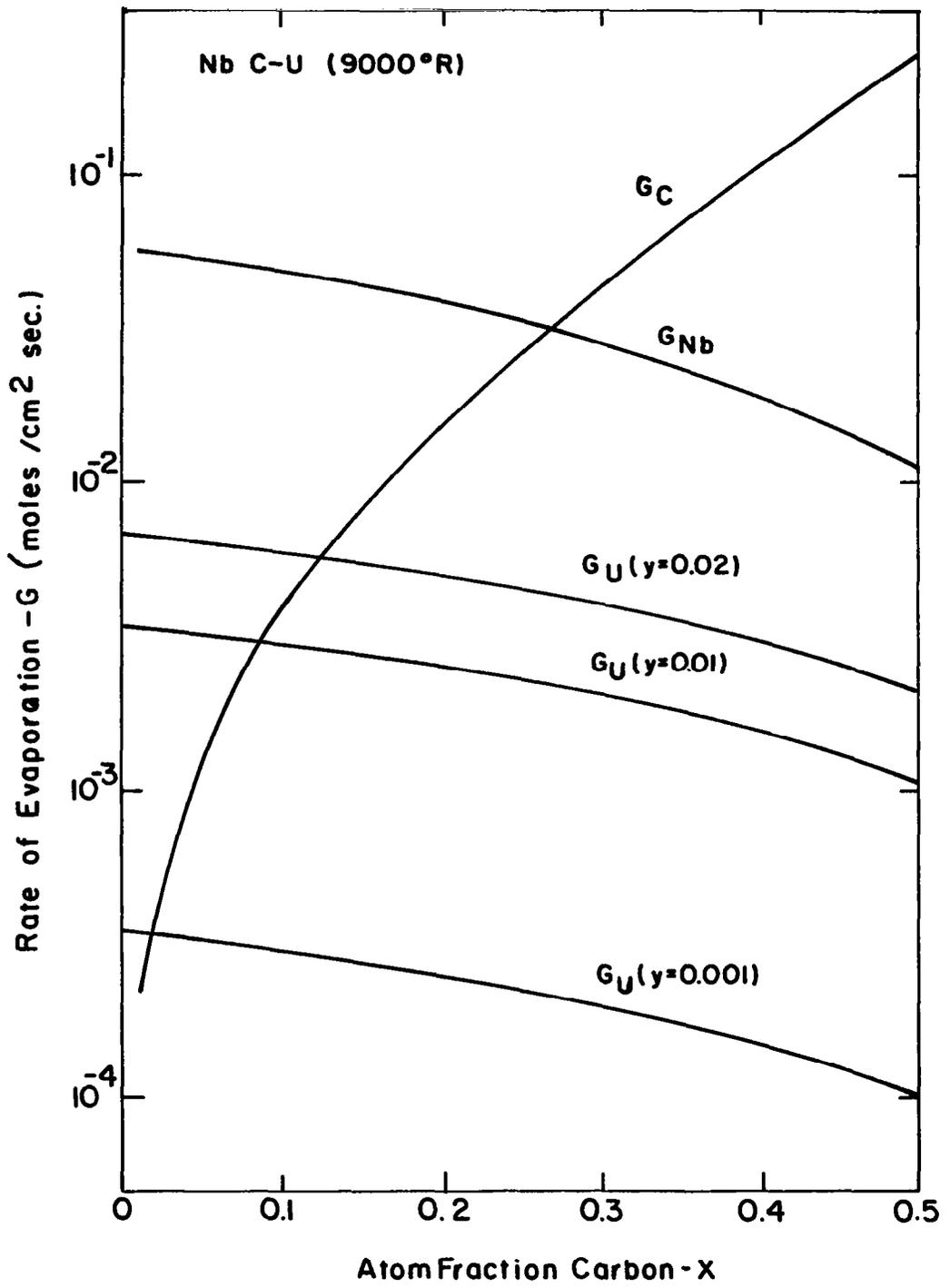
Figure 6. Rates of Evaporation of Nb, C and U in Nb-C-U Alloys at 9000°R.
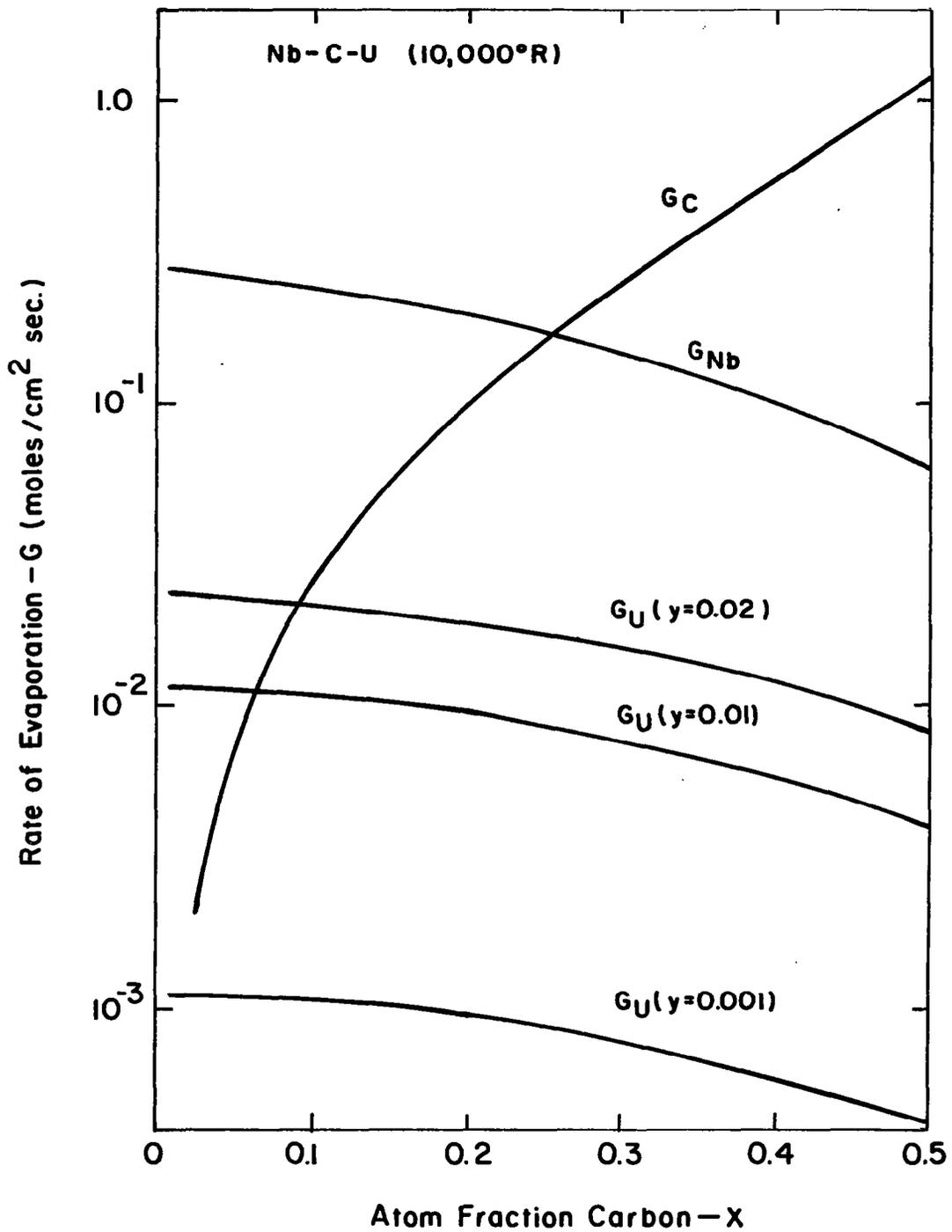
Figure 7. Rates of Evaporation of Nb, C and U in Nb-C-U Alloys at 10,000°R.

