Name ______________________

Please put answers within boxes provided.

Chemistry 342

November 23, 1998

Third Exam

1. In the following figures (a)-(h) attach these equation labels (A)-(Z') to each one of the appropriate straight or curved lines to which the equation applies. An equation may be used more than once, some equations may not be used at all, and some lines may not have applicable equations from the list.

Equations:

(A) $p_A/p^*_A = x_A$

(B) $y_A = p^*_A/p$

(C) $y_A - X_A = (n_{A(VAP)}/n_{(VAP)}) - (n_A/n)$

(D) $p = p^*_A p^*_B / \{p^*_A + (p^*_B - p^*_A)y_A)\}$

(E) $p = p_A + p_B$

(F) $p_B = K_H x_B$

(G) $p = p^*_A x_A + p^*_B (1 - x_A)$

(H) $dp/dT = \Delta_{vap}\boldsymbol{H} / \{T(V_{m,\text{gas}} - V_{m,\text{liquid}})\}$

(I) $\ln x_A = \Delta_{fus}\boldsymbol{H}/R \left[-\frac{1}{T} + \frac{1}{T^*} \right]$

(J) $(\partial\mu_{gas}/\partial T)_p = -\boldsymbol{S}_{m,gas}$

(K) $\mu^*_{\text{A,vap}} = \mu^{\ominus}_T + RT\ln(p^*_A/1)$

(L) $\mu_{\text{A,liquid}}(T,p,x_A) = \mu_{\text{A,solid}}(T,p)$

(M) $\mu_A(T) = \mu_A{}^*{}_T + RT\ln x_A$

(N) $(\partial[\Delta_{\text{rxn}}\boldsymbol{G}^{\ominus}/T]/\partial T)_p = -(\Delta_{\text{rxn}}\boldsymbol{H}^{\ominus}/T^2)$

(O) $\ln\gamma_{\pm} = z_+ z_- I^{1/2} (e^2/10\varepsilon k_B T)^{3/2} \{2\pi\rho N_{\text{Avog}}\}^{1/2}$

(P) $g_B(T,p) = \mu_B{}^*(T,p) + RT\ln K_H/p_B{}^*$

(Q) $\ln K = 2\ln C_s + 2\ln\gamma_{\pm}$

(R) $\mathcal{E} = \mathcal{E}^{\ominus} - (RT/\nu\mathcal{F})\ln Q_{\text{rxn}}$

(S) F = 0

(T) F = 1 F′ = 0

(U) F = 2 F′ = 1

(V) $\mu(T) = \mu^{\ominus}_T + RT\ln\frac{f}{1}$

(W) $\ln\frac{f}{p} = \int_0^p \frac{(Z-1)}{p}\,dp$

(X) $\mathcal{E}\,dQ = \mu'_{e-}\,dn - \mu_{e-}\,dn$

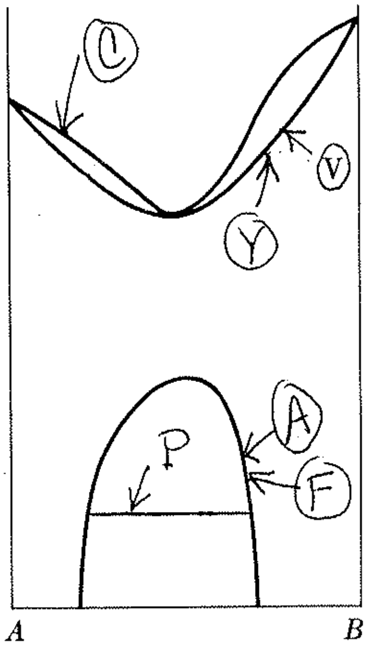
(X') $\boldsymbol{G}_{T,p} = \sum_i n_i\mu_i$

