Print in upper case the first three letters of your last name here: ☐☐☐

Your name: ***Jameson key***

Please put answers within boxes provided.

Chemistry 342

December 7, 1999

Final Exam (3 hours)

1 J = 1 kg m^2 s^{-2} k_B = 1.38066×10^{-23} J K^{-1} $R = N_{Avogadro}k_B$

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

$[p+a(n/V)^2](V-nb) = nRT$ van der Waals equation of state

$(\partial S/\partial V)_T = (\partial p/\partial T)_V$

$(\partial S/\partial p)_T = -(\partial V/\partial T)_p$

$(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$

$(\partial H/\partial p)_T = -T(\partial V/\partial T)_p + V = \{p + (\partial U/\partial V)_T\}(\partial V/\partial p)_T + V$

$C_p - C_V = \{p + (\partial U/\partial V)_T\}(\partial V/\partial T)_p$

monatomic gas molar heat capacity: $C_V = (3/2)R$

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, $\ln \gamma_\pm = z_+z_-I^{1/2}(1.17223)$

$\ln a_A = \Delta_{fus}H/R\left[-\frac{1}{T} + \frac{1}{T^*}\right]$ ionic strength ≡ ½$\sum m_i z_i^2$

❖❖

If insufficient information is provided, you may assume ideal behavior (and you must clearly state that you are doing so), <u>provided</u> that there is nothing in the problem that contradicts this assumption. Otherwise, you must assume that explicitly non-ideal systems are under consideration.

1. (a) Suppose that a piece of metal with a volume of 0.1 liter at 1 atm is compressed adiabatically by a shock wave of 10^5 atm to a volume of 0.090 liter. **Calculate** the ΔU and ΔH of metal. (Assume the compression occurs at a constant pressure of 10^5 atm.)

initial (0.1 L, 1 atm) → final (0.090 L, 10^5 atm)

p_{op} = 10^5 atm

$\Delta U = q + W$ $q = 0$ (adiabatic)

$dW = -p_{op}dV$ p_{op} = constant = 10^5 atm

$W = -10^5 \text{ atm} \int_{0.10}^{0.090} dV = 10^3$ L atm = 101.3 kJ   *Answer*

/

$\Delta \boldsymbol{H} = \Delta \boldsymbol{U} + \Delta(pV)$

$\Delta(pV) = [10^5(0.090) - 1(0.1)]\ 8.3144/0.082057 = 9.119\times10^5$ J

$\Delta \boldsymbol{H} = 101.3 + 911.9 = 1013.2$ kJ *Answer*

(b) When tungsten carbide WC was burned with excess oxygen in a bomb calorimeter, it was found for the reaction

$$WC(s) + (5/2)O_2\ (g) \rightarrow WO_3(s) + CO_2(g)$$

that $\Delta_{rxn}\boldsymbol{U}$ (300 K) = -1192 kJ mol^{-1}. **Calculate** $\Delta_{rxn}\boldsymbol{H}$ at 300 K.

$\Delta \boldsymbol{H} = \Delta \boldsymbol{U} + \Delta(pV)$

$\Delta(pV) = (n_{g,products} - n_{g,reactants})RT$ (ideal gas) = (1 - 5/2) R300

$\Delta \boldsymbol{H} = -1192\times10^3 + (1 - 5/2)\times8.3144\times300$ J mol^{-1} = - 1195.7 kJ mol^{-1}

Answer

(c) **Calculate** $\Delta_{formation}\boldsymbol{H}$ of tungsten carbide WC from its elements if the $\Delta \boldsymbol{H}$ of combustion of pure C and pure W at 300 K are, respectively, -393.5 kJ mol^{-1} and -837.5 kJ mol^{-1}.

$\Delta_f \boldsymbol{H}$

	$W(s) + 3/2O_2(s) \rightarrow WO_3(s)$	$\Delta \boldsymbol{H}$ = -837.5 kJ mol^{-1}
	$C(s) + O_2(s) \rightarrow CO_2(g)$	$\Delta \boldsymbol{H}$ = -393.5 kJ mol^{-1}
- {	$W(s) + C(s) \rightarrow WC(s)$	$\Delta_f \boldsymbol{H}$= ? }
	$WC(s) + (5/2)O_2\ (g) \rightarrow WO_3(s) + CO_2(g)$	$\Delta \boldsymbol{H}$ = -1195.7 kJ mol^{-1}

-1195.7 = [-837.5 -393.5 - $\Delta_f \boldsymbol{H}$]

$\Delta_f \boldsymbol{H}$ = -35.3 kJ mol^{-1} *Answer*

(d) One mole of an ideal gas, initially at 400 K and 10 atm, is adiabatically expanded against a constant pressure of 5 atm until equilibrium is re-attained. If $C_V = 18.8 + 0.021T$ J K^{-1} mol^{-1}, **calculate** ΔU, ΔH, and ΔS for the change in the gas.

initial (400 K, 10 atm) $\rightarrow$ final (T_f, 5 atm)

p_{op} = 5 atm

that is, equilibrium is re-attained when p_{gas} reaches p_{op}.

$\Delta \boldsymbol{U} = q + W$ $\quad$ $q = 0$ (adiabatic)

$p_{op} = 5$ atm $= p_f$ $\quad$ $W = -5 \int_{R400/10}^{RTf/5} dV = \Delta \boldsymbol{U} = -R(T_f - 200)$

$(\partial \boldsymbol{U}/\partial V)_T = 0$ (ideal gas)

$\Delta \boldsymbol{U} = \int_{400}^{Tf} C_V dT + \int (\partial \boldsymbol{U}/\partial V)_T \, dV$

$\Delta \boldsymbol{U} = \int_{400}^{Tf} \{18.8 + 0.021T\} dT = 18.8(T_f - 400) + (0.021/2)(T_f^2 - 400^2)$

$-R(T_f - 200) = 18.8(T_f - 400) + (0.021/2)(T_f^2 - 400^2)$

$0.0105T_f^2 + 27.1144T_f - 10862.88 = 0$ $\quad$ Solve for T_f,

$T_f = 352.5$ K

Substitute into $\Delta \boldsymbol{U} = -R(T_f - 200) = -8.3144\ (352.5 - 200) = -1268$ J mol^{-1}

Answer

$\Delta \boldsymbol{H}$

ideal gas, $\Delta(pV) = \Delta(RT) = R(T_f - 400)$

$\Delta \boldsymbol{H} = \Delta \boldsymbol{U} + R(T_f - 400) = -1268 - 395 = -1663$ J mol^{-1} $\quad$ Answer

$\Delta \boldsymbol{S}$

$d\boldsymbol{S} = C_p dT/T + (\partial \boldsymbol{S}/\partial p)_T \, dp$

$(\partial \boldsymbol{S}/\partial p)_T = -(\partial V/\partial T)_p = -R/p$ for an ideal gas $\quad$ also $C_p = C_V + R$ (ideal gas)

$\Delta \boldsymbol{S} = \int_{400}^{Tf} \{18.8 + 8.3144 + 0.021T\} dT/T + \int_{10}^{5} -R\, dp/p$

$\quad = \int_{400}^{Tf} \{27.1144\, d(\ln T) + 0.021 dT\} - 8.3144 \int_{10}^{5} d(\ln p)$

$\Delta \boldsymbol{S} = 27.1144 \ln(T_f/400) + 0.021(T_f - 400) - 8.3144 \ln(5/10)$

$\quad = -4.425 + 5.763 = +1.338$ J K^{-1}mol^{-1} $\quad$ Answer

2. When 2.00 mol of an ideal gas at 330 K and 3.50 atm is subjected to isothermal compression, its entropy decreases by 25.0 J K^{-1}. **Calculate** the final pressure of the gas and $\Delta \boldsymbol{G}$ for the compression.

p_f

To do this problem, we need to know how $\boldsymbol{S}$ and $\boldsymbol{G}$ change with p. From the given $\Delta \boldsymbol{S} = -25$ J K^{-1}, we should be able to get p_f.

