EXAM 1

18 September 1992

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a few words of explanation. If possible, please write on one side of the paper only.

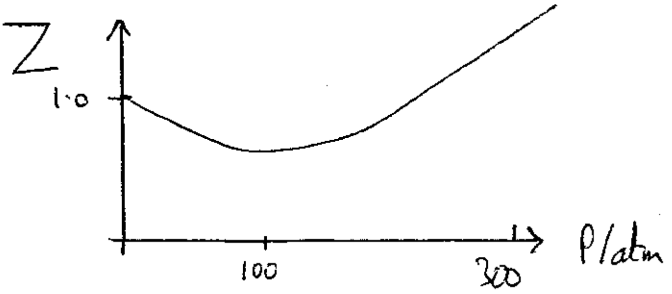
$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$

(1) *20 points (only a few lines are needed for full credit in each part of this question)*

a) Interpret the van der Waals *a* and *b* in terms of assumptions about ideal gases.

b) The system is a sample of gas in a piston. What is ΔU if 1000 J of heat are absorbed and the gas expands by 0.001 m^3 against a constant external pressure of 10^5 Pa?

c) Define the *compression factor*, Z, for a gas. A plot of Z versus pressure p for a gas is shown below; explain how in this case Z is qualitatively related to intermolecular forces (a) at p = 100 atm, (b) at p = 300 atm.



d) What is the difference between *closed* and *isolated* systems?

e) Draw a pV diagram and on it sketch the shape of a typical *isotherm* for an ideal gas.

(2) *10 points*

a) Starting from the ideal gas law, derive an expression for the density ρ of an ideal gas in terms of p, V, T and the molar mass M.

b) A sample of ideal gas, with volume 2 m^3, has a density of 2.6 kg m^{-3} at 400 K and a pressure of 10^5 Pa. What is the molar mass? *Give units!*

c) The gas in (b) is now compressed to 0.5 m^3, and the temperature is lowered to 300 K. What is the new pressure of the gas? *Give units!*

(3) *20 points*

The van der Waals equation of state for one mole of gas is

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

a) Find two relations between *a* and *b* and the critical properties from the information that the first and second derivatives of p with respect to V are zero at the critical point p_c, V_c, T_c.

b) Show that your relations are satisfied by $V_c = 3b$, $p_c = a/(27b^2)$ and $T_c = 8a/(27Rb)$.

PHYSICAL CHEMISTRY 3510
EXAM 2
October 21, 1992

Please write neatly and clearly, and show all working. Allocate time to each question in proportion to the available credit. Keep explanations brief and to the point.

DATA: $L = 6.022 \times 10^{23}$ mol^{-1}. $R = 8.314$ J K^{-1} mol^{-1}. 1 atm = 101325 Pa.

1. *20 points.*
Along an adiabat pV^{γ} is constant. Imagine that 1 mol of ideal gas (the system), with $C_V = 20$ J K^{-1}, is expanded reversibly and adiabatically from 1 m^3 to 3 m^3. The initial temperature is 400 K. Work out q, ΔU, ΔH and w for the system, clearly stating any extra results or relations you rely on.

2. *10 points.*

i) Starting with the definitions of C_p and H and the result that

$$\left[\frac{\partial U}{\partial T}\right]_p = \left[\frac{\partial V}{\partial T}\right]_p \left[\frac{\partial U}{\partial V}\right]_T + C_V$$

show that in general for any material

$$C_p - C_V = \left[\frac{\partial V}{\partial T}\right]_p \left[p + \left[\frac{\partial U}{\partial V}\right]_T\right]$$

ii) Use the above result to derive $C_p - C_V$ for 1 mol of ideal gas.

3. *20 points.*
Consider the hydrogenation of acetylene to ethane:
$C_2H_2(g) + 2\ H_2(g) \rightarrow C_2H_6(g)$
C_p for C_2H_2, H_2 and C_2H_6 is $30 + 0.1T$, $20 + 0.1T$ and $40 + 0.1T$ J K^{-1} mol^{-1}, respectively, where T is the temperature. ΔH for combustion to $CO_2(g)$ and/or $H_2O(l)$ for C_2H_2, H_2 and C_2H_6 at 298 K is -1300, -286 and -1560 kJ mol^{-1}, respectively.

i) Show that ΔH for hydrogenation at 298 K is -312 kJ mol^{-1}.
ii) Calculate ΔU for hydrogenation at 298 K.
iii) Calculate ΔH for hydrogenation at 500 K.

SOLUTIONS for EXAM 2 10-21-92

1. Adiabatic $\therefore q = 0$.

$pV^{\gamma} =$ constant. Initial $p_1 = \frac{RT_1}{V_1} = \frac{R \times 400}{1}$ Pa $=$ 3326 Pa

$\therefore$ 3326 Pa $\times 1^{\gamma} = p_2 \times 3^{\gamma}$ and $\gamma = C_p/C_V = \frac{C_V + R}{C_V} = 1.416$

$\therefore p_2 = \frac{3326 \text{ Pa}}{3^{1.416}} = 702$ Pa. $T_2 = \frac{p_2 V_2}{R} = 253$ K.

$\Delta U = C_V \cdot (T_2 - T_1) = -2940$ J. $q = 0 \therefore w = \Delta U$.

$\Delta H = C_p \cdot (T_2 - T_1) = -4162$ J.

2\. i) $C_p = \left(\frac{\partial H}{\partial T}\right)_p$ and $H = U + pV$ $\therefore C_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$

$$\therefore C_p - C_V = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_p + \left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial U}{\partial V}\right)_T$$

$$= \left(\frac{\partial V}{\partial T}\right)_p \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right].$$

ii) For an ideal gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$, $V = \frac{RT}{p} \therefore \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}$

$\therefore C_p - C_V = \frac{R}{p}[0 + p] = R$.

