

Chemistry 230 — Fall 2001
Exam 2 Solutions

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NAME: KEY
(please print)

CHEMISTRY 230 — Tellinghuisen
2nd Hour Exam — 11/8/01

Honor Code Pledge and Signature:

Fundamental Constants: $R = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1} = 0.0820578 \text{ L atm mol}^{-1} \text{ K}^{-1} = 1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}$

- I. (35) **The Third Degree.** The molar heat capacity of a solid substance at $P = P^*$ can be represented over a certain range of temperatures as a polynomial in T , $C_{p,m} = a + bT + cT^2$.
- Obtain expressions for ΔH_m° and ΔS_m° for heating this substance from T_1 to T_2 .
 - For $\text{CS}_2(s)$ in the range 15 K – 60 K, $a = -11.53 \text{ J mol}^{-1} \text{ K}^{-1}$, $b = 1.365 \text{ J mol}^{-1} \text{ K}^{-2}$, and $c = -0.0095 \text{ J mol}^{-1} \text{ K}^{-3}$. Calculate ΔH_m° and ΔS_m° for heating $\text{CS}_2(s)$ from 15.0 K to 60.0 K.
 - Use the Debye theory for the heat capacity at low temperatures to estimate S_m° for $\text{CS}_2(s)$ at 15.0 K; then calculate S_m° at 60.0 K.
 - Can this information be used to evaluate ΔG_m° for the heating of $\text{CS}_2(s)$ from 15.0 K to 60.0 K? Explain very briefly.

A.
$$\Delta H_m^\circ = \int_{T_1}^{T_2} C_{p,m}^\circ dT = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3)$$

$$\Delta S_m^\circ = \int_{T_1}^{T_2} \frac{C_{p,m}^\circ}{T} dT = a \ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1) + \frac{c}{2}(T_2^2 - T_1^2)$$

B. $\Delta H_m^\circ = 1111 \text{ J/mol}$; $\Delta S_m^\circ = 29.41 \frac{\text{J}}{\text{mol K}}$

C. Debye: $C_{p,m}^\circ = aT^3$ at low T

$$\hookrightarrow S_{m,T}^\circ = \int_0^T aT'^2 dT' = \frac{1}{3} aT^3 = \frac{1}{3} C_{p,m}^\circ(T)$$

At 15.0 K, $C_{p,m}^\circ = 6.81 \frac{\text{J}}{\text{mol} \cdot \text{K}} \rightarrow S_{m,15}^\circ = 2.27 \frac{\text{J}}{\text{mol K}}$

$$\hookrightarrow S_{m,60}^\circ = 2.27 + 29.41 = 31.68 \frac{\text{J}}{\text{mol K}}$$

D. YES.
$$\Delta G_m^\circ = G_{m,2}^\circ - G_{m,1}^\circ = (H_m^\circ - TS_m^\circ)_2 - (H_m^\circ - TS_m^\circ)_1$$

$$= \Delta H_m^\circ + T_1 S_{m,1}^\circ - T_2 S_{m,2}^\circ$$

All these quantities are known.

- II. (25) **Shifty Reactions.** The shift reaction — $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$ — is important in the commercial production of hydrogen. Use tabulated values of the free energy function given below to calculate K° for this reaction at 1000 K.

Let $Z = -\frac{G_T^\circ - H_0^\circ}{RT}$. Then $G_T^\circ = H_0^\circ - ZRT$

$$\Delta G_T^\circ = \sum \nu_i G_{T,i}^\circ = \sum \nu_i H_{0,i}^\circ - RT \sum \nu_i Z_i$$

$$= \Delta H_0^\circ - RT \sum \nu_i Z_i$$

$$\Delta H_0^\circ = 10^3 \text{ RK} [-47.29 + 0 + 13.69 + 28.736]$$

$$= -4.864 \times 10^3 \text{ K R}$$

$$\sum \nu_i Z_i = 27.246 + 16.485 - 24.558 - 23.674$$

$$= -4.501$$

$$\Delta G^\circ = -4.864 \times 10^3 \text{ K R} + RT \times 4.501$$

$$\hookrightarrow \frac{\Delta G^\circ}{RT} = 4.501 - 4.864 = -0.363$$

$$\hookrightarrow K^\circ = \exp\left[-\frac{\Delta G^\circ}{RT}\right] = 1.438$$