Start with $d\boldsymbol{G} = V dp - \boldsymbol{S} dT$

$d\boldsymbol{G}$ is an exact differential, therefore the mixed derivatives are equal:

$(\partial V/\partial T)_p = -(\partial \boldsymbol{S}/\partial p)_T$

$d\boldsymbol{S} = (1/T)C_p\, dT - (\partial V/\partial T)_p\, dp$

Now we are ready to apply to this problem: isothermal $dT = 0$ leads to

$d\boldsymbol{S} = -(\partial V/\partial T)_p\, dp$ which integrates to $\int d\boldsymbol{S} = \int -(\partial V/\partial T)_p\, dp$

ideal gas $pV = nRT$ leads to $V = nRT/p$ so that $(\partial V/\partial T)_p = nR/p$

$\Delta \boldsymbol{S} = \int d\boldsymbol{S} = \int -nR\, dp/p = -nR \ln(p_f/p_i)$

$-25 \text{ J K}^{-1} = -2 \text{ mol} \times 8.3144 \text{ J K}^{-1}\text{mol}^{-1} \ln(p_f/3.5)$

Solve for p_f, $p_f = 15.7$ atm — *Answer*

$\Delta \boldsymbol{G}$

From $d\boldsymbol{G} = V dp - \boldsymbol{S} dT$

$\int d\boldsymbol{G} = \int V dp$ when isothermal

The ideal gas eqn $V = nRT/p$ leads to $\Delta \boldsymbol{G} = \int nRT dp/p$

isothermal leads to $\Delta \boldsymbol{G} = nRT \ln p_f/p_i$

$\Delta \boldsymbol{G} = -T\Delta \boldsymbol{S} = -330 \text{ K} \times \{-25 \text{ J K}^{-1}\}$

$= +8.25$ kJ — *Answer*

Alternatively,

$\Delta \boldsymbol{G}_T = \Delta \boldsymbol{H} - T\Delta \boldsymbol{S}$

ideal gas $(\partial \boldsymbol{H}/\partial p)_T = 0$, and $dT = 0$ gives $\Delta \boldsymbol{H} = 0$ also leads to

$\Delta \boldsymbol{G}_T = -T\Delta \boldsymbol{S}$ for this problem.

3. At -5°C, the vapor pressure of ice is 0.00396 atm and that of supercooled liquid water is 0.00416 atm. The enthalpy of fusion of ice is 5.85 kJ mol^{-1} at -5°C. **Calculate** ΔG and ΔS per mole for the transition at -5°C,

water→ ice

ΔG: The transition being considered is

liq (0.00416 atm, -5°C) → solid (0.00396 atm, -5°C) ΔG =?

$\Delta G = \mu_{H2O}(\text{solid, 0.00396 atm, -5°C}) - \mu_{H2O}(\text{liq, 0.00416 atm, -5°C})$

We know the following:

(1) $\mu_{H2O}(\text{liq, 0.00416 atm, -5°C}) = \mu_{H2O}(\text{gas, 0.00416 atm, -5°C})$

(2) $\mu_{H2O}(\text{solid, 0.00396 atm, -5°C}) = \mu_{H2O}(\text{gas, 0.00396 atm, -5°C})$

For the gas, we assume ideal gas law: since $dG = Vdp - SdT$, for the gas,

$$\mu_{H2O}(\text{gas, 0.00396 atm, -5°C}) = \mu_{H2O}(\text{gas, 1 atm, 0°C}) + \int_1^{0.00396} RTdp/p - \int_{268}^{273} S_{gas} dT$$

from (2) $$\mu_{H2O}(\text{solid, 0.00396 atm, -5°C}) = \mu_{H2O}(\text{gas, 1 atm, 0°C}) + \int_1^{0.00396} RTdp/p - \int_{268}^{273} S_{gas} dT$$

from (1) $$\mu_{H2O}(\text{liq, 0.00416 atm, -5°C}) = \mu_{H2O}(\text{gas, 1 atm, 0°C}) + \int_1^{0.00416} RTdp/p - \int_{268}^{273} S_{gas} dT$$

Subtracting these two eqns., we obtain:

$$\mu_{H2O}(\text{solid, 0.00396 atm, -5°C}) - \mu_{H2O}(\text{liq, 0.00416 atm, -5°C}) = \int_{0.00416}^{0.00396} RTdp/p = 8.3144(268)\ln(0.00396/0.00416)$$
$$= -109.79 \text{ J mol}^{-1}$$ Answer

ΔS

$\Delta G_T = \Delta_{fus}H_T - T\Delta S_T$

$\Delta G_{268} = \Delta_{fus}H_{268} - 268\,\Delta S_{268}$

$-109.79 \text{ J mol}^{-1} = 5.85\times10^3 - 268\Delta S_{268}$

$\Delta S_{268} = +22.238 \text{ J K}^{-1} \text{ mol}^{-1}$ Answer

4. The normal melting point of mercury is -38.87°C. At this temperature, the specific volume of the liquid is 0.07324 $cm^3\ g^{-1}$ and that of the solid is 0.07014 $cm^3\ g^{-1}$. The heat of fusion is 11.63 $J\ g^{-1}$. Assume these quantities are all independent of T and p.

(a) **Calculate** ΔS and ΔG when 1 g liquid mercury freezes at -38.87°C.

ΔS

LIQ (−38.87°C, 1atm) → SOLID (−38.87°C, 1atm)

$q_p = -\Delta_{fus}H = q_{REV} = -11.63\ J\ g^{-1}$

$dS = \frac{dq_{REV}}{T} \rightarrow \Delta S = \frac{q_{REV}}{T} = \frac{-11.63}{(-38.87+273.1)}\ J\ g^{-1}K^{-1}$

$= -0.0497\ J\ g^{-1}K^{-1}$

ΔG at equilibrium at normal melting point

$\Delta G = 0$

(b) **Calculate** the melting point of mercury under a pressure of 200 atm.

$dG_{LIQ} = V_{LIQ}\,dp - S_{LIQ}\,dT$

$dG_{SOLID} = V_{SOLID}\,dp - S_{SOLID}\,dT$

at equil $dG_{LIQ} = dG_{SOLID}$

$(V_{LIQ} - V_{SOLID})\,dp = (S_{LIQ} - S_{SOLID})\,dT$

$\int_{1atm}^{200atm} (V_{LIQ} - V_{SOLID})\,dp = \int_{-38.87+273}^{T} (S_{LIQ} - S_{SOLID})\,dT$

$(.07324 - .07014)\ cm^3 g^{-1}\ (200-1)\ atm \times 10^{-3} \frac{L}{cm^3} \times \frac{8.3144}{.082057} = 11.63\ J g^{-1} \int_{-38.87+273}^{T} \frac{dT}{T}$

$= 11.63 \ln \frac{T}{(-38.87+273)}$

solve for T

T = 235.6 K

(c) The vapor pressure of solid iodine is 0.000329 atm, and its density is 4.93 g cm^{-3} at 293 K. **Calculate the vapor pressure** of iodine under 1000 atm pressure of argon assuming that the argon does not dissolve in the iodine.