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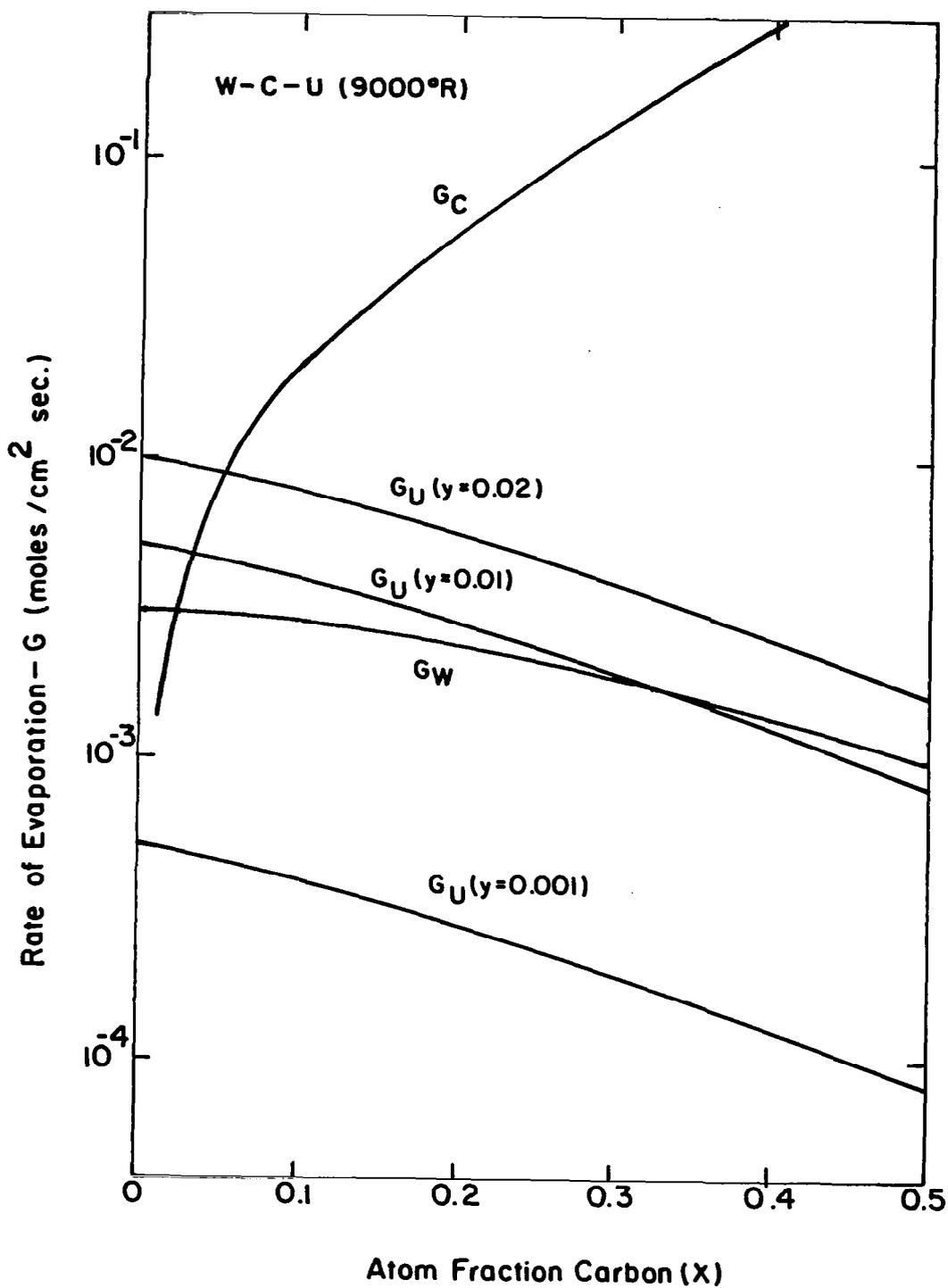
Figure 8. Rates of Evaporation of W, C and U in W-C-U Alloys at 9000°R.