Gaseous elements and compounds with values referenced to H_0°

	$-(G_T - H_0^\circ)/RT$					$(H_{298}^\circ - H_0^\circ)/R$ (K)	$\Delta H_f^\circ/R$ (10^3 K)
	298.15 K	500 K	1000 K	1500 K	2000 K		
H ₂	12.301	14.076	16.485	17.921	18.968	1018.5	-
O ₂	21.173	22.992	25.521	27.088	28.243	1044.0	-
CO	20.275	22.086	24.558	26.069	27.183	1042.9	-13.69 ± 0.02
CO ₂	21.934	24.001	27.246	29.445	31.138	1126.4	-47.29 ± 0.01
H ₂ O	18.716	20.802	23.674	25.493	26.881	1191.3	-28.736 ± 0.005
CH ₄	18.376	20.531	24.00	26.63	28.82	1204.7	-7.999

- III. (35) **Upping the Pressure (vapor, that is).** Consider the process, $\text{Br}_2(l) \rightleftharpoons \text{Br}_2(g)$.
- Use thermodynamic data tabulated below to calculate ΔH°_{298} , ΔS°_{298} , and ΔG°_{298} for this process.
 - Specify precisely what states of reactants and products are implied for these calculated quantities. Then construct a 4-step, constant- T path that accomplishes the conversion from reactant to product and includes the equilibrium conversion of liquid to gas at the vapor pressure P of $\text{Br}_2(l)$ at 25.0°C .
 - Use your results from A (and B) to calculate ΔH_{vap} and the approximate vapor pressure of $\text{Br}_2(l)$ at 25°C .
 - V_m of $\text{Br}_2(l)$ is $51.2 \text{ cm}^3/\text{mol}$. Calculate the activity of $\text{Br}_2(l)$ under Ar gas at $P_{\text{Ar}} = 777 \text{ atm}$.
 - Hence, what is the approximate vapor pressure of $\text{Br}_2(l)$ at $P_{\text{Ar}} = 777 \text{ atm}$? (Neglect the effect of the Ar on the fugacity of $\text{Br}_2(g)$.)
 - In discussing the vapor/condensed-phase equilibrium processes of Br_2 in class, we illustrated with a figure showing two intersecting straight lines. What was plotted on the two axes, and why were there two lines?

STANDARD-STATE THERMODYNAMIC PROPERTIES AT 25°C AND 1 BAR

Substance	$\Delta H^\circ_{f,298}$ (kJ/mol)	$\Delta G^\circ_{f,298}$ (kJ/mol)	$S^\circ_{m,298}$ ($\frac{\text{J}}{\text{mol K}}$)	$C^\circ_{p,m,298}$ ($\frac{\text{J}}{\text{mol K}}$)
$\text{Br}(g)$	111.884	82.396	175.022	20.786
$\text{Br}(aq)$	-121.55	-103.97	82.4	-141.8
$\text{Br}_2(l)$	0	0	152.231	75.689
$\text{Br}_2(g)$	30.907	3.110	245.463	36.02

- A. $\Delta H^\circ_{298} = 30.907 \frac{\text{kJ}}{\text{mol}}$; $\Delta G^\circ_{298} = 3.110 \frac{\text{kJ}}{\text{mol}}$
- $\Delta S^\circ_{298} = \sum \nu_i S^\circ_{m,i} = 93.232 \frac{\text{J}}{\text{mol K}}$
- B. (liq, real, 25°C , P^*) \rightarrow (ideal gas, 25°C , P^*)
 \downarrow ①
 (liq, real, 25°C , P) \rightarrow (gas, real, 25°C , P) \rightarrow (gas, ideal, 25°C , P)
 ② ③ ④
- C. $\Delta H_4 = 0$; $\Delta H_1 \approx \Delta H_3 \approx 0 \Rightarrow \Delta H_{\text{vap}} \approx \Delta H^\circ = 30.907 \frac{\text{kJ}}{\text{mol}}$
- $K^\circ = \exp\left[-\frac{\Delta G^\circ}{RT}\right] = \frac{f_{\text{Br}_2(g)}/P^\circ}{a_{\text{Br}_2(l)}} \approx \frac{P/P^\circ}{1}$
- $K^\circ = e^{-1.255} = 0.2852 = P/P^\circ \rightarrow P = 0.2852 P^\circ \approx 214 \text{ torr}$