(1) μ_{I_2}(SOLID, 293 K, .000329 atm) = μ_{I_2}(GAS, 293, .000329 atm)

(2) μ_{I_2}(SOLID, 293 K, 1000 atm) = μ_{I_2}(GAS, 293, P)

Eq(2) − Eq(1) gives

$$\int_{.000329}^{1000} V_{\text{SOLID } I_2 \text{ at } 293}\, dp = \int_{.000329\text{ atm}}^{P} \frac{RT}{P}\, dp$$

$V_{\text{GAS } I_2}$ at 293 assume ideal

∴ Molecular weight of I_2 = 127×2 g mol^{-1}

$$V_{SOLID} = \frac{10^{-3}\ L}{4.93\ g} * 127\times 2\ g/mol = 5.15\times10^{-2}\ L\ mol^{-1}$$

$$5.15\times10^{-2}\ L\ mol^{-1}(1000\ atm - .00033)\times\frac{8.3144}{0.082057} = 8.3144(293)\ln\frac{P}{0.000329}$$

solve for P

P = 0.00280 atm

(d) Given the following data:
At 298 K, the standard enthalpy of combustion of diamond is -395.3 kJ mol^{-1} and that of graphite is -393.4 kJ mol^{-1}. The densities of diamond and graphite are 3.513 and 2.260 g cm^{-3} respectively. The molar entropies of diamond and graphite are 2.439 and 5.694 J K^{-1} mol^{-1}, respectively.

Find $\Delta G^{\ominus}_{298\,K}$ for the transition graphite→diamond at 298 K.

process: graphite (1 bar, 298 K) →diamond (1 bar, 298 K)

$\Delta \boldsymbol{G}^{\ominus}_{298\,K} = \Delta \boldsymbol{H}^{\ominus}_{298\,K} - T\ \Delta \boldsymbol{S}^{\ominus}_{298\,K}$ so we need to find $\Delta \boldsymbol{H}^{\ominus}_{298\,K}$ first.

graphite (1 bar, 298 K) + O_2 → CO_2(g, 1 bar, 298 K) $\Delta \boldsymbol{H}^{\ominus}_{298\,K}$= -393.4
- {diamond (1 bar, 298 K) + O_2 → CO_2(g, 1 bar, 298 K) $\Delta \boldsymbol{H}^{\ominus}_{298\,K}$= -395.3}
graphite (1 bar, 298 K) →diamond (1 bar, 298 K) $\Delta \boldsymbol{H}^{\ominus}_{298\,K}$= 1.9 kJ mol^{-1}

$\Delta \boldsymbol{S}^{\ominus}_{298\,K} = \boldsymbol{S}^{\ominus}_{298\,K}$(diamond) - ($\boldsymbol{S}^{\ominus}_{298\,K}$(graphite)= 2.439 - 5.694
= -3.255 J K^{-1} mol^{-1}

$\Delta \boldsymbol{G}^{\ominus}_{298\,K} = 1.9\times10^3 - (298)(-3.255) = +2870$ J mol^{-1} Answer

(e) **Calculate the pressure** at which diamond and graphite would be in equilibrium at 298 K.

$$\begin{array}{ccc}
 & b & \\
\text{graphite (298 K, } p) & \rightarrow & \text{diamond (298 K, } p) \\
a\uparrow & & c\downarrow \\
\text{graphite (298 K, 1 bar)} & \leftarrow & \text{diamond (298 K, 1 bar)} \\
 & d &
\end{array}$$

$\Delta \boldsymbol{G}_{298} = 0 = \Delta \boldsymbol{G}_a + \Delta \boldsymbol{G}_b + \Delta \boldsymbol{G}_c + \Delta \boldsymbol{G}_d$
$d\boldsymbol{G} = Vdp - \boldsymbol{S}dT,\ dT = 0$
$\Delta \boldsymbol{G}_a = \int_{1\,bar}^{p} V(\text{graphite, 298 K})\, dp = V(\text{graphite, 298 K})(p-1)$
$\Delta \boldsymbol{G}_b = 0$ (at equilibrium)
$\Delta \boldsymbol{G}_c = -\int_{1\,bar}^{p} V(\text{diamond, 298 K})\, dp = -V(\text{diamond, 298 K})(p-1)$
$\Delta \boldsymbol{G}_d = -\Delta \boldsymbol{G}^{\ominus}_{298\,K} = -2870$ J mol^{-1} from above.
$0 = \Delta \boldsymbol{G}_a + \Delta \boldsymbol{G}_b + \Delta \boldsymbol{G}_c + \Delta \boldsymbol{G}_d = \{V(\text{graphite}) - V(\text{diamond})\}(p-1) + 0 - 2870$
$0=(10^{-3}\ \text{L}\times12\ \text{g mol}^{-1})\cdot\{(1/2.260) - (1/3.513)\}(p-1) - 2870 \times 0.01\text{L bar/J}$
Solve for p. $p = 1.51\times10^4$ bar Answer

5. The partial pressure of acetic acid above acetic acid - benzene solutions at 50°C are shown below:

x_a(%)	1.60	4.39	8.35	11.38	17.14	29.79	36.96	58.34	66.04	84.35	99.35	100
p_a (torr)	3.63	7.25	11.51	14.2	18.4	24.8	28.7	36.3	40.2	50.7	54.7	54.9

The vapor pressure of pure benzene at 50°C is 152 torr.

You may use the space below to derive any relations you need to answer the questions that follow.

$a = P_a / P_a^*$ $\quad \gamma_a = \dfrac{a_a}{x_a}$ $\quad P_{a\,ideal} = x_a P_a^*$

$\lim_{x_a \to 0} P_a = K_H x_a$

Henry's law

Consider a (acetic acid+benzene) liquid solution that is 17.14 mole percent in acetic acid. **Calculate the activity and the activity coefficient** of acetic acid in this solution, using the rational system.

$a = p_a/p_a{}^* = 18.4/54.9 = 0.335$ $\qquad \gamma_a = 0.335/0.1714 = 1.955$

What would the partial pressure have been if this solution had been ideal?

$p_a = 0.1714 \times 54.9 = 9.41$ torr

What would the partial pressure have been if this solution obeyed Henry's law?

$p_a / x_a = 3.63/0.016 = 226.875$ at the limit of x_a very small.. ∴ $K_H = 2.26875$,
$p_a = x_a K_H = 0.1714 \times 226.875 = 38.9$ torr

Had the solution been an ideal solution, **write an equation** (with all the known constants explicitly written into it) that would describe the straight line that expresses the relation between the total vapor pressure and the molefraction of acetic acid in the liquid phase.