25
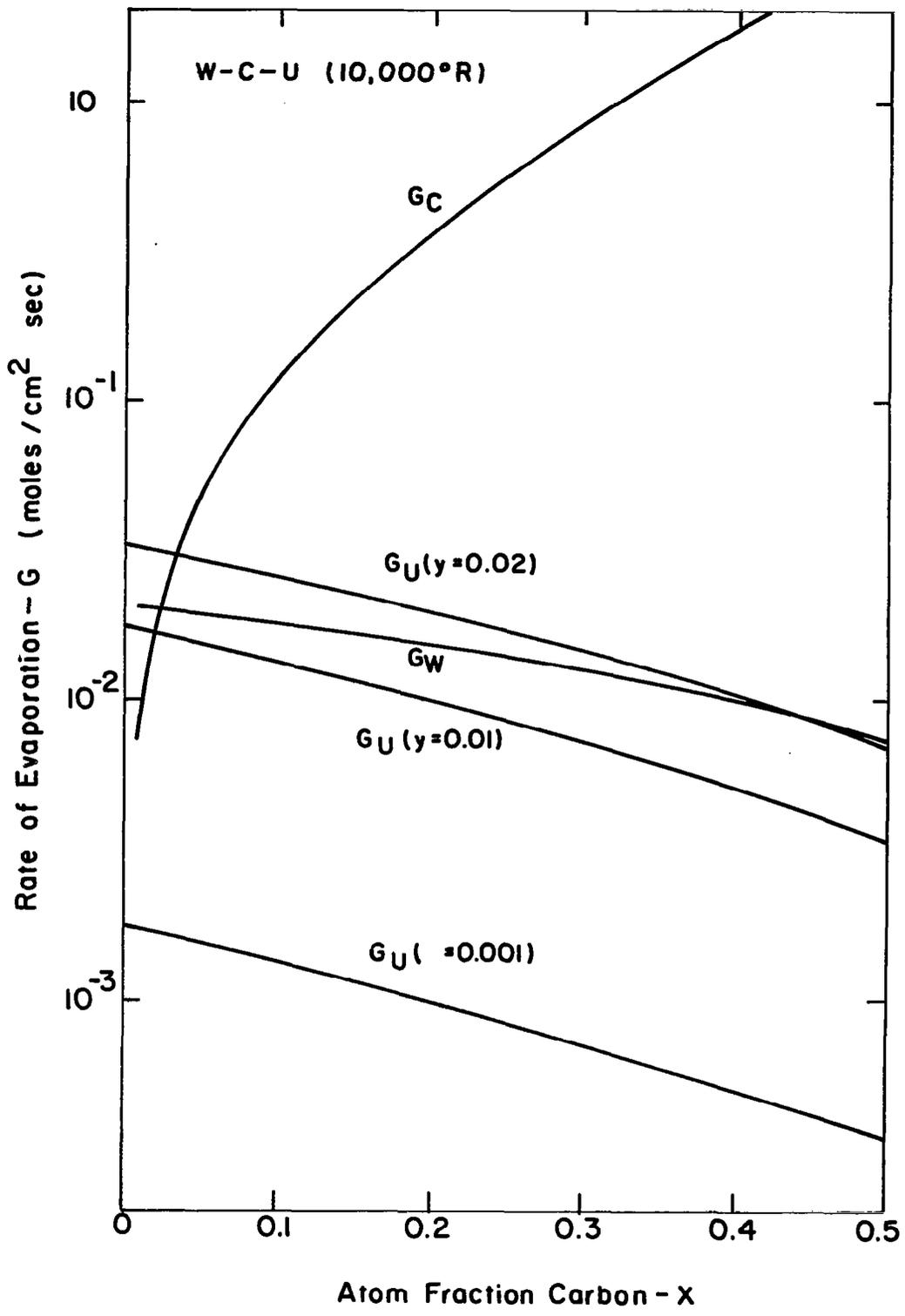
Figure 9. Rates of Evaporation of W, C and U in W-C-U Alloys at 10,000°R.

According to Eq. (4), the binary congruencies for the ternary systems investigated are given by:

$$G_C/G_{Me} = x/(1-x) \qquad (5a)$$

$$G_C/G_U = x/y \qquad (5b)$$

$$G_{Me}/G_U = (1-x)/y \qquad (5c)$$

By plotting the left hand side (LHS) and right hand side (RHS) of Eq. (5) as functions of x, one establishes a congruent composition by the intersection of LHS and RHS. If, however, LHS and RHS do not intersect, there is no congruency.

Plots of LHS and RHS (Eq. (5)) vs. x for the selected systems and temperatures are given in Figures 10-15. The limited range of uranium content variation, y = 0.001 to y = 0.02, is not sufficient to cause variation in congruent composition. For example, the congruencies for C and U in the Zr-C-U system at $9,000^{\circ}$R are of identical composition for y = 0.001, y = 0.01 and y = 0.02, as shown in Figure 11. Consequently, uranium content was held constant at y = 0.01 for the other systems and temperatures. A tabulation of the observed congruencies is given in Table 7.

It is of interest to consider the variation in alloy composition with time for the case where no ternary congruencies are observed. Consider the Zr-C-U system at 9000°R. A binary Zr-C congruency occurs at x = 0.195. If the starting composition is 0.805 Zr - 0.195 C - 0.010 U, one has $(1-x)/y = 80.5$ atoms Zr/atoms U in the liquid alloy. From Figure 10, G_{Zr}/G_U at x = 0.195 is 37.5 and

$$\frac{G_{Zr}}{G_U} = 37.5 \text{ atoms Zr/atom U}$$

in the vapor. Therefore, there is a continuous depletion of uranium in the
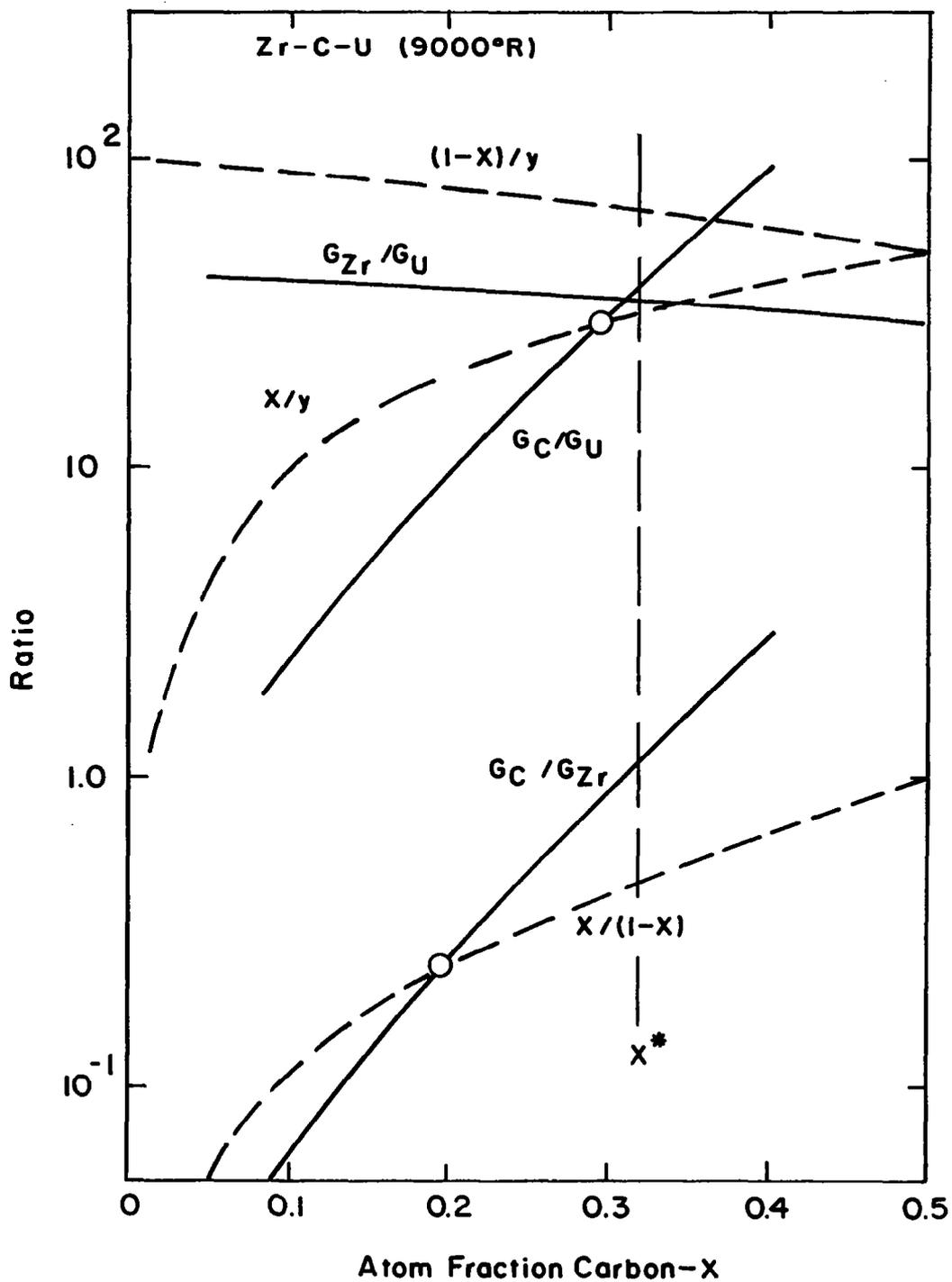
Figure 10. Establishment of Binary Congruencies in Zr-C-U Alloys at 9000°R.

