CHEM 330 – PHYSICAL CHEMISTRY I – Fall 2026

EXAM 3

Closed book, closed notes
No electronics allowed (discovery of use is an automatic 0)
Calculators may be used (do not use the calculator on your electronic devices)
Write your name clearly in the provided answer book

Time: 1 hour 30 minutes

Problem 1 (10 points)
One mole of CO_2 expands reversibly and isothermally at 350 K from 1.50 L to 6.00 L. Treating it as a Van der Waals gas with b = 0.04267 L mol^{-1}, calculate ΔS. Compare your answer with the value for an ideal gas. Utilize the Maxwell relations for A (with dA = −SdT – PdV).
A Van der Waals gas has the following equation of state:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Problem 2 (15 points)
For the decomposition of calcium carbonate,

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

$\Delta_rH°$ = +178.3 kJ mol^{-1} and $\Delta_rG°$ = +130.4 kJ mol^{-1} at 298.15 K. Assume that $\Delta_rH°$ and $\Delta_rS°$ do not depend on temperature.
Note that the Gibbs-Helmholtz equation is given by:

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$

and $\Delta_r G = -RTln(K_P)$

(a) Is the reaction spontaneous under standard conditions at 298.15 K? Calculate $\Delta_rS°$. [4 points]
(b) Use the Gibbs–Helmholtz equation to estimate $\Delta_rG°$ at 1000 K. [4 points]
(c) Above what temperature is the reaction spontaneous under standard conditions? [4 points]
(d) Calculate K_p at 1000 K. Since CO_2 is the only gas, $K_p = P_{CO2}/P°$. What is the equilibrium pressure of CO_2 above the solids at 1000 K? [3 points]

Problem 3 (15 points)
Consider the gas-phase reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

for which K_p = 54.0 at 700 K.

(a) Calculate $\Delta_rG°$ at 700 K. [3 points]
(b) A vessel initially contains 1.00 mol H_2 and 1.00 mol I_2, and no HI. Write the number of moles of each species at equilibrium in terms of the extent of reaction ξ, and find ξ_{eq} at 700 K. [5 points]
(c) Would ξ_{eq} change if the total pressure were doubled at 700 K? Explain briefly. [3 points]
(d) $\Delta_rH°$ = −9.46 kJ mol^{-1} and may be taken as independent of temperature. Estimate K_p at 800 K. Does raising the temperature favor reactants or products? [4 points]

Problem 4 (10 points)
The Helmholtz energy is defined as A = U − TS, and dA = −SdT − PdV.
(a) Using the natural variables of A and the corresponding Maxwell relation, show that $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$. [6 points]
(b) Hence show that $(\partial U/\partial V)_T = 0$ for an ideal gas. [4 points]

Use:
R = 8.314 J K^{-1} mol^{-1}
P° = 1 bar
1 L = 10^{-3} m^3
1 Pa m^3 = 1 J

Exam 3 -Solutions

Solution 1

Maxwell relation for A (from $dA = -SdT - PdV$):

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

For 1 mole of a Van der Waals gas,

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} = \left(\frac{\partial S}{\partial V}\right)_T$$

Integrating at constant T from V_1 to V_2,

$$\Delta S = \int_{V_1}^{V_2} \frac{R\,dV}{V-b} = R \ln \frac{V_2 - b}{V_1 - b}$$

With V_1 = 1.50 L, V_2 = 6.00 L and b = 0.04267 L mol^{-1},

$$\Delta S = (8.314) \ln \frac{6.00 - 0.04267}{1.50 - 0.04267} = (8.314) \ln \frac{5.957}{1.457} = (8.314)(1.4080)$$

$$\Delta S = +11.71 \text{ J K}^{-1}$$

For an ideal gas (b = 0),

$$\Delta S = R \ln \frac{V_2}{V_1} = (8.314) \ln \frac{6.00}{1.50} = (8.314)(1.3863) = +11.53 \text{ J K}^{-1}$$

The Van der Waals gas gains slightly more entropy (0.18 J K^{-1}, about 1.6%): the molecules' own volume b makes the fractional gain in free volume larger. Note that ΔS does not depend on a, or on T, so the temperature of 350 K is not needed.

Solution 2

(a) $\Delta_r G^\circ = +130.4\ \text{kJ mol}^{-1} > 0$, so the reaction is **not** spontaneous under standard conditions at 298.15 K.

