

**COLLEGE OF ENGINEERING**  
**Department of Metallurgical & Materials Engineering**  
**The University of Alabama**

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MTE 562

Thermodynamics

**QUIZ II**

**Q.1**

a) (5 pts)

Define Gibbs Phase Rule

b) (10 pts)

Show that for a two phase equilibrium,

$$\frac{dT}{dP} = \frac{(V^{\text{II}} - V^{\text{I}}) T}{\Delta H}$$

This relationship is called Clapeyron equation.

c) (20 pts) The vapor pressures (in Torr) of solid and liquid uranium hexafluoride are:

$$\log P_s = 10.648 - 2559.5/T \quad \text{and} \quad \log P_l = 7.540 - 1511.3/T$$

a) Calculate the temperature of the triple point.

b) Assuming the latent heats of vaporization and sublimation to be independent of temperature, calculate their values.

**Q.2**

a) (5 pts)

Explain the conditions for the feasibility of chemical reactions

b) (10 pts)

For a chemical reaction,



derive that  $\Delta_r G = \Delta_r G^\circ + RT \ln J$

c) (20 pts)

Calculate  $\Delta_r G^\circ$ ,  $\Delta_r H^\circ$ , and  $\Delta_r S^\circ$  at 1100 K for the following reaction by using the attached tables.



**Q.3**

a) (10 pts)

Explain the following:

1. Raoult's Law
2. Henry's Law

b) (20 pts)

The vapor pressures (in mm Hg) of solid silver and solid silver-palladium alloys were expressed as functions of temperature (in the range 1092-1221 K) as follows:

For pure solid silver,

$$\log P_{\text{Ag}} = -13,696/T + 8.727$$

For solid Ag-Pd alloy,  $X_{\text{Ag}} = 0.802$  (the vapor above the alloy contains no Pd),

$$\log P_{\text{Ag}} = -13,795/T + 8.649$$

(a) Calculate the fugacity of silver in the pure state and in the alloy at 1200K.

(b) Calculate the activity and activity coefficient for silver in Ag-Pd solid Solution at 1200 K.

**Table 12.1** Thermodynamic properties of Al in its standard reference state.  
Reproduced from Gen. Ref. (1).

$T/K$	$(J K^{-1} mol^{-1})^{\circ}$			$(kJ mol^{-1})^{\circ}$			
	$C_p^{\circ}$	$S^{\circ}$	$-[G^{\circ}-H^{\circ}(T_r)]/T$	$H^{\circ}-H^{\circ}(T_r)$	$\Delta_f H^{\circ}$	$\Delta_f G^{\circ}$	$Log K_f$
0	0.	0.	Infinite	-4.539	0.	0.	0.
100	12.997	6.987	47.543	-4.056	0.	0.	0.
200	21.338	19.144	30.413	-2.254	0.	0.	0.
298.15	24.209	28.275	28.275	0.	0.	0.	0.
300	24.247	28.425	28.276	0.045	0.	0.	0.
400	25.784	35.630	29.248	2.553	0.	0.	0.
500	26.842	41.501	31.129	5.186	0.	0.	0.
600	27.886	46.485	33.283	7.921	0.	0.	0.
700	29.100	50.872	35.488	10.769	0.	0.	0.
800	30.562	54.850	37.663	13.749	0.	0.	0.
900	32.308	58.548	39.780	16.890	0.	0.	0.
933.450	32.959	59.738	40.474	17.982	Crystal $\leftrightarrow$ Liquid		
933.450	31.751	71.213	40.474	28.693	Transition		
1000	31.751	73.400	42.594	30.806	0.	0.	0.
1100	31.751	76.426	45.534	33.981	0.	0.	0.
1200	31.751	79.189	48.225	37.156	0.	0.	0.
1300	31.751	81.730	50.706	40.331	0.	0.	0.
1400	31.751	84.083	53.007	43.506	0.	0.	0.
1500	31.751	86.273	55.153	46.681	0.	0.	0.
1600	31.751	88.323	57.162	49.856	0.	0.	0.
1700	31.751	90.247	59.052	53.031	0.	0.	0.
1800	31.751	92.062	60.836	56.207	0.	0.	0.
1900	31.751	93.779	62.525	59.382	0.	0.	0.
2000	31.751	95.408	64.129	62.557	0.	0.	0.
2100	31.751	96.957	65.656	65.732	0.	0.	0.
2200	31.751	98.434	67.112	68.907	0.	0.	0.
2300	31.751	99.845	68.505	72.082	0.	0.	0.
2400	31.751	101.196	69.839	75.257	0.	0.	0.
2500	31.751	102.493	71.120	78.432	0.	0.	0.
2600	31.751	103.738	72.350	81.607	0.	0.	0.
2700	31.751	104.936	73.535	84.782	0.	0.	0.
2790.812	31.751	105.986	74.574	87.665	Liquid $\leftrightarrow$ Ideal Gas		
2790.812	20.795	211.333	74.574	381.667	Fugacity = 1 bar		
2800	20.795	211.401	75.023	381.858	0.	0.	0.
2900	20.796	212.131	79.738	383.938	0.	0.	0.
3000	20.798	212.836	84.163	386.017	0.	0.	0.
3100	20.800	213.518	88.325	388.097	0.	0.	0.
3200	20.804	214.178	92.248	390.178	0.	0.	0.