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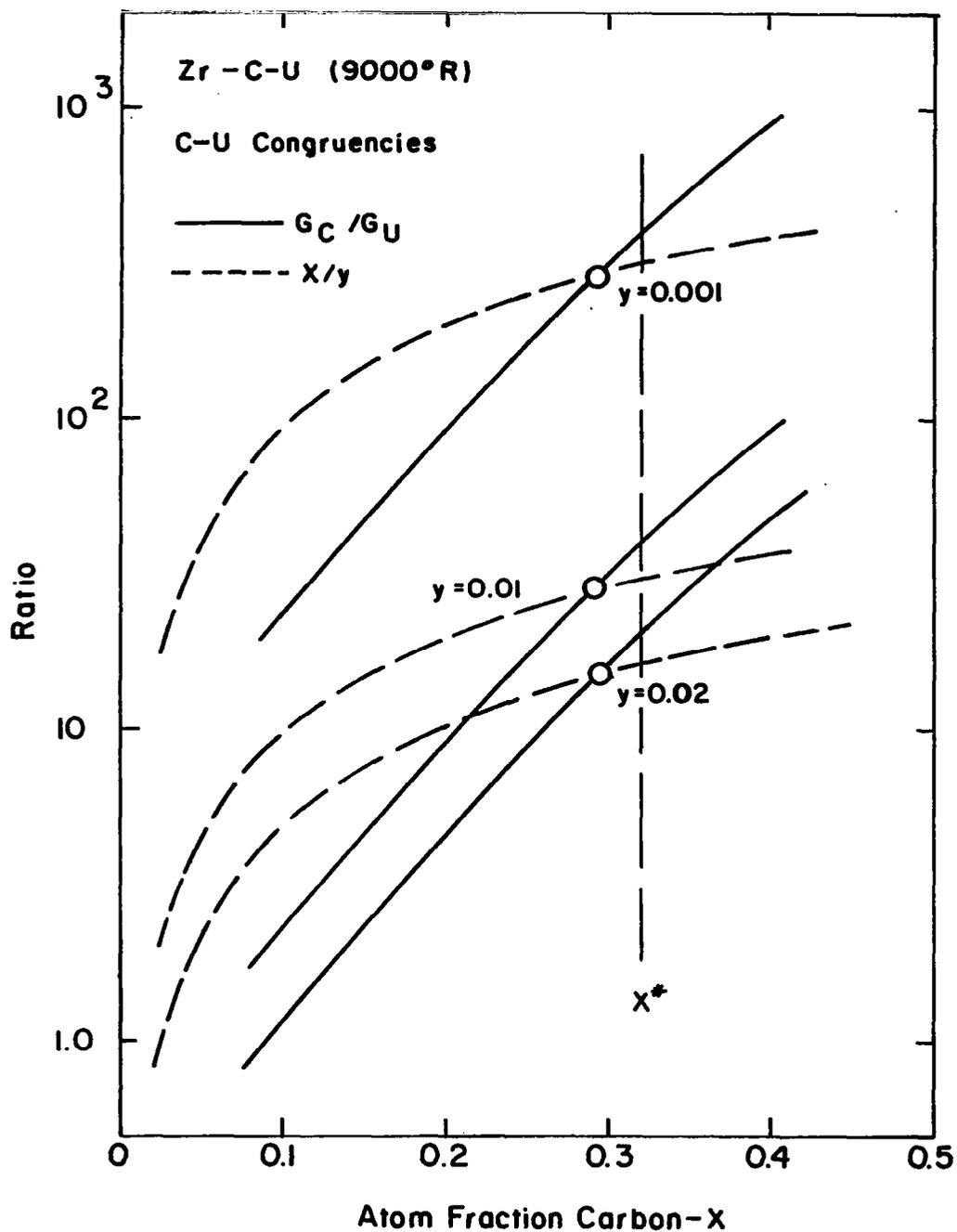
Figure 11. Effect of Uranium Content on U-C Congruency in Zr-C-U Alloys at 9000°R.
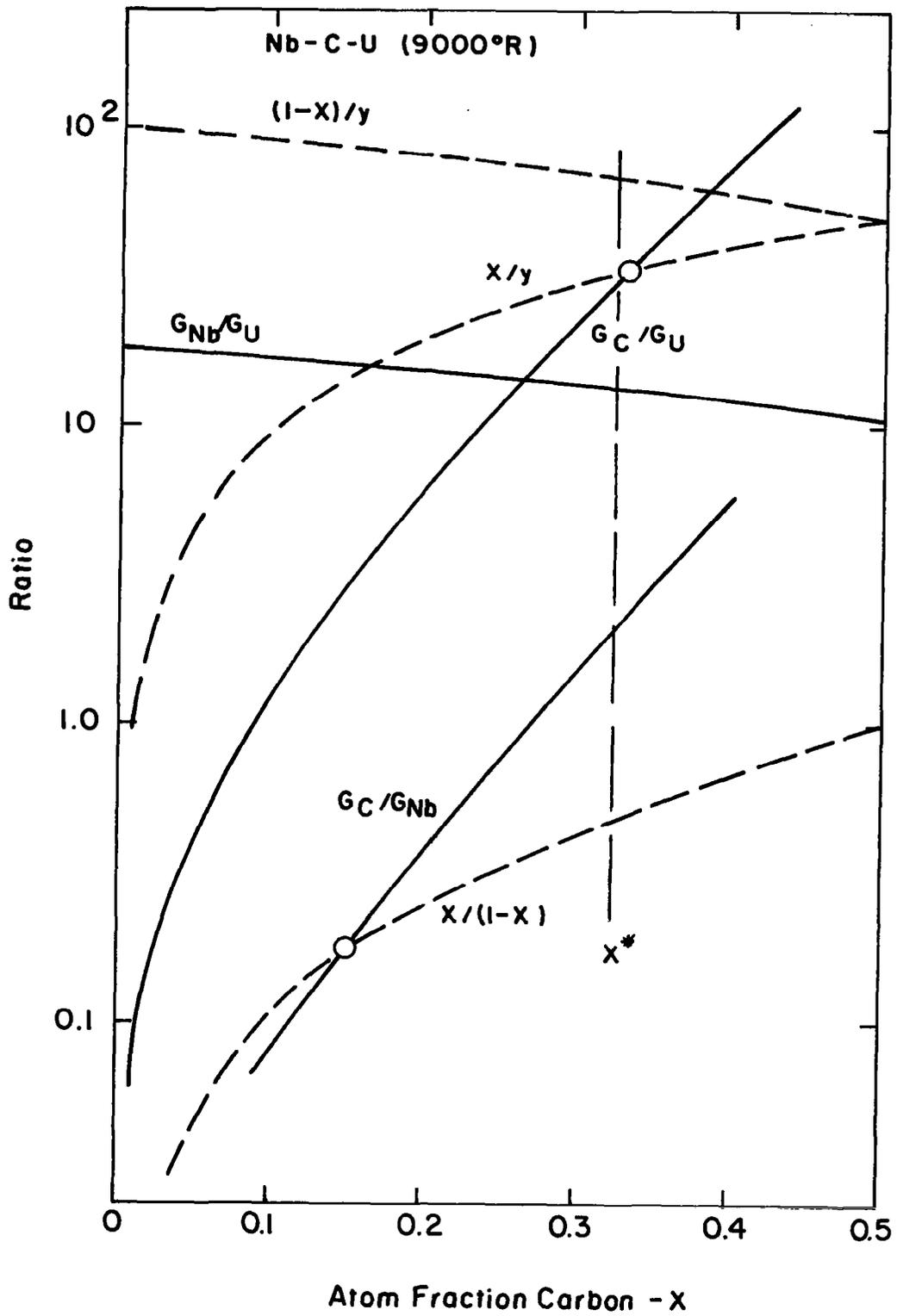