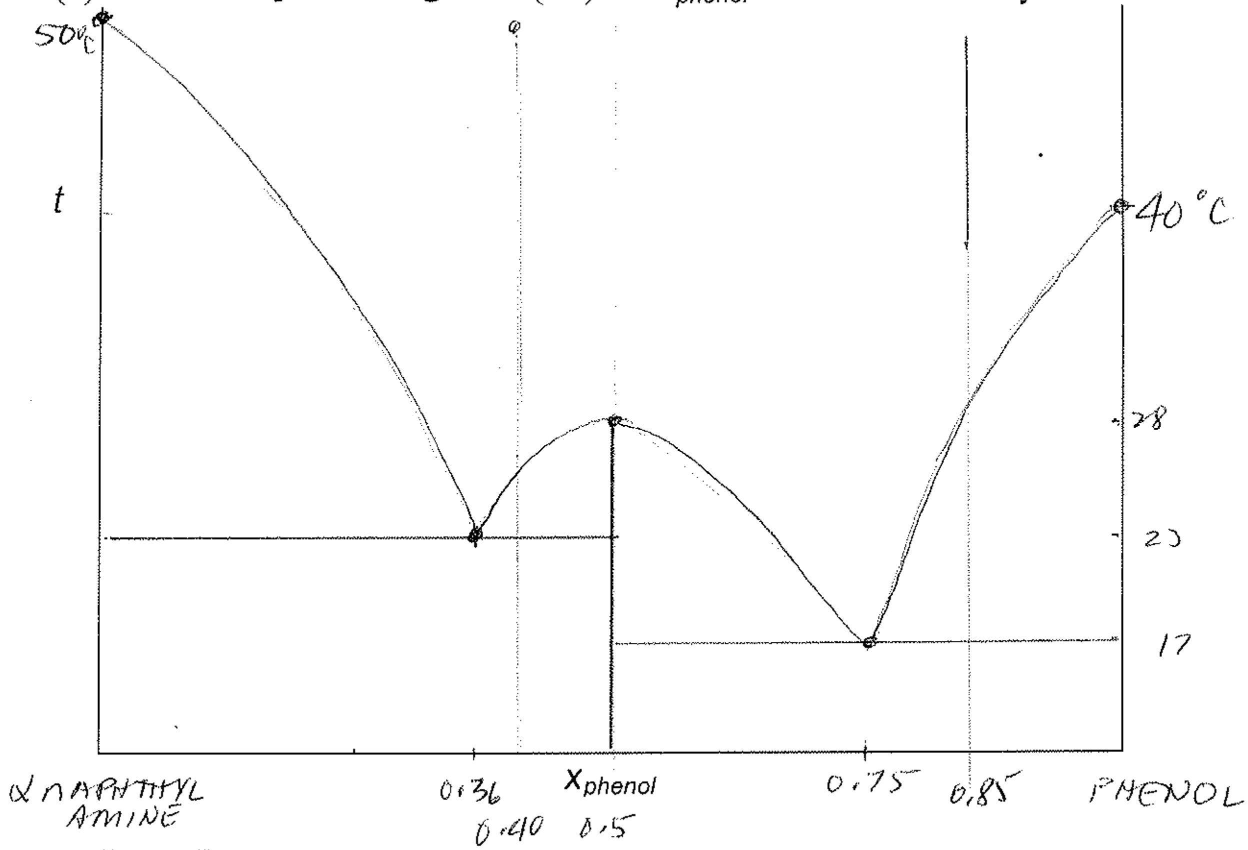
$p = x_a 54.9 + (1 - x_a)152$

Would the total vapor pressure of (acetic acid+benzene) liquid solutions be **greater or less** (which one?) than that given by that straight line? **Explain.**

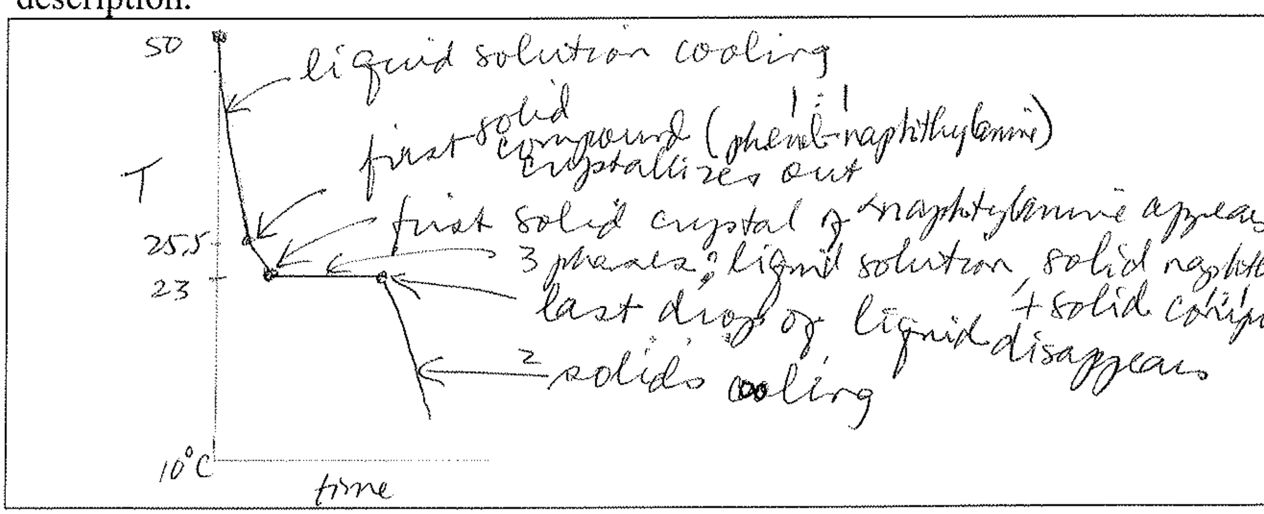
$\gamma > 1$ Therefore, total vapor pressure will be greater than ideal.

6. Phenol melts at 40°C; α-naphthylamine melts at 50°C. In the binary system, there are eutectics at 75 mol% phenol and 17°C, and 36 mol % phenol and 23°C. A compound is formed at 50 mol% phenol with a melting point of 28°C. All these data are at 1 atm.

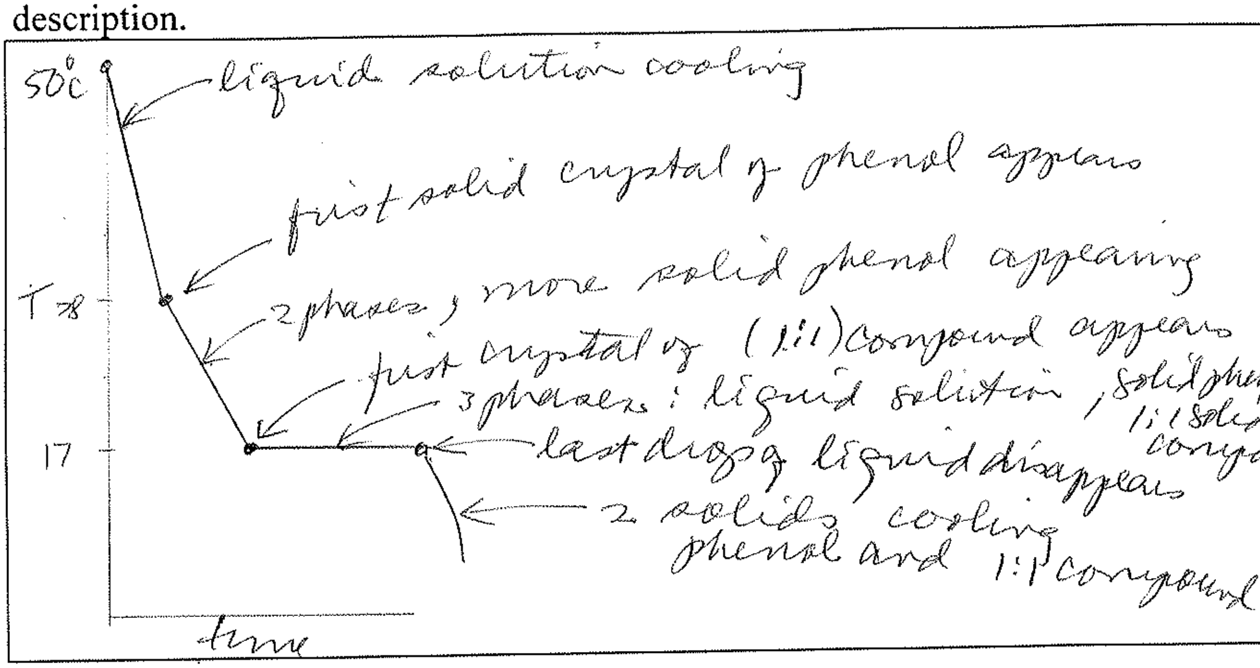
(a) **Sketch the phase diagram** t (°C) vs. x_{phenol} at 1 atm for this system.