(Y) $(\partial\boldsymbol{G}/\partial T)_p = -\boldsymbol{S}$

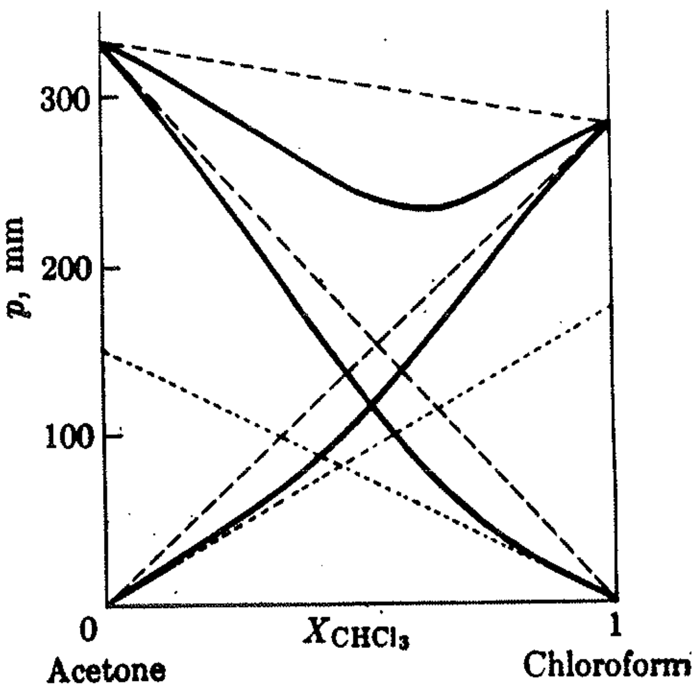
(Z) $\Delta_{\text{rxn}}\boldsymbol{G} = (c\mu_C + e\mu_E) - (a\mu_A + b\mu_B)$

(Z') $\Delta_{\text{rxn}}\boldsymbol{H}^{\ominus} = -\nu\mathcal{F}\{\mathcal{E}^{\ominus} - T(d\mathcal{E}^{\ominus}/dT)\}$

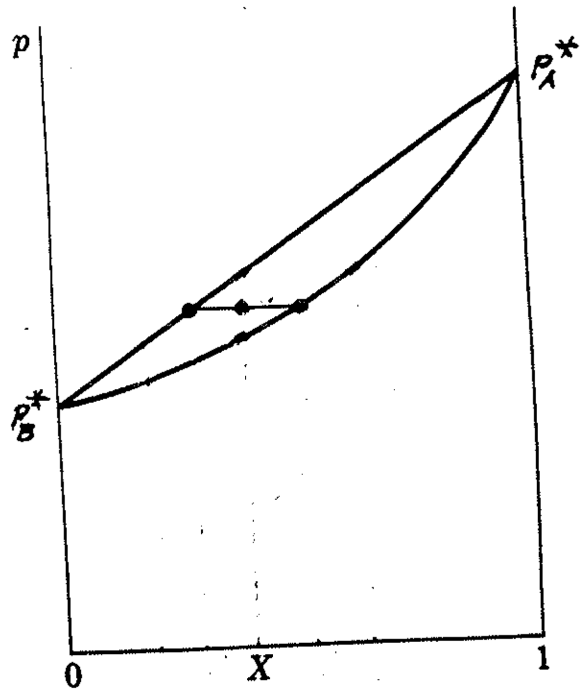
Your answer should look like the following example:



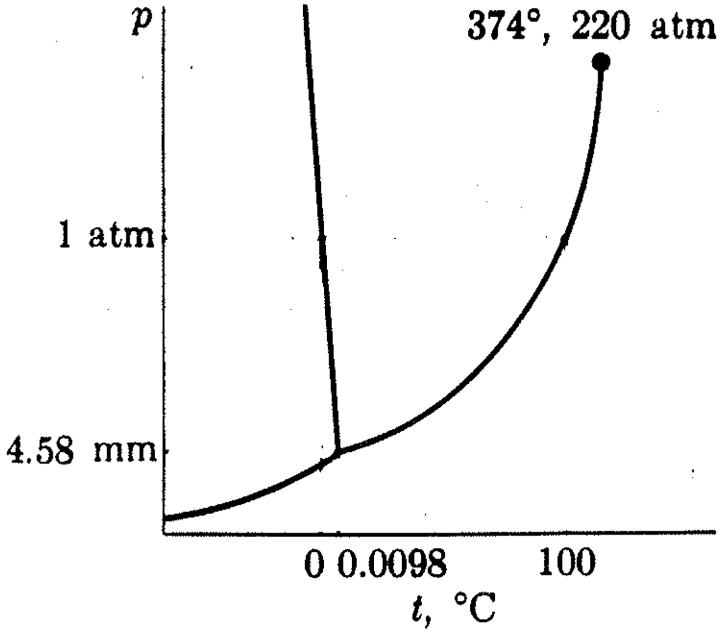
(a)