Figure 12. Establishment of Binary Congruencies in Nb-C-U Alloys at 9000°R.
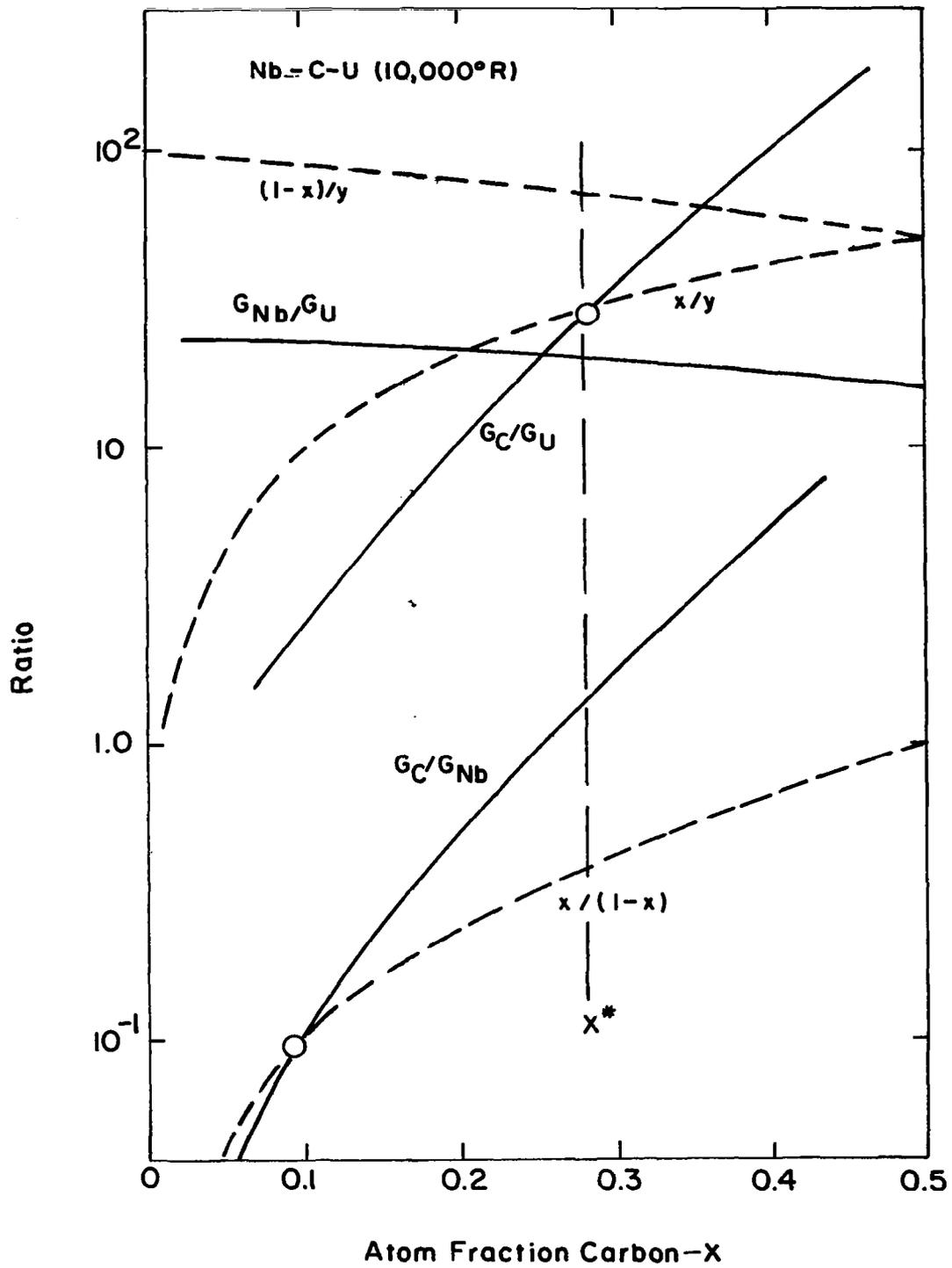
Figure 13. Establishment of Binary Congruencies in Nb-C-U Alloys at 10,000°R.