- D. $\ln a = \int_{P^\circ}^P \frac{V_m}{RT} dP \approx \frac{V_m}{RT} (P - P^\circ) \approx \frac{51.2 \text{ cm}^3}{RT} \times 776 \text{ atm}$
 $= 1.624 \rightarrow a = 5.07$
- E. $K^\circ \approx \frac{P/P^\circ}{a_l} \rightarrow P = P^\circ K^\circ a_l = 1.447 P^\circ$
- F. $\ln P$ vs $\frac{1}{T(\text{K})}$. The steeper line represented the solid-vapor equilibrium, while the other was for liquid-vapor. The two intersected at the triple point.

IV. (45) **Short Shots. Do JUST 3 of the following.**

- A. Consider the ideal gas dissociation equilibrium, $\text{A}(g) \rightleftharpoons \text{B}(g) + 2\text{C}(g)$.
- Give the equilibrium expression for K°_P in terms of the partial pressures of reactants and products.
 - Obtain an equation which could be solved to yield the degree of dissociation α in terms of K°_P and the total pressure P . [Hint: Start with n_0 mols of A and no B or C.]

1. $K^\circ_P = \frac{(P_B/P^\circ)(P_C/P^\circ)^2}{(P_A/P^\circ)}$

2. $\text{A} \rightleftharpoons \text{B} + 2\text{C}$

m_0 0 0

$m_0(1-\alpha)$ αn_0 $2\alpha n_0$ $\rightarrow \text{total} = m_0(1+2\alpha)$

X_i : $\frac{1-\alpha}{1+2\alpha}$ $\frac{\alpha}{1+2\alpha}$ $\frac{2\alpha}{1+2\alpha}$

P_i : $P \times$ " " "

$K^\circ_P = \left(\frac{P}{P^\circ}\right)^2 \frac{4\alpha^3}{(1-\alpha)(1+2\alpha)^2}$

Prob I _____

II _____

III _____

IV _____



B. Consider the virial 2 equation (i.e., the version that is a power series in P).

1. Give this equation through the term that includes the third virial coefficient.
2. Define the compressibility factor Z for a gas that obeys this equation.
3. Obtain expressions for the fugacity coefficient ϕ and the fugacity f for such a gas.

$$1. PV_m = RT [1 + B^+(T)P + C^+(T)P^2 + \dots]$$

$$2. Z \equiv \frac{PV_m}{RT} = [1 + B^+(T)P + C^+(T)P^2 + \dots]$$

$$3. \ln \phi = \int_0^P \left[\frac{V_m}{RT} - \frac{1}{P'} \right] dP' = \int_0^P \left[\frac{1}{P'} + B^+ + C^+P' - \frac{1}{P'} \right] dP'$$

$$= \int_0^P [B^+ + C^+P'] dP' = B^+P + \frac{C^+}{2}P^2$$

$$\hookrightarrow \phi = \exp [B^+P + \frac{1}{2}C^+P^2] ; f = \phi P = P e^{B^+P + \frac{1}{2}C^+P^2}$$

C. Long ago we determined that the Joule-Thomson coefficient μ_{JT} is related to C_p and $(\partial H/\partial P)_T$ by $(\partial H/\partial P)_T = -C_p \mu_{JT}$. Use this result to evaluate ΔH for the isothermal ($T = 300$ K) compression of 1.00 mol of CO_2 from 1.00 atm to 50.00 atm, given the following expressions for $C_p(T)$ and $\mu_{JT}(P)$:

$$C_{p,m} = 26.00 + 0.0435 T - 1.483 \times 10^{-5} T^2 \text{ (units J mol}^{-1} \text{ K}^{-1}; T \text{ in K)}$$

$$\mu_{JT} = 1.107 - 0.0023 P \text{ (units K atm}^{-1}, P \text{ in atm, } T = 300 \text{ K)}$$