Since $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$,

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{(178.3 - 130.4) \times 10^3\ \text{J mol}^{-1}}{298.15\ \text{K}}$$

$$\Delta_r S^\circ = +160.7\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(b) Gibbs–Helmholtz equation:

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$

Integrating from $T_1 = 298.15$ K to $T_2 = 1000$ K with ΔH constant,

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\frac{\Delta G(1000)}{1000} = \frac{130.4 \times 10^3}{298.15} + (178.3 \times 10^3)\left(\frac{1}{1000} - \frac{1}{298.15}\right)$$

$$= 437.4 - 419.7 = 17.64\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$\Delta_r G^\circ(1000\ \text{K}) = (1000)(17.64) = +17.6\ \text{kJ mol}^{-1}$$

Check: $\Delta_r H^\circ - T\Delta_r S^\circ = 178.3 - (1000)(0.1607) = +17.6\ \text{kJ mol}^{-1}$, the same answer.

(c) $\Delta_r G^\circ$ changes sign when $\Delta_r H^\circ = T\Delta_r S^\circ$:

$$T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ} = \frac{178.3 \times 10^3}{160.7} = 1110\ \text{K}$$

Above about 1110 K the reaction is spontaneous under standard conditions. $\Delta_r S^\circ > 0$ (a gas is formed), so heating favors the products.

(d) Using $\Delta_r G^\circ = -RT \ln K_p$:

$$\ln K_p = -\frac{\Delta_r G^\circ}{RT} = -\frac{17.64 \times 10^3}{(8.314)(1000)} = -2.122$$

$$K_p = e^{-2.122} = 0.120 \qquad P_{CO_2} = K_p P^\circ = 0.12\ \text{bar}$$

At 1000 K the equilibrium pressure of CO_2 above the solids is about 0.12 bar, still below 1 bar, as expected since $\Delta_r G^\circ > 0$ at this temperature.

Solution 3

(a) Using $\Delta_r G^\circ = -RT \ln K_p$:

$$\Delta_r G^\circ = -RT \ln K_p = -(8.314)(700)\ln(54.0) = -(5820)(3.989)$$

$$\Delta_r G^\circ = -2.32 \times 10^4\ \text{J mol}^{-1} = -23.2\ \text{kJ mol}^{-1}$$

(b) At equilibrium, starting from 1.00 mol H_2 and 1.00 mol I_2:

$$H_2: \ 1-\xi \qquad I_2: \ 1-\xi \qquad HI: \ 2\xi$$

Total number of moles: $(1-\xi) + (1-\xi) + 2\xi = 2$

$$K_p = \frac{(P_{HI}/P^\circ)^2}{(P_{H_2}/P^\circ)(P_{I_2}/P^\circ)}, \qquad P_j = \frac{n_j}{\sum n_j} P$$

$$K_p = \frac{(2\xi)^2}{(1-\xi)(1-\xi)} = \frac{(2\xi)^2}{(1-\xi)^2}$$

The total pressure and the total number of moles cancel. Taking the square root of both sides,

$$\frac{2\xi}{1-\xi} = (54.0)^{1/2} = 7.348 \qquad \xi_{eq} = \frac{7.348}{2+7.348} = 0.786\ \text{mol}$$

At equilibrium: 0.214 mol H_2, 0.214 mol I_2, 1.57 mol HI.

(c) No. $\Delta\nu = 2 - (1+1) = 0$, so P/P° cancels from the expression for K_p in (b), and ξ_{eq} does not depend on the total pressure. Neither side has fewer moles of gas, so by Le Châtelier's Principle a change in pressure gives no shift.

(d) Integrated van 't Hoff equation (from Gibbs–Helmholtz, with $\Delta_r H^\circ$ constant):

$$\ln\frac{K_p(T_2)}{K_p(T_1)} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$= -\frac{(-9460)}{8.314}\left(\frac{1}{800} - \frac{1}{700}\right) = (1138)(-1.786\times10^{-4}) = -0.203$$

$$K_p(800\ \text{K}) = (54.0)\,e^{-0.203} = (54.0)(0.816) = 44.1$$

K_p falls from 54.0 to 44.1: the reaction is exothermic, so raising T favors the reactants (ξ_{eq} drops from 0.786 to 0.768 mol).

Solution 4

(a) Differentiating $A = U - TS$ with respect to V at constant T,

$$\left(\frac{\partial A}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T$$

$A = f(T, V)$, so

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

Comparing the coefficients of dT and dV with $dA = -SdT - PdV$,

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \qquad \left(\frac{\partial A}{\partial T}\right)_V = -S$$

The Maxwell relation for A (cross derivatives of A are equal):

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Substituting both into the first equation,

$$-P = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

This is the thermodynamic equation of state.

(b) For one mole of an ideal gas,

$$P = \frac{RT}{V} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \qquad \left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V} - P = 0$$

U of an ideal gas does not depend on V at constant T (no intermolecular forces).