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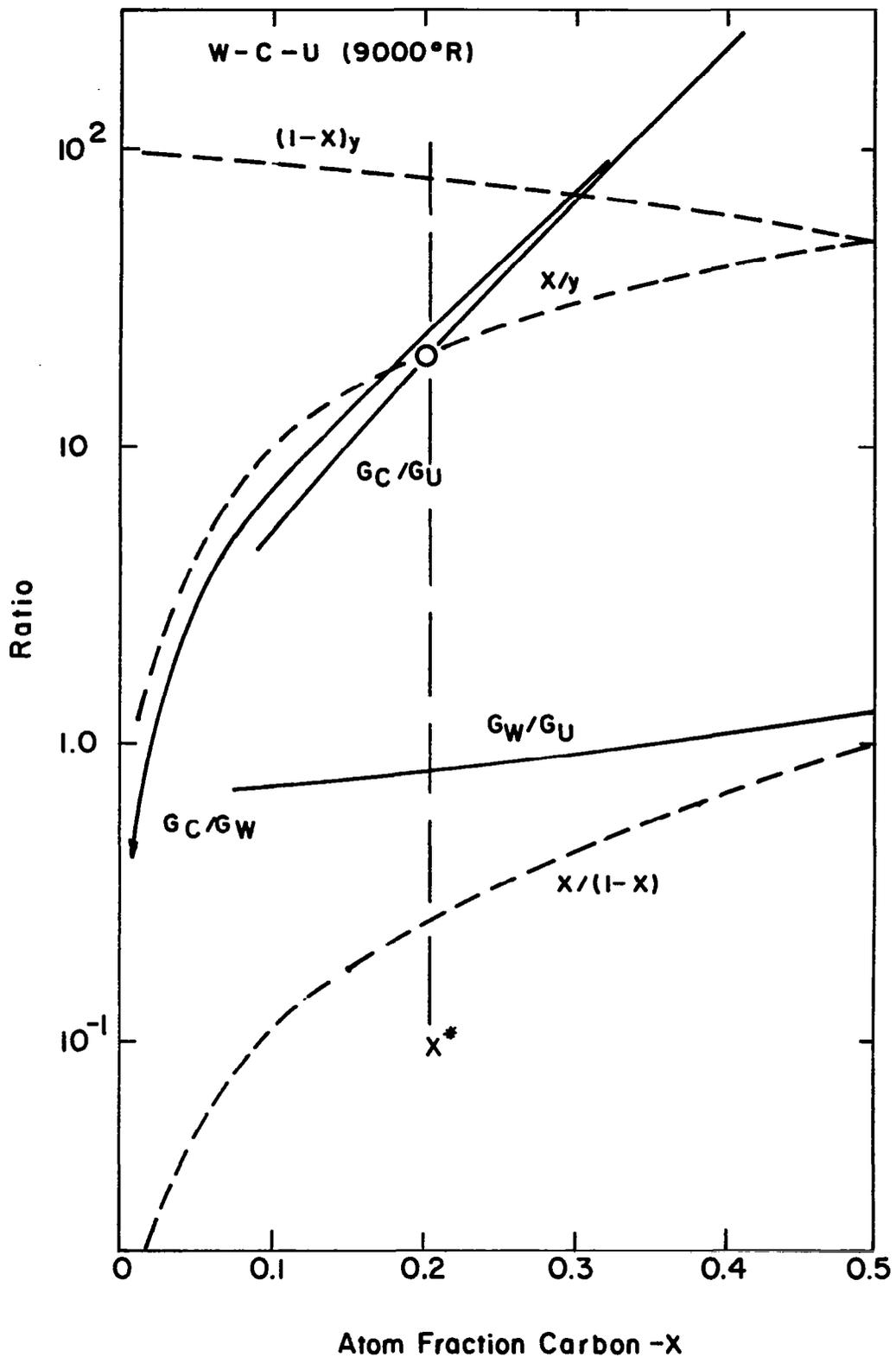
Figure 14. Establishment of Binary Congruencies in W-C-U Alloys at 9000°R.
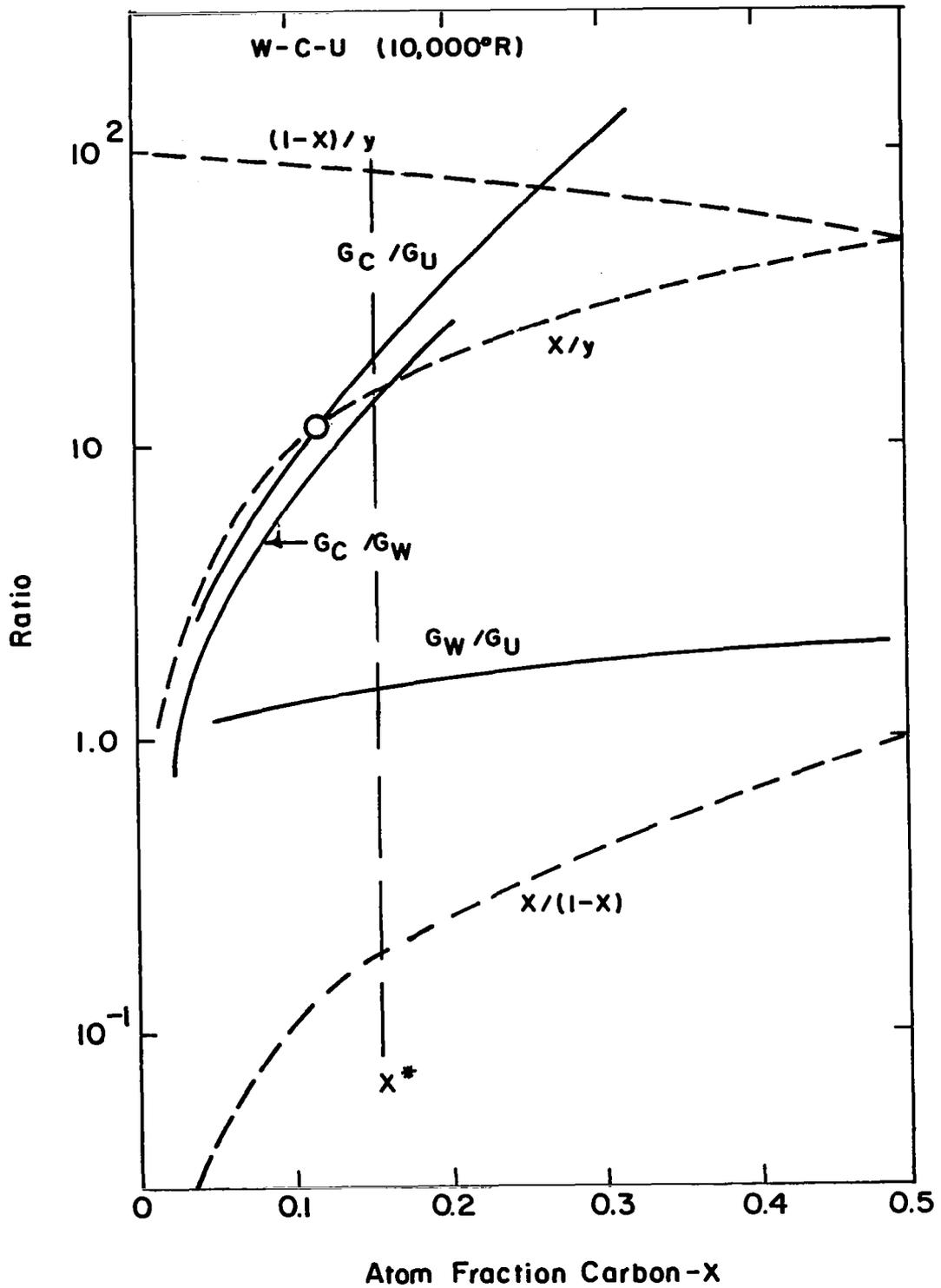
Figure 15. Establishment of Binary Congruencies in W-C-U Alloys at 10,000°R.