(b) **Describe** clearly what happens if a mixture containing 40 mol% phenol is cooled from 50°C to 10°C. Include a labeled cooling curve to illustrate your description.

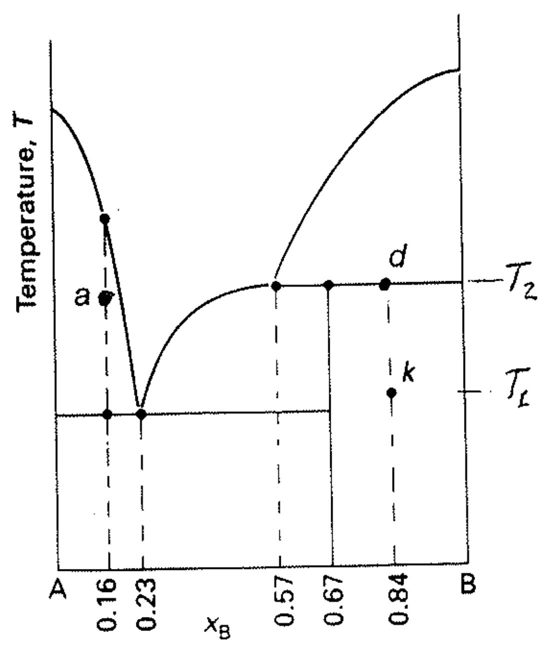


(c) **Describe** clearly what happens if a mixture containing 85 mol% phenol is cooled from 50°C to 10°C. Include a labeled cooling curve to illustrate your description.



(d) Given the phase diagram below which represents a solid-liquid equilibrium system, **completely describe the system** at each of the state points (a), (d), and (k) indicated, **following the format of the example.**

For example, "At t = 60°C and overall composition $X_{acetone}$ = 0.30, two phases: a liquid solution of composition $x_{acetone}$ = 0.25 and a gas mixture with composition $y_{acetone}$ = 0.42"



state point (a)

At T_2 and overall composition $X_B = 0.16$, two phases: a liquid solution of composition $x_B = 0.20$ and pure solid A

state point (d)

At T_2 and overall composition $X_B = 0.84$, three phases at equilibrium: a liquid solution of composition $X_B = 0.57$, pure solid B and pure solid compound AB_2

state point (k)

At T_1 and overall composition $X_B = 0.84$, Two phases: pure solid B and pure solid compound AB_2 are present

7. For each of the following processes, **state which** of the quantities ΔT, $\Delta \boldsymbol{U}$, $\Delta \boldsymbol{H}$, $\Delta \boldsymbol{S}$, $\Delta \boldsymbol{G}$, q, W **are equal to zero** for the system specified. **For those which are not zero, state whether the value is positive or negative.** If information is not available to determine the sign of a non-zero value, use NA. Hint: Only ~~four~~ five NA

(a) A <u>non-ideal gas</u> is taken around an <u>irreversible</u> cycle.

(b) At 25°C a solution is formed by mixing 0.3 mol of liquid C_6H_{14} with 0.5 mol of liquid C_7H_{16}, forming an ideal solution.

(c) H_2 and O_2 react to form H_2O inside an insulated bomb calorimeter.

(d) One mole of liquid benzene is vaporized at 80°C (its normal boiling point) and 1 atm in a canister fitted with a frictionless weightless piston and immersed in a heat reservoir that is maintained at 80°C.

(e) C_2H_6 is burned with excess oxygen inside an insulated canister fitted with a frictionless weightless piston.

(f) A reaction occurs in an electrochemical cell that has $\mathcal{E} = +\,0.50$ volt at constant T and p. In another experiment, $\mathcal{E}$ of this cell is found to have a <u>negative</u> temperature coefficient. No gases are involved at either electrode of this cell.

(g) Heat is withdrawn slowly at a uniform rate from a liquid-solid system at 1 atm at its eutectic temperature without any work being done.

(h) A <u>non-ideal</u> gas [having negative values for both $(\partial \boldsymbol{U}/\partial V)_T$ and $(\partial \boldsymbol{H}/\partial p)_T$] originally at V_1 expands isothermally into an evacuated volume so as to make its final volume equal to $3V_1$.

(i) Two ideal gases A and B each at 0.5 atm and 300 K separately occupy two glass bulbs joined by a stopcock. The stopcock is opened and all thermometer and pressure gauge readings are unchanged.

(j) Reactants in dilute aqueous solutions are combined in a open flask immersed in a thermostatted bath, and an exothermic reaction occurs until chemical equilibrium is achieved. No gases are involved in this reaction.

Enter 0, +, - , or NA **into the appropriate box in the table and provide a brief explanation on the next page**

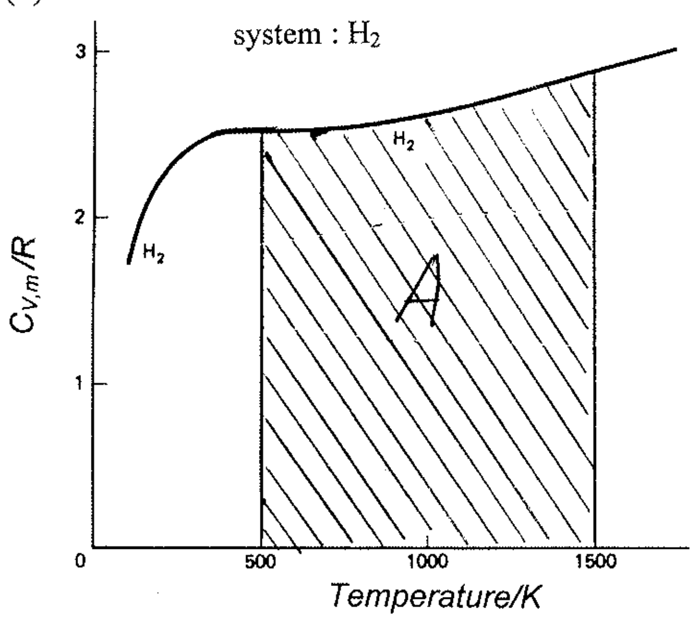
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)
ΔT	0	0	+	0	+	0	0	0	0	0
$\Delta \boldsymbol{U}$	0	0	0	NA	−	−	−	−	0	−
$\Delta \boldsymbol{H}$	0	0	NA	+	0	−	−	+	0	−
$\Delta \boldsymbol{S}$	0	+	+	+	+	−	−	+	+	NA
$\Delta \boldsymbol{G}$	0	−	−	0	−	−	0	−	−	−
q	NA	0	0	+	0	−	−	−	0	−
W	NA	0	0	−	−	−	0	0	0	0