Compare your result with that which would be obtained for an ideal gas.

$$\left(\frac{\partial H}{\partial P} \right)_T = -C_p \mu_{JT} \rightarrow dH_T = -C_p \mu_{JT} dP_T$$

$$\hookrightarrow \Delta H = -C_p \int_{1.00}^{50.00 \text{ atm}} \mu_{JT} dP = -C_p \int_1^{50} [a - bP] dP$$

$$= -C_p \left[49a - \frac{b}{2}(50^2 - 1) \right]$$

$$C_p \text{ at } 300 \text{ K} = 1.00 \text{ mol} \times C_{p,m} = 37.715 \frac{\text{J}}{\text{K}}$$

$$\hookrightarrow \Delta H = -1937 \text{ J}$$

$$\Delta H_{\text{id.gas}} = 0.$$

D. Consider the reaction, (1) $2 \text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{NOCl}(g)$. At 300°C this reaction has an equilibrium constant $K_1^\circ = 2.73$.

1. Give the conditions for chemical reaction equilibrium in this reaction, in terms of chemical potentials. Be specific.
2. Calculate K° (call it K_2°) for the reaction, (2) $\text{NOCl}(g) \rightleftharpoons \text{NO}(g) + \frac{1}{2} \text{Cl}_2(g)$, at 300°C .
3. A reaction vessel is charged initially with $1.00 P^\circ$ of NO , $2.00 P^\circ$ of Cl_2 , and $1.50 P^\circ$ of NOCl at 300°C . Calculate the reaction quotient Q_1 , and predict the direction in which Reaction 1 will proceed.
4. Suppose the volume of the vessel is such that it contains 0.60 mol NO under the conditions stated in 3. Calculate the amounts of the other two components.
5. Starting with the conditions in 4, what are the maximum and minimum possible values of the extent of reaction ξ : (i) for Reaction 1; and (ii) for Reaction 2?

$$1. \sum \nu_i \mu_i = 0 \Rightarrow 2\mu_{\text{NO}} + \mu_{\text{Cl}_2} = 2\mu_{\text{NOCl}}$$

$$2. R_x 2 = \frac{1}{2} \times \text{reverse of (1)} \Rightarrow K_2^\circ = K_1^\circ^{-1/2} = 0.605$$

$$3. K_1^\circ = \frac{(P_{\text{NOCl}}/P^\circ)^2}{(P_{\text{NO}}/P^\circ)^2 (P_{\text{Cl}_2}/P^\circ)} \Rightarrow Q_1 = \frac{(1.50)^2}{1.00^2 \times 2.00} = 1.125$$

$Q_1 < K_1^\circ$, so R_x proceeds toward the right.

$$4. \text{NO} : P = 1.00 P^\circ ; n = 0.60 \text{ mol}$$

$$\text{Cl}_2 : P = 2.00 P^\circ \Rightarrow n = 1.20 \text{ mol}$$

$$\text{NOCl} : P = 1.50 P^\circ \Rightarrow n = 0.90 \text{ mol}$$

$$5. (1) 2 \text{NO} + \text{Cl}_2 \rightleftharpoons 2 \text{NOCl}$$

$$(0.60 - 2\xi) \quad (1.20 - \xi) \quad (0.90 + 2\xi) \Rightarrow \xi_{\text{max}} = 0.30 \text{ mol}$$

$$\xi_{\text{min}} = -0.45 \text{ mol}$$

$$(2) \text{NOCl} \rightleftharpoons \text{NO} + \frac{1}{2} \text{Cl}_2$$

$$(0.90 - \xi) \quad (0.60 + \xi) \quad (1.20 + \frac{1}{2}\xi)$$

$$\hookrightarrow \xi_{\text{max}} = 0.90 \text{ mol}$$

$$\xi_{\text{min}} = -0.60 \text{ mol}$$