TABLE 7

SUMMARY OF CALCULATED CONGRUENCIES
OCCURRING IN THE SYSTEMS Zr-C-U,
Nb-C-U, AND W-C-U AT 9000 AND $10,000^{\circ}$R

| System | x_c - Congruent Composition | |
	$9,000^{\circ}$R	$10,000^{\circ}$R
Zr-C	0.195	- - - - -
C-U	0.290	- - - - -
Zr-U	nc*	- - - - -
Nb-C	0.150	0.092
C-U	0.340	0.282
Nb-U	nc	nc
W-C	nc	nc
C-U	0.200	0.115
W-U	nc	nc

* nc = no congruency.

liquid with time. The same trend in uranium depletion with time is found for the other alloys and temperatures studied. One could therefore maintain a pseudo-ternary congruency by continually adding uranium to the alloy which, for the case described above, would be at a rate of 0.325 gr. uranium/cm^2-sec.

4. ESTIMATE OF COMPONENT MASS LOSS RATES

It is of interest to make an approximate calculation of the controlling reaction for mass loss rate from the engine system. For a first guess, it is assumed that the evaporated vapor is of constant composition throughout the volume of the pipe, i.e., back pressure effects due to the hydrogen stream or to component evaporation upstream are ignored. Mass loss rate due to evaporation from the liquid is designated G_{vac} and mass loss rate by stream ejection into the surroundings is designated G_{vel}. A typical engine system is described by the following parameters:

1) Length of furnace pipe (L) = 10'

2) Inner diameter of furnace pipe (D) = 4"

3) Velocity of gas stream (v) = 100'/sec. and therefore

4) Volume ejected to surroundings/sec. = 2.47 x 10^5 cm^3/sec.

If we assume the instream gas is ideal, n (moles) = PV/RT, and

$$G_{vel} = n/sec = PV_s/RT = 5424 \ P(atm)/T-^oR \ moles/sec. \qquad (6)$$

Also $\quad G_{vac} = G \ \pi \ DL = 9729 \ G \ moles/sec.$ $\qquad\qquad\qquad\qquad$ (7)

Therefore, $\qquad\qquad G_{vac}/G_{vel} = 1.794 \ GT(^oR)/P(atm)$ $\qquad\qquad$ (8)

Eq. (8) has been evaluated for the three systems investigated, with selected variation in x, y and T. The results are given in Table 8.

For all cases, $G_{vac}/G_{vel} \approx 10^3$ and mass loss rate is controlled by stream velocity. The buildup of the stream back pressure undoubtedly reduces the component evaporation rates that have been presented earlier. More refined calculations of mass loss rates are being carried out by NASA personnel.

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TABLE 8

MASS LOSS RATES THROUGH HYDROGEN TRANSPORT AND VAPORIZATION

System	x	y	$T - {}^{o}R$	$G_{vac}/G_{vel} \times 10^{-3}$	$G_{vel}(moles/sec)$
Zr-C-U	0.2	0.001	9000	1.061	1.101
	0.2	0.01	9000	1.049	1.135
	0.2	0.02	9000	1.036	1.172
Nb-C-U	0.1	0.01	9000	1.069	0.511
	0.2	0.01	9000	1.233	0.455
	0.1	0.01	10,000	1.111	2.355
W-C-U	0.1	0.01	9000	2.098	0.161
	0.1	0.01	10,000	1.849	0.822

5. CONSIDERATION OF THE VAPOR-LIQUID-GRAPHITE TRIPLE

POINT FOR CARBON

The vapor pressure of carbon in its various forms (i.e., C, C_2, C_3, etc.) has been previously tabulated ([1]). This information has been taken from the JANAF compilation ([4]) and is shown as a sum of components in Figure 16. The total pressure is seen to reach one atmosphere at about 4100° K. Recently, Berkowitz and Chupka ([5]) have performed a mass spectrograph experiment at about 4000° K by means of laser flash heating. They found that the relative abundance of gaseous polymers were in relatively good agreement with the values given by the JANAF compilation. Surprisingly however, the extension of this curve shown as a dashed curve H-I in Figure 16 indicates a temperature near 5200° K at 100 atmospheres. This is very much higher than the reported triple point pressure ([6,7]) for the vapor, liquid and graphitic forms of carbon at 4000° K and 110 atmospheres. The latter has been determined by heating graphite in an autoclave filled with argon at pressures between 50 and 150 atmospheres and observing conditions for the formation of molten graphite. The triple point pressure has been definitely determined as 110 atmospheres, and while the triple point temperature of 4000° K (measured optically) is open to some question, an error of 1200° K seems outside the range of experimental error. Also shown in Figure 16 are the reported liquid/graphite equilibrium lines observed by Fateeva et al ([9]) and Bundy ([8]) measured at high pressures. These curves differ substantially, but support the 110 atmosphere-4000° K location of the triple point. The insert in Figure 16 which shows the anticipated behavior illustrates the present dilemma. If the vapor pressure results are taken at face value, then

Figure 16. Summary of Phase Equilibria Data Relevant to the Vapor-Liquid-Graphite
Equilibria for Carbon.

the triple point temperature is much higher than heretofore reported. On the other hand, if the high pressure observations are accepted, then the true vapor pressure of carbon is substantially _higher_ than indicated by the JANAF tabulation.