300
200
100
p, mm
0
X_{CHCl_3}
1
Acetone
Chloroform

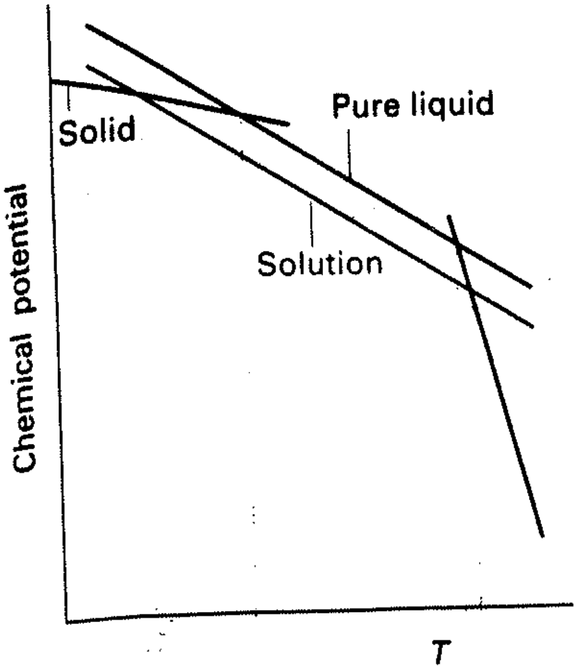
(b)


p
p_A^*
p_B^*
0
X
1

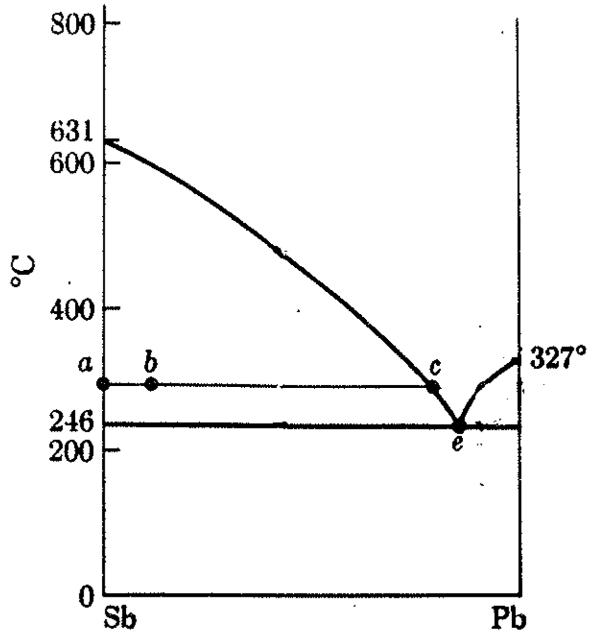
(c)