Continued

**Table 12.6** Thermodynamic properties of HF(g); adapted from Gen. Ref. (3).

<i>T, K</i>	<i>(J/(mol · K))</i>			<i>J/mol</i>		
	<i>C<sub>p</sub><sup>o</sup></i>	<i>S<sup>o</sup></i>	$-(G^o - H_{298}^o)/T$	$H^o - H_{298}^o$	$\Delta H_f^o$	$\Delta G_f^o$
1000.00	30.142	209.285	188.636	20,649	-274,532	-278,455
1100.00	30.516	212.178	190.647	23,684	-274,870	-278,830
1200.00	30.934	214.850	192.554	26,756	-275,202	-279,176
1300.00	31.384	217.344	194.366	29,872	-275,519	-279,494
1400.00	31.832	219.686	196.091	33,033	-275,822	-279,788

**Table 12.7** Thermodynamic properties of AlF<sub>3</sub>(c); adapted from gen. Ref. (3).

<i>T, K</i>	<i>(J/(mol · K))</i>			<i>J/mol</i>		
	<i>C<sub>p</sub><sup>o</sup></i>	<i>S<sup>o</sup></i>	$-(G^o - H_{298}^o)/T$	$H^o - H_{298}^o$	$\Delta H_f^o$	$\Delta G_f^o$
1000.00	100.831	179.487	112.139	67,348	-1,510,890	-1250,016
1100.00	101.893	189.147	118.707	77,485	-1,509,488	-1223,996
1200.00	102.917	198.057	124.953	87,725	-1,508,014	-1198,107
1300.00	103.915	206.334	130.898	98,067	-1,506,467	-1172,343
1400.00	104.894	214.071	136.566	108,508	-1,504,845	-1146,702

**Table 12.8** Thermodynamic properties of H<sub>2</sub>(g); adapted from Gen. Ref. (3).

<i>T, K</i>	<i>(J/(mol · K))</i>			<i>(J/mol)</i>
	<i>C<sub>p</sub><sup>o</sup></i>	<i>S<sup>o</sup></i>	$-(G^o - H_{298}^o)/T$	$H^o - H_{298}^o$
1000.00	30.205	166.216	145.536	20,680
1100.00	30.579	169.112	147.550	23,719
1200.00	30.992	171.790	149.460	26,797
1300.00	31.424	174.288	151.275	29,918
1400.00	31.863	176.633	153.003	33,082

Daojie Zhang

7. The freedom of a system is related to its component  $C$  and phases  $p$ .

5 Degrees of freedom =  $C - p + 2$ . ✓

where 2 represents the temperature and pressure.

$$\frac{100}{100}$$

At equilibrium,  $dG^I = dG^{II}$ .

Since  $dG = Vdp - SdT$ , we get assumptions

0  $V^I dp - S^I dT = V^{II} dp - S^{II} dT$

i.e.  $\frac{dT}{dp} = \frac{V^{II} - V^I}{S^{II} - S^I} = \frac{V^{II} - V^I}{\Delta S}$

Noting that,  $\Delta S = \Delta H/T$

the equation transforms into  $\frac{dT}{dp} = \frac{(V^{II} - V^I)T}{\Delta H}$  ✓

$\ln P_s = (10.648 - 2539.5/T) \ln 10 = 24.518 - 5893.5/T$

$\ln P_l = (7.560 - 1511.3/T) \ln 10 = 17.361 - 3480.0/T$

At equilibrium,  $G_l = G_s$ . i.e.  $RT \ln P_s = RT \ln P_l$ .