Prior to the mass spectrographic measurements of Drowart et al (10) (which form the basis of the current vapor pressure tabulations (1, 4)) Pitzer and Clementi (11) performed a molecular orbital calculation of the relative abundences of polyatomic gaseous species of carbon. These calculations were cognizant of the triple point at 110 atmospheres and 4000°K and took the one atmosphere vaporization temperature to be 3700°K. At the time of the Pitzer-Clementi computation, vapor pressure data for C, C_2 and C_3 were available. Information on the higher polymers were not. By coupling the available pressure measurements with the one atmosphere vaporization temperature and the triple point conditions, Pitzer and Clementi produced pressure-temperature calculations for C_4, C_5 to C_{13}. These computations indicated that C_5 and _higher_ polymers became dominant at temperatures above 2000°K.

Subsequently, the mass spectrographic study of Drowart et al (10) at temperatures between 1800°K and 2700°K indicated that C_4 and C_5 _did_ _not_ _dominate_ up to 2700°K. The abovementioned results of Berkowitz and Chupka (5) are also in disagreement with the conclusions of Pitzer and Clementi.

Under the present circumstances, it appears that resolution of this problem will require a re-evaluation of the triple point conditions and the vapor pressure data on an experimental as well as a theoretical basis.

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APPENDIX A

CALCULATION OF INTERACTION PARAMETERS
FOR THE W-C-U TERNARY SYSTEM

The W-C phase diagram[*]contains three intermediate phases which have the following properties.

Phase	ΔF (**)	$\overline{T}$	$\overline{x}$
β	-4800 cal/g-at.	$3050^{\circ}K$	0.31
β'	-5100	3000	0.39
σ	-5100	3050	0.50 ($x^{L\sigma}=0.42$)

where ΔF is the free energy of formation, $\overline{T}$ is the melting point, and x is atom fraction of carbon.

The free energy of the liquid is given by:

$$F^{L}=(1-x) F^{L}_{W} + F^{L}_{C} + RT ((1-x) ln(1-x) + x \, lnx) + x(1-x)L_{W-C} \tag{A1}$$

and, of the solid phases, by

$$F^{\beta} = \Delta F^{\beta} + (1-x^{\beta})F^{\alpha}_{W} + x^{\beta}F^{\gamma}_{C} \tag{A2a}$$

$$F^{\beta'} = \Delta F^{\beta'} + (1-x^{\beta'})F^{\alpha}_{W} + x^{\beta'}F^{\gamma}_{C} \tag{A2b}$$

$$F^{\sigma} = \Delta F^{\sigma} + (1-x^{\sigma})F^{\alpha}_{W} + x^{\sigma}F^{\gamma}_{C} \tag{A2c}$$

By applying the lever rule

$$F^{\sigma} = (\frac{1-x^{\sigma}}{1-x^{L\sigma}}) F^{L} + (\frac{x^{\sigma}-x^{L\sigma}}{1-x^{L\sigma}}) F^{\gamma}_{C} \tag{A3}$$

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[*] E. Rudy and D. P. Harmon, "Ternary Phase Equilibria in Transition Metal Boron Carbon Silicon Systems", Aerojet-General Corp., Progress Report #3, AF Contract No. AF33(615)-1249.

[**] E. Rudy and Y. Chang, Metals for the Space Age, 5th Plansee Proceedings, F. Benesovski, Ed.,Metallwerk Plansee, Reutte, Tyrol, Austria, 1964, p.813.

The free energies of transformation of tungsten and carbon are[*]

$$\Delta F_C^{L \to \gamma} = F_C^{\gamma} - F_C^{L} = -21,600 + 5.4T \tag{A4a}$$

$$\Delta F_W^{L \to \alpha} = F_C^{\alpha} - F_C^{L} = -8420 + 2.28T \tag{A4b}$$

At $\overline{T}$ and $\overline{x}$, by definition

$$F^{L} \equiv F^{\beta} \quad (3050^{\circ}K, \ \overline{x} = 0.31)$$

$$F^{L} \equiv F^{\beta'} \quad (3000^{\circ}K, \ \overline{x} = 0.39)$$

Solution of Eqs. (A1), (A2), and (A4) yields

$$L^{\beta} = -17,065$$

$$L^{\beta'} = -17,590$$

Likewise, solution of Eqs. (A1), (A2c), and (A3) at $T = 3050^{\circ}K$, $x^{\sigma} = 0.50$, and $x^{L\sigma} = 0.42$,

$$L^{\sigma} = -19,645$$

Averaging L^{β}, $L^{\beta'}$, and L^{σ}, one obtains

$$L_{W-C} \approx -18,100 \tag{A5}$$

The W-U phase diagram[**] contains a peritectic reaction very near

pure uranium. By definition, the partial molar free energy of liquid tungsten is:

$$\overline{F}_W^{L} = F_W^{L} - y \frac{\partial F^{L}}{\partial y} \tag{A6}$$

where y = atom fraction of uranium.

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[*] J. Elliott and M. Gleisser, <u>Thermochemistry for Steelmaking</u> (Addison-Wesley Publishing Company, Reading, Mass., 1960).

[**] M. Hansen and K. Anderko, <u>Constitution of Binary Alloys</u> (McGraw Hill Book Company, New York, N.Y., 1958).

By differentiating the expression for the free energy of the liquid (comparable to Eq. (A1)) and substituting into Eq. (A6), one has, with rearrangement

$$\bar{F}_W^L - F_W^L = y^2 L + RT \ln(1-y) \tag{A7}$$

For any temperature T, where $\bar{T}_W > T > \bar{T}_U$,

$$\bar{F}_W^L \bigg|_{y_{L\alpha}} \equiv \bar{F}_W^\alpha \bigg|_{y_{\alpha L}}$$

Assuming no solid solubility of carbon in α, $y_{\alpha L} = 0$ and

$$F_W^\alpha - F_W^L = \Delta F_W^{L \to \alpha} = y^2 L + RT \ln(1-y) \tag{A8}$$

Values of $y_{L\alpha}$ and T are selected from the liquidus of the W-U phase diagram and are introduced into Eq. (A8). Solution with Eq. (A4b) yields

T	y	L
2750°K	0.75	+9,640
2525	0.85	+10,510
2075	0.95	+10,280

By averaging

$$L_{W-U} \approx +10,100 \tag{A9}$$

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