p
374°, 220 atm
1 atm
4.58 mm
0 0.0098
100
t, °C

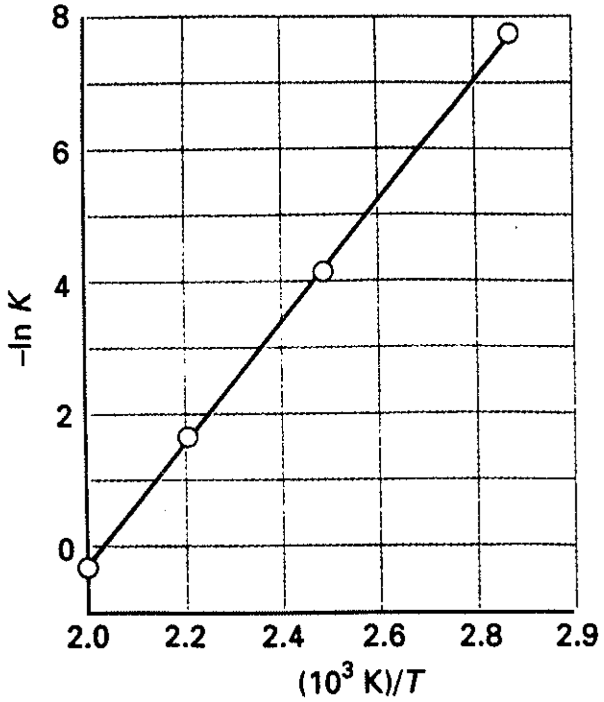
(d)


Pure liquid
Solid
Solution
Chemical potential
T

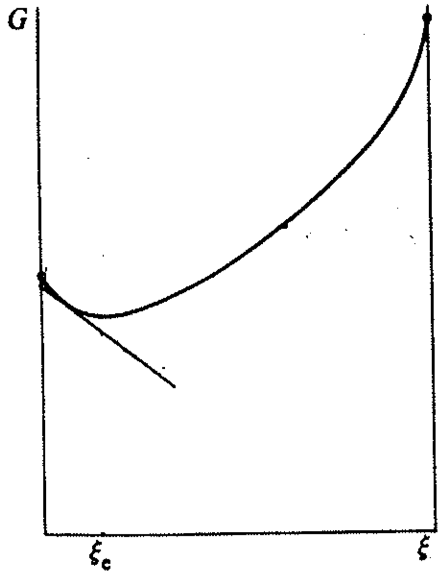
(e)


800
631
600
°C
400
a
b
c
327°
246
200
e
0
Sb
Pb

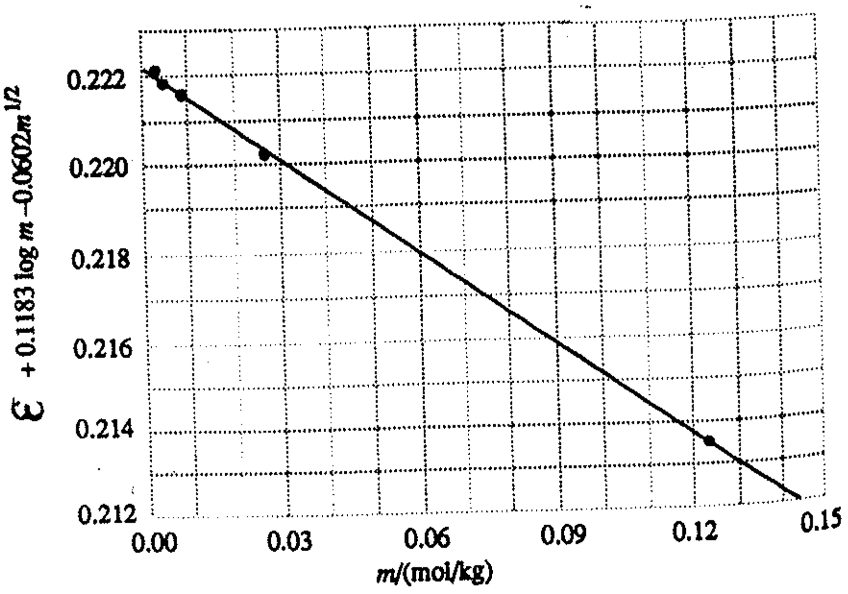
(f)


8
6
4
2
0
−ln K
2.0
2.2
2.4
2.6
2.8
2.9
(10³ K)/T

(g)


G
ξe
ξ

(h)


ℰ + 0.1183 log m −0.0602m^1/2
0.222
0.220
0.218
0.216
0.214
0.212
0.00
0.03
0.06
0.09
0.12
0.15
m/(mol/kg)