	The key to each answer of 0,+, or - in each case	Fill the table, following the key points:
(a)	*cycle* makes all Δ(state function) = 0	q and W opposite signs but NA
(b)	$dT = 0$, *ideal liquid solution* means $(\Delta V, \Delta \boldsymbol{H}, q) = 0$ upon mixing.	$\Delta T = 0$, $\Delta \boldsymbol{H} = 0$, $q = 0$, $\Delta V = 0$ gives $W = 0$, $\Delta \boldsymbol{U} = q+W = 0$, $\Delta \boldsymbol{S}_{mixing} > 0$ since greater disorder in the mixture than in separate pure liquids, $\Delta \boldsymbol{G} = \Delta \boldsymbol{H} - T\Delta \boldsymbol{S} = 0 - [+] = [-]$
(c)	$q = 0$, $dV = 0$, isolated system, spontaneous reaction, $\Delta n_{gas} = -1$	$\Delta T > 0$ since *adiabatic* combustion, $W=0$, $\Delta \boldsymbol{U} = q_V = 0$, spontaneous, $\therefore$ $\Delta \boldsymbol{S}_{isol\ sys} > 0$ and $\Delta_{rxn} \boldsymbol{G} < 0$ $\Delta \boldsymbol{H} = \Delta \boldsymbol{U} + \Delta(n_{gas}RT) = 0 + R(T_f - 1.5T_i) =$ NA
(d)	$dT = 0$, $dp = 0$, $dV +$, two phases are at equilibrium during the liq$\rightarrow$gas transformn	$\Delta \boldsymbol{G} = 0$ at equilibrium, $\Delta \boldsymbol{S} > 0$ since $\boldsymbol{S}_{gas} > \boldsymbol{S}_{liq}$, $\Delta_{vap} \boldsymbol{H} > 0$ since $\boldsymbol{H}_{gas} > \boldsymbol{H}_{liq}$, $q_p = \Delta \boldsymbol{H} > 0$, $\Delta \boldsymbol{U} = q_p - p\Delta V =$ NA
(e)	$q = 0$, $dp = 0$, $\Delta n_{gas} = +½$, $dV +$, spontaneous reaction	$\Delta T > 0$ since *adiabatic* combustion, $q = 0$, $\Delta \boldsymbol{H} = q_p = 0$, $W = -p\Delta V < 0$, $\Delta \boldsymbol{U} = 0 + W < 0$ spontaneous, $\therefore \Delta \boldsymbol{G} < 0$, $\Delta \boldsymbol{H} - T\Delta \boldsymbol{S} < 0$ leads to $\Delta \boldsymbol{S} > 0$
(f)	$dT = 0$, $dp = 0$, $\Delta n_{gas} = 0$, $\mathcal{E} > 0$ $(\partial \mathcal{E}/\partial T)_p < 0$, $\Delta_{rxn} \boldsymbol{G} = -\nu \mathcal{F} \mathcal{E} = W_{elec}$ $\nu \mathcal{F} (\partial \mathcal{E}/\partial T)_p = \Delta_{rxn} \boldsymbol{S}$, $\Delta_{rxn} \boldsymbol{H} = -\nu \mathcal{F} \cdot \{ \mathcal{E} - T(\partial \mathcal{E}/\partial T)_p \}$	From signs of $\mathcal{E}$ and $(\partial \mathcal{E}/\partial T)_p$, $W_{elec} < 0$, $\Delta_{rxn} \boldsymbol{G} < 0$, $\Delta_{rxn} \boldsymbol{S} < 0$, $\Delta_{rxn} \boldsymbol{H} < 0$ $q_p = \Delta \boldsymbol{H} < 0$, $\Delta \boldsymbol{U} = q + W_{elec} < 0$
(g)	$dT = 0$, $dp = 0$, $W = 0$, $q < 0$, 3 phases remain at equilibrium at $T_{eutectic}$,	$\Delta \boldsymbol{G} = 0$ at equilibrium, $\Delta \boldsymbol{U} = q + W < 0$ $\Delta \boldsymbol{H} = q_p < 0$, $\Delta \boldsymbol{H} - T\Delta \boldsymbol{S} = 0$ leads to $\Delta \boldsymbol{S} < 0$
(h)	$dT = 0$, $dV > 0$, $p_{op} = 0$, spontaneous $(\partial \boldsymbol{U}/\partial V)_T < 0$, $(\partial \boldsymbol{H}/\partial p)_T < 0$ ideal gas $d\boldsymbol{S} = C_V dT + nR\,dV/V$ $\Delta \boldsymbol{S}_T = nR \int dV/V$	$d\boldsymbol{U} = C_V dT + (\partial \boldsymbol{U}/\partial V)_T dV = 0+(-)(+) = [-]$ $d\boldsymbol{H} = C_p dT + (\partial \boldsymbol{H}/\partial p)_T dp = 0+(-)(-) = [+]$ $W = 0$, $q = \Delta \boldsymbol{U} - W = [-] - 0 = [-]$ spontaneous, thus $\Delta \boldsymbol{G} < 0$ $\Delta \boldsymbol{S}_T > 0$ (also greater space disorder)
(i)	$dT = 0$, $dp = 0$, $dV_{tot} = 0$, spontaneous mixing, ideal: $\boldsymbol{U} = \boldsymbol{U}(T)$, $\boldsymbol{H} = \boldsymbol{H}(T)$	$dV_{tot} = 0 \therefore W = 0$, $dT = 0 \therefore \Delta \boldsymbol{U} = \Delta \boldsymbol{H} = 0$ $q = \Delta \boldsymbol{U} - W = 0$, no q and $W \therefore$ an isolated system, which has $\Delta \boldsymbol{S} > 0$ for spontaneous change, spontaneous, $\therefore$ $\Delta \boldsymbol{G}_{T,p} < 0$
(j)	$dT = 0$, $dp = 0$, $q < 0$, $\Delta n_{gas} = 0$ spontaneous reaction	$\Delta n_{gas} = 0 \therefore W = 0$, $\Delta \boldsymbol{U} = q+W = [-] +0$ $\Delta \boldsymbol{H} = \Delta \boldsymbol{U} + \Delta(pV) = [-] +0$ spontaneous, $\therefore$ $\Delta_{rxn} \boldsymbol{G}_{T,p} < 0$ $\Delta \boldsymbol{G} = \Delta \boldsymbol{H} - T\Delta \boldsymbol{S}$ leads to $[-] = [-] - T\Delta \boldsymbol{S}$ $\therefore \Delta \boldsymbol{S} =$ NA

8. In each of the following plots, given the numerical value for the area $|A|$ in the units appropriate to the graph, **write an equation defining the area, following the format of the example.**

For example, "$\Delta G_T = \int_{1\text{ atm}}^{20\text{atm}} V_m\, dp = A$ L atm mol^{-1}".