$24.518 - 5893.5/T = 17.361 - 3480.0/T$

which yields,  $T = 337.2 \text{ K}$ . ✓

~~$RT \ln P = \Delta H - T \Delta S \Rightarrow \ln P = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$~~   $\frac{d \ln P}{dT} = \frac{\Delta H}{RT^2}$

since the latent heats of vaporization and sublimation are assumed to be independent of temperature,

1)  $\Delta H_{vap} = 15.11 \cdot 3480.0 R = 28934.5 \text{ J/mol}$  ✓

$\Delta H_{sub} = 5893.5 R = 49001.6 \text{ J/mol}$  ✓



2)  $J = K_p$  or  $\Delta G = 0$  at equilibrium. ✓

$J > K_p$  or  $\Delta G > 0$  the reaction tends to occur spontaneously in the opposite direction. ✓

$J < K_p$  or  $\Delta G < 0$  the reaction tends to occur spontaneously. ✓

$$\Delta_r G = (\cancel{c} G_c + d G_d + \dots) - (a G_A + b G_B + \dots)$$

$$= (c G_c^\circ + c R T \ln a_c + d G_d^\circ + d R T \ln a_d + \dots) - (a G_A^\circ + a R T \ln a_A + b G_B^\circ + b R T \ln a_B + \dots)$$

Noting that  $\Delta_r G^\circ = c G_c^\circ + d G_d^\circ + \dots - (a G_A^\circ + b G_B^\circ + \dots)$

— assumptions

$$1) \Delta_r G = \Delta_r G^\circ + R T \ln \frac{a_c \cdot a_d \cdot \dots}{a_A \cdot a_B \cdot \dots} = \Delta_r G^\circ + R T \ln J$$

where  $J = \frac{a_c \cdot a_d \cdot \dots}{a_A \cdot a_B \cdot \dots}$  ✓

$$2) \Delta_r G = -1.5 \Delta_r G^\circ = \Delta_r G^\circ_{\text{AlF}_3} - 3 \cdot \Delta_r G^\circ_{\text{HF}} = -1223996 + 278830 \times 3 = -387506 \text{ J/mol}$$

$$20 \Delta_r S^\circ = 1.5 \Delta_r S^\circ_{\text{H}_2} + \Delta_r S^\circ_{\text{AlF}_3} - 3 \cdot \Delta_r S^\circ_{\text{HF}} - \Delta_r S^\circ_{\text{Al}}$$

$$= 1.5 \times 169.112 + 189.147 - 3 \times 212.178 - 76.426$$

$$= -270.145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \quad \checkmark$$

$$\Delta_r H^\circ = \Delta_r G^\circ + T \cdot \Delta_r S^\circ = -387506 - 1100 \times 270.145 = -684665.5 \text{ J/mol} \quad \checkmark$$

a). Raoult's Law: the activity is equal to its mole fraction when  $x_i \rightarrow 1$ !

$$a_i = x_i \quad \lim_{x_i \rightarrow 1} \gamma_i = 1 \quad \checkmark$$

10 Henry's Law: the activity is proportional to its mole fraction for an infinite dilute solution.

$$a_i = \gamma_i^\infty \cdot x_i \quad \lim_{x_i \rightarrow 0} \gamma_i = \gamma_i^\infty \quad \checkmark$$

$$1) \text{ For pure solid silver. } \ln P_{\text{Ag}} = (-13696/T + 8.727) \ln 10 = -31536.2/T + 20.095$$

$$\text{For solid Ag-Pd alloy. } \ln P_{\text{Ag}} = (-13795/T + 8.649) \ln 10 = -31764.2/T + 19.915$$

a) The fugacity is equal to the vapor pressure, at 1200 K.

$$\text{For pure solid silver. } f_{\text{Ag}} = P_{\text{Ag}} = 10^{(-13696/1200 + 8.727)} = 2.059 \times 10^3 \text{ mm} \cdot \text{Hg}$$

$$\text{For solid Ag-Pd alloy. } f_{\text{Ag}} = P_{\text{Ag}} = 10^{(-13795/1200 + 8.649)} = 1.423 \times 10^3 \text{ mm} \cdot \text{Hg}$$

\* Since in Ag-Pd solid solution, the vapor ~~contains~~ above the alloy contains no Pd, the activity ~~of~~ for silver is,

$$a_{\text{Ag}} = \frac{f_{\text{Ag}}}{f_{\text{Ag}}^{\circ}} = \frac{1.423 \times 10^{-3}}{2.059 \times 10^{-3}} = 0.691. \checkmark$$

the activity coefficient for silver is,

$$\gamma_{\text{Ag}} = \frac{a_{\text{Ag}}}{x_{\text{Ag}}} = \frac{0.691}{0.802} = 0.862. \checkmark$$

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