$1\ \mathrm{J} = 1\ \mathrm{kg\ m^2\ s^{-2}}$ $k_B = 1.38066\times10^{-23}\ \mathrm{J\ K^{-1}}$ $R = N_{Avogadro}k_B$

$R = 8.31441\ \mathrm{J\ mol^{-1}\ K^{-1}} = 1.98718\ \mathrm{cal\ mol^{-1}\ K^{-1}} = 0.082057\ \mathrm{L\ atm\ mol^{-1}\ K^{-1}}$

The limiting Debye-Hückel eqn: $\ln \gamma_\pm = z_+z_- I^{1/2}\,(e^2/10\varepsilon k_B T)^{3/2}\,\{2\pi\rho N_{Avog}\}^{1/2}$

for water at 25°C as the solvent, $\ln \gamma_\pm = z_+z_- I^{1/2}\,(1.17223)$

ionic strength $= \frac{1}{2}\sum m_i z_i^2$

$$\ln x_A = \Delta_{fus}H/R\left[\frac{-1}{T} + \frac{1}{T^*}\right]$$

2. From the attached graph determine the following and place your answers in the table below:

(a) The mole fraction of B in the vapor at 35°C and a pressure of 65 mm Hg for a system having over all 20 mole % B

(b) The mole fraction of A in the liquid at 35°C and a pressure of 65 mm Hg for a system having over all 20 mole % B

(c) The relative amounts of liquid and vapor for a system having over all 20 mole % B at 35°C and a pressure of 65 mm Hg

(d) Are the A-B intermolecular interactions stronger or weaker (which one?) than the A-A and B-B interactions?

(e) What is the vapor pressure of pure A at 35°C?

(f) What is the vapor pressure of pure B at 35°C?

(g) If an azeotrope is formed by this system, what is the approximate composition of the azeotropic mixture?

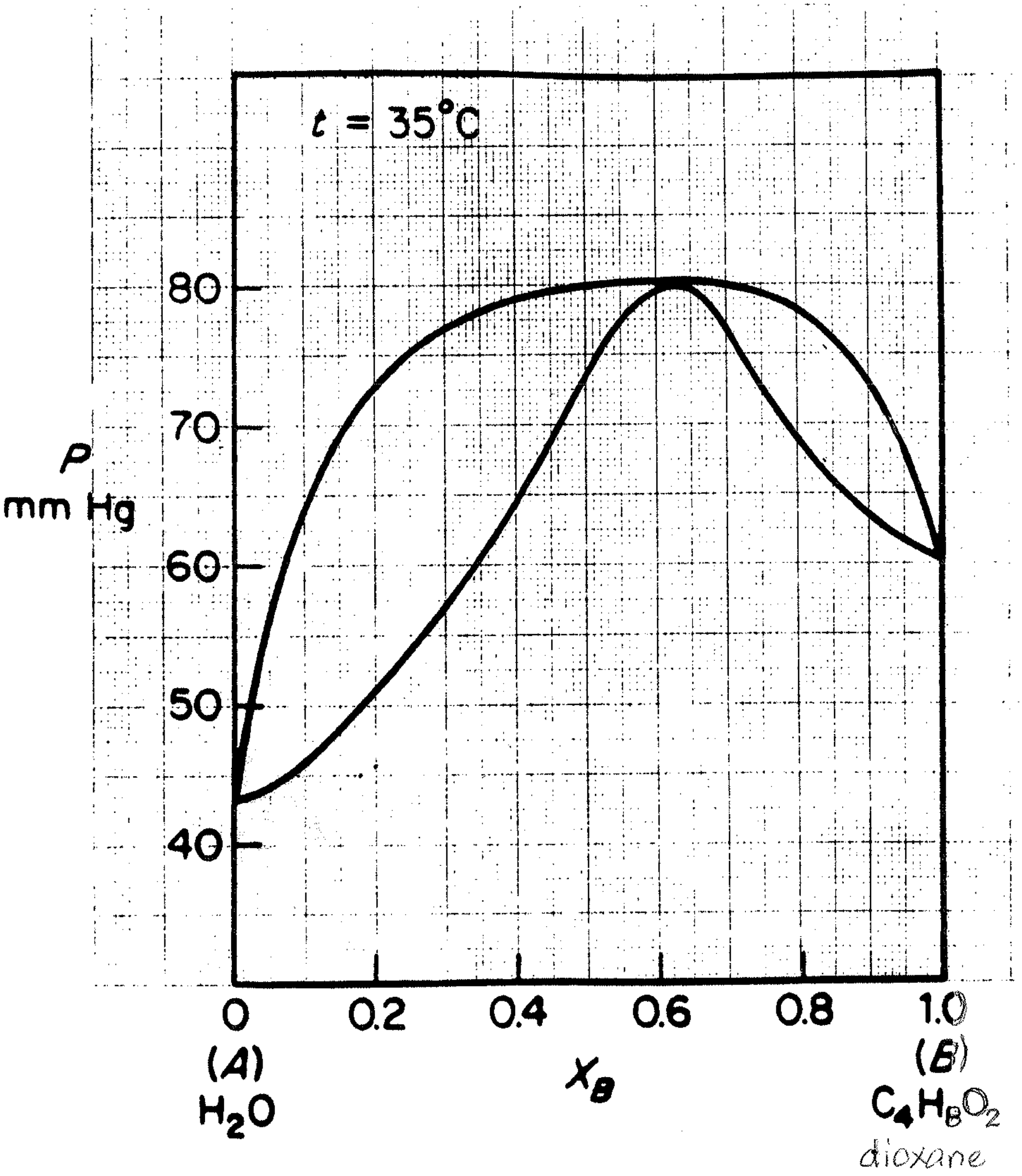
(h) If an azeotrope is formed by this system, would it boil at a higher or lower temperature (which one) than both A and B?