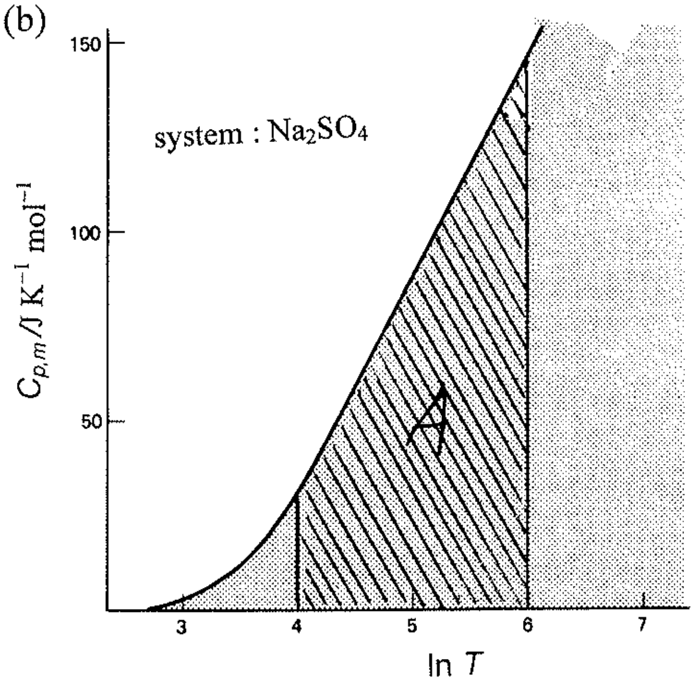
(a)



Answer:

$$\Delta U = \int_{500}^{1500K} C_v\, dT = 8.3144A \text{ J mol}^{-1}$$

(b)

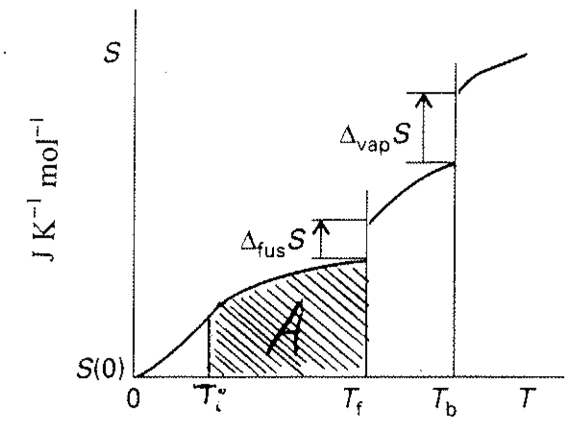


Answer:

$$\Delta S = \int_{54.6K}^{403.4K} C_p \frac{dT}{T} = A \text{ J K}^{-1}\text{ mol}^{-1}$$

(c)

system: solid at 1 atm



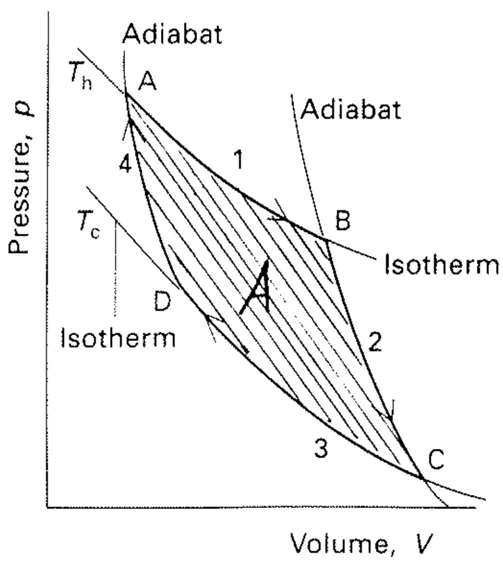
Answer:

at constant p

$$\Delta G = \int_{T_i}^{T_f} -S\,dT = -A \quad \text{J mol}^{-1}$$

(d)

system : gas in a Carnot cycle



Answer:

$$W = -\int p_{op}\,dV \overset{\text{reversible}}{=} -\int p\,dV$$

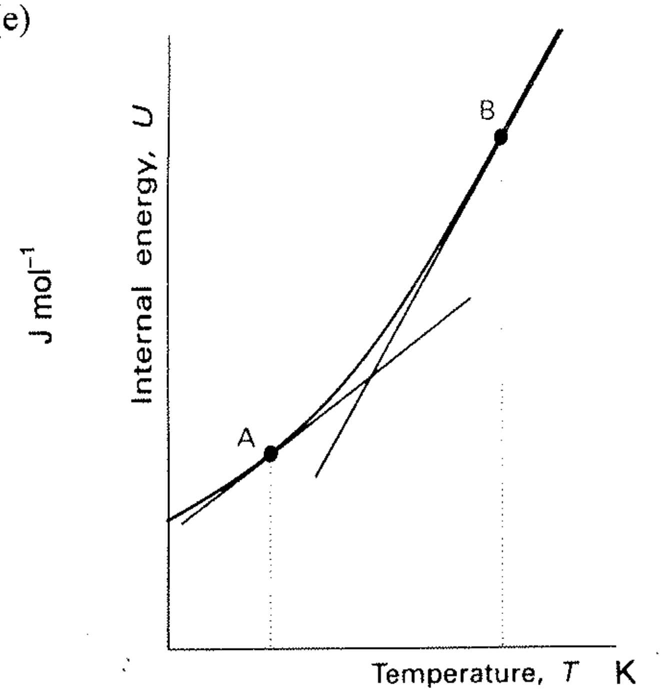
$$W_{TOTAL} = A \quad \text{L atm mol}^{-1}$$

is the algebraic sum of four areas each one of the form $-\int p\,dV$

In each of the following plots, given the straight line with a value of the slope as shown in units that are appropriate to the plot, **write an equation describing the straight line, following the format of the example.**

For example, "$p_A = p^*_A x_A$, where the slope is p^*_A = 33.5 mm Hg"

(e)

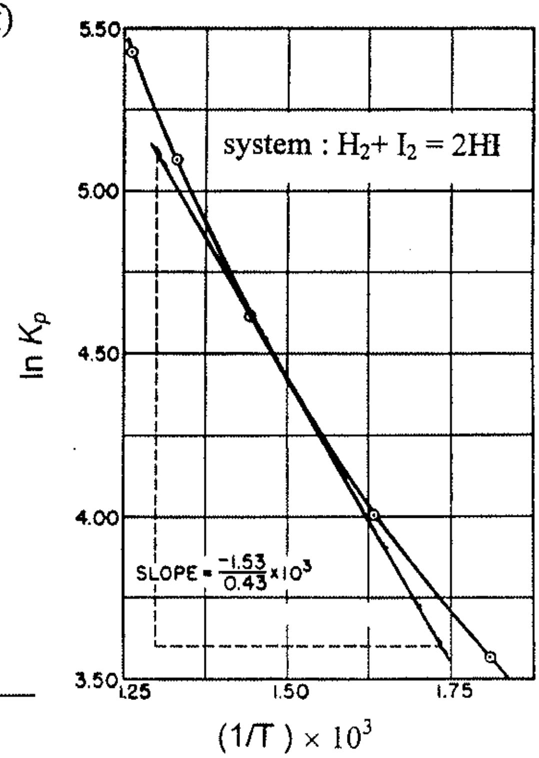


Answer:

slope is

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

(f)