(i) Would the activity coefficient of B in a liquid solution of A+B be smaller or greater (which one?) than 1.0?

(j) Would the activity coefficient of A in a liquid solution of A+B be smaller or greater (which one?) than 1.0?

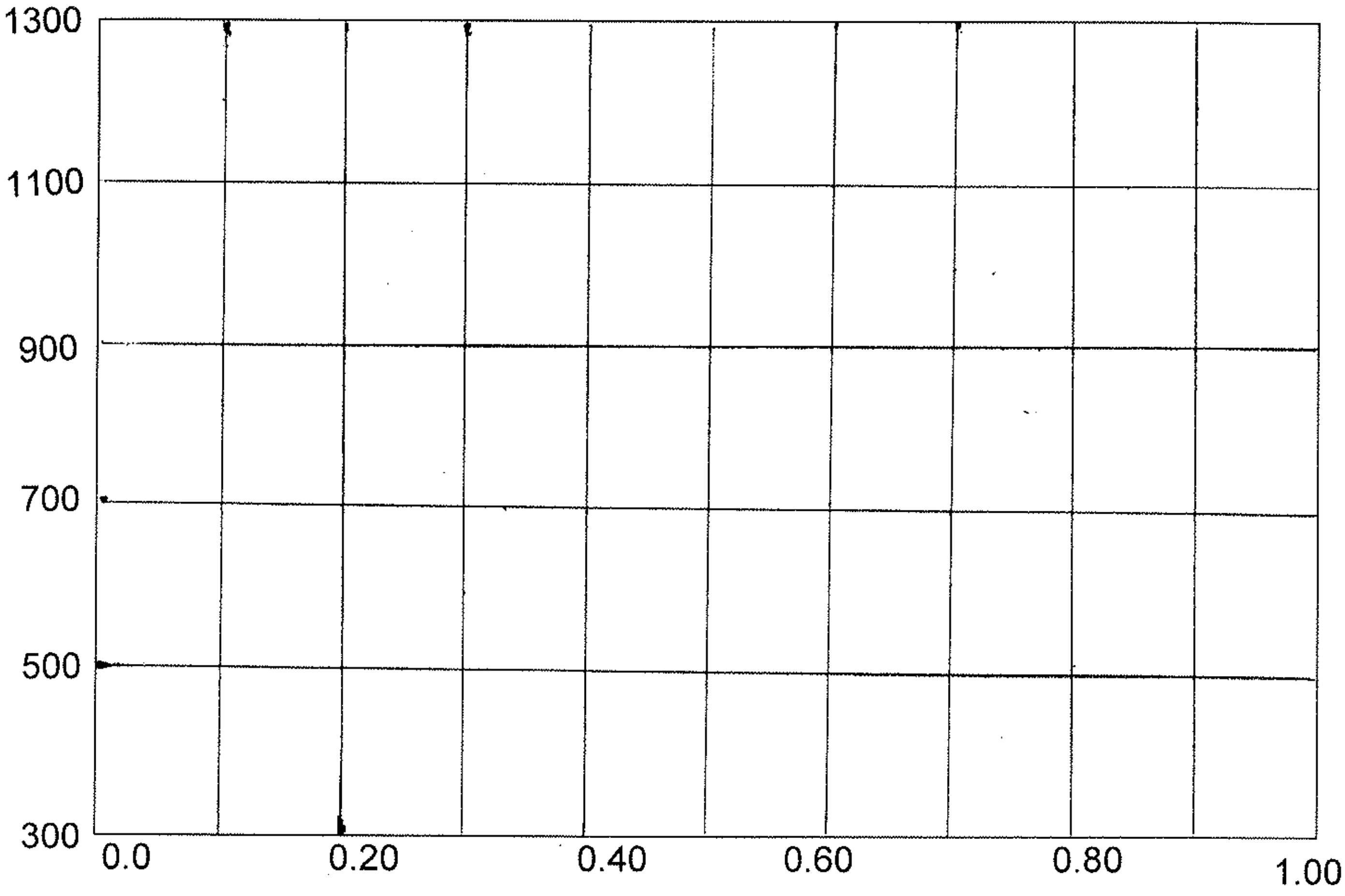
(a)	(b)	(c)	(d)	(e)

(f)	(g)	(h)	(i)	(j)


t = 35°C
80
70
60
50
40
P
mm Hg
0
0.2
0.4
0.6
0.8
1.0
(A)
H_2O
X_B
(B)
$C_4H_8O_2$
dioxane

3. The table below gives the break and halt (plateau in the cooling curve) temperatures found in the cooling curves of two metals A and B. Construct a phase diagram consistent with the data of these curves. Label the regions of the diagram, stating what phases and substances are present. Give the probable formula of any compounds that form

x_B	break, t °C	first halt, t °C	second halt, t °C
0.0		1100	
0.10	1060	700	
0.20	1000	700	
0.30	940	700	400
0.40	850	700	400
0.50	750	700	400
0.60	670	400	
0.70	550	400	
0.80		400	
0.90	450	400	
1.00		500	



4. For the reaction: $C(graphite) + 2H_2(g) \rightarrow CH_4(g)$
the change in enthalpy is -21 045 cal mol^{-1} at 600°C.
The third law entropies (cal mol^{-1} K^{-1} at 600°C and 1 atm are:
4.98 for C(graphite); 38.9 for $H_2(g)$; 56.6 for $CH_4(g)$

(a) Calculate the equilibrium constant for the reaction at 600°C.

(b) What experimental information would you need, besides that given above, in order to be able to evaluate K_p at any temperature? Make a suitable approximation that is adequate over a short temperature range and use it to estimate the equilibrium constant at 750°C.

(c) Is it better to use high or low temperatures to get the maximum yield of $CH_4(g)$? High or low pressures? Explain.

T	p

5 The activity of pure liquid water at 1 atm is 1 according to the definition of the standard state as a pure liquid at 1 atm. Calculate the activity of pure liquid water at 50°C and 10^4 atm, given that the integral $\int V_m \, dp$ between 1 atm and 10^4 atm is = 161.450 L atm for liquid water at 50°C.