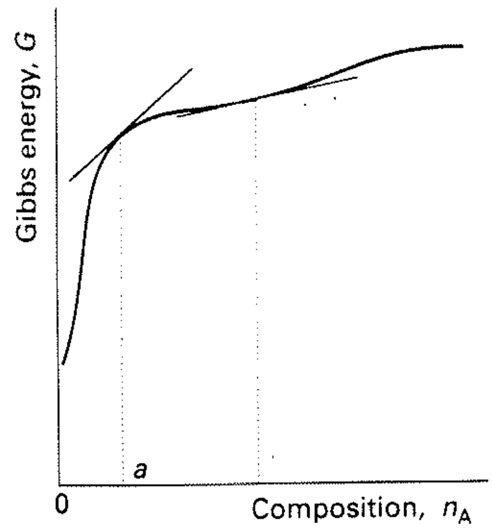


Answer:

$$\frac{d \ln K_p}{d\left(\frac{1}{T}\right)} = \overbrace{\frac{-\Delta_{rxn} H^\ominus}{R}}^{\text{slope}}$$

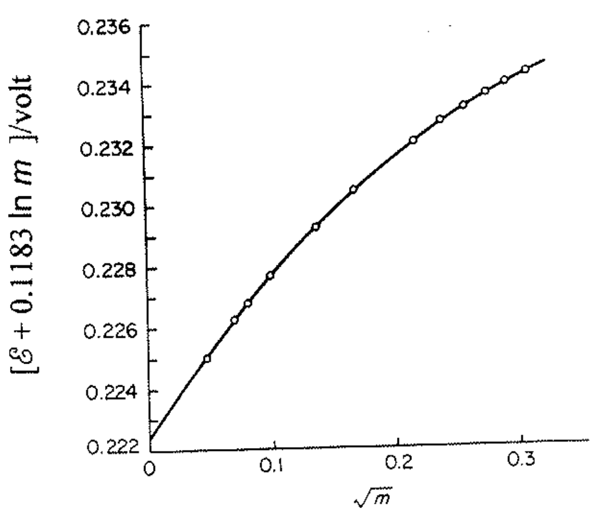
$$\ln K_p = \frac{-\Delta_{rxn} H^\ominus}{RT} + \ldots$$

$$A \ln T + BT + CT^2 + \ldots$$

(g)	Answer:
	$\mu_A(T,p,x_A) = \left(\frac{\partial G}{\partial n_A}\right)_{T,p,n_B}$ the slope is the numerical value of the chemical potential of A in the liquid solution of this composition

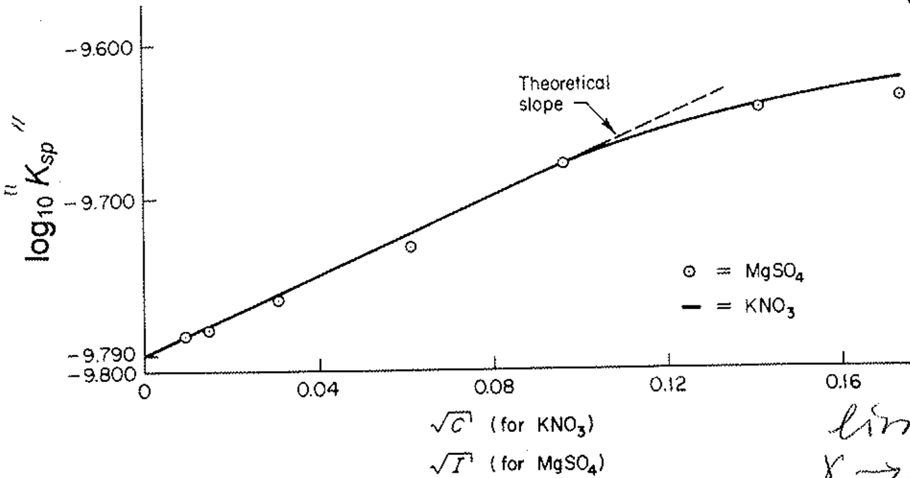
In each of the following plots, given the data curve that is extrapolated to the appropriate limit to find the intercept, shown in units that are appropriate to the plot, **write an equation describing the intercept , following the format of the example.**

For example, "lim (as p→0) $(pV_m/RT) = (pV_m/RT)_{ideal} = 1$"

(h)	Answer:
	$\lim_{\gamma_\pm \to 1} \left[\mathcal{E} + \frac{2RT}{\mathcal{F}} \ln\left(\frac{m}{1}\right) \right]$ $= \lim_{\gamma_\pm \to 1} \left[\mathcal{E}^\ominus - \frac{2RT}{\mathcal{F}} \ln \gamma_\pm \right]$ $= \mathcal{E}^\ominus$ since $\nu = 1$, $s = 2$, $\ln \gamma_\pm = A m^{\frac{1}{2}}$

(i)

system: AgCl at 25°C
with increasing KNO_3 concentration
and increasing $Mg(SO_4)$ concentration



Answer:

$$\text{true } K_{sp} = \gamma_\pm^2 \overbrace{m_{Ag^+} m_{Cl^-}}^{"K_{sp}"} = \gamma_\pm^2 m^2$$

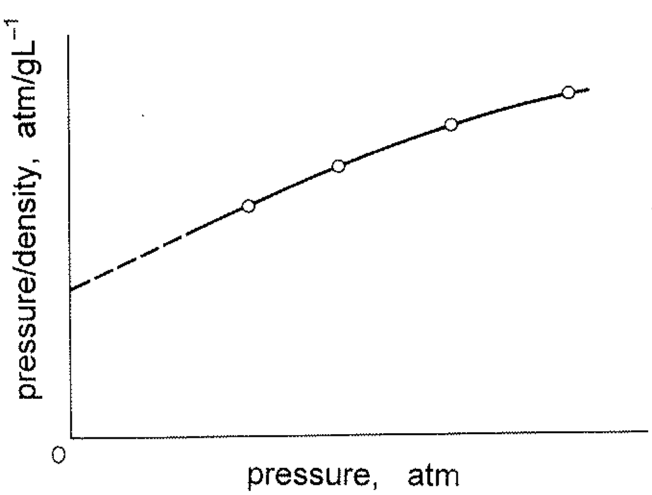
$$\log_{10} K_{sp\,\text{true}} = 2\log_{10}\gamma_\pm + 2\log_{10} m$$

$$2\log_{10} m = \log_{10} K_{sp\,\text{true}} - 2\underbrace{\log_{10}\gamma_\pm}_{AI^{1/2}}$$

$$\lim_{\gamma_\pm \to 1} (2\log_{10} m) = \log_{10} K_{sp\,\text{true}}$$

(j)

system: a non-ideal gas
of unknown molecular weight



Answer:

ideal gas $pV = nRT$

$$p = \underbrace{\frac{g}{V}}_{\text{density}} \frac{RT}{\underbrace{M}_{\text{molec. wt}}}$$

$$\frac{P}{g/V} = \frac{RT}{M}$$

$$\lim_{P \to 0} \frac{P}{(g/V)} = \frac{RT}{M}$$