3 i)

$$\begin{tikzcd}
3\tfrac{1}{2}O_2 + 2H_2 + C_2H_2 \arrow[r, "x"] \arrow[d, "{-1300 \atop -2\times286}\ \text{kJ/mol}"] & 3\tfrac{1}{2}O_2 + C_2H_6 \arrow[dl, "-1560\ \text{kJ mol}^{-1}"] \\
2CO_2 + 3H_2O &
\end{tikzcd}$$

$x - 1560$ kJ mol^{-1} $= -1300 - 2(286)$ kJ mol^{-1} $\therefore x = -312$ kJ mol^{-1}.

ii) $\Delta H = \Delta U + \Delta(pV)$ and $pV = nRT \therefore \Delta U = \Delta H - \Delta n . RT$

where $\Delta n = -2$ $\therefore$ $\Delta U = \Delta H + 2.RT$

$= -312000 + 2 \times 8.314 \times 298$ J mol^{-1}

$= -307$ kJ mol^{-1}.

iii) $\Delta C_p = 40 + 0.1T - (30 + 0.1T + 2(20 + 0.1T)) = -30 - 0.2T$.

$$\Delta H_{500} = \Delta H_{298} + \int_{298}^{500} \Delta C_p . dT = \Delta H_{298} - \left[30T + 0.1T^2\right]_{298}^{500}$$

$= -312000 - 15000 - 25000 + 8940 + 8880$ J mol^{-1}

$= -334$ kJ mol^{-1}.

PHYSICAL CHEMISTRY 3510
EXAM 3
October 23, 1992

Please write neatly and clearly, and show all working. Allocate time to each question in proportion to the available credit. Keep explanations brief and to the point.

DATA: L or N_A = 6.022×10^{23} mol^{-1}. R = 8.314 J K^{-1} mol^{-1}. 1 atm = 101325 Pa.

1. *20 points.*

i) Give one example of an *irreversible* change, and outline the *entropy* implications.

ii) ΔH_{vap} for the vaporization of liquid ethanol is 2100 J K^{-1} mol^{-1} at the boiling point, 350 K. Calculate ΔS_{vap}, and interpret the sign of your answer in terms of changes in the degree of order or disorder in the system.

iii) A change in a system has $\Delta H = +15$ kJ mol^{-1} and $\Delta S = +100$ J K^{-1} mol^{-1} at 298 K. What is ΔG? Will the change be *spontaneous* if it occurs in a system at constant temperature and pressure?

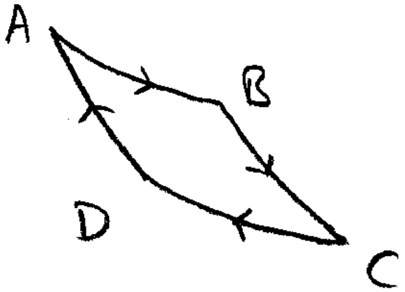
2. *10 points.*

i) A material with $C_p = 50$ J K^{-1} is *reversibly* heated from 400 to 500 K. Starting from the general definition of dS, calculate ΔS for the material.

ii) How would ΔS differ if the material had been heated *irreversibly*?

3. *20 points.*

Here is a reversible Carnot cycle for 1 mole of an ideal gas.



i) The thermodynamic efficiency ϵ of a Carnot engine is $\epsilon = (T_h - T_c)/T_h$. Calculate ϵ here.

ii) Using your answer to (ii), or otherwise, find the amount of heat that must be absorbed at 800 K to obtain 100 J of work from this engine. How much heat is rejected at the lower temperature?

iii) Which segment (i.e. A to B, C to D etc.) corresponds to an *adiabatic compression*? What is ΔS for the gas for this adiabatic compression?

SOLUTIONS for EXAM 3 10-23-92

1 i) See notes. ΔS_{univ} must be greater than zero.

ii) Because this is reversible, $\Delta S = \frac{\Delta H}{T} = \frac{2100 \text{ J mol}^{-1}}{350 \text{ K}} = 6 \text{ J K}^{-1} \text{mol}^{-1}$.

Positive because disorder increases – C_2H_5OH molecules have more freedom.

iii) $\Delta G = \Delta H - T\Delta S = 15000 - 298 \times 100 \text{ J mol}^{-1} = -14800 \text{ J mol}^{-1}$ or -14.8kJ/mol.

$\Delta G < 0$ ∴ change is spontaneous.

2 i) $dS = \frac{dq_{rev}}{T} = \frac{C_p\, dT}{T}$ ∴ $\Delta S = \int_{400}^{500} C_p \cdot \frac{dT}{T} = C_p \ln \frac{500}{400}$
$= 11.2 \text{ J K}^{-1}$.

ii) S is a fn. of state ∴ ΔS would remain the same.

3 i) $\epsilon = \frac{800-500}{800} = 0.375$.

ii) work = ϵ × heat absorbed ∴ $q_{800} = \frac{100 \text{ J}}{0.375} = 267 \text{ J}$.

Heat rejected + work = heat absorbed ∴ $-q_{500} = 267 - 100 \text{ J} = 167 \text{ J}$.

iii) D to A. $q = 0$ (adiabatic) ∴ $\int \frac{dq}{T} = 0$ ∴ $\Delta S = 0$.

EXAM 4
20 November 1992

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a few words of explanation.

For a particle with velocity u and mass m, momentum = mu and kinetic energy = $0.5\,mu^2$.
$k_B = 1.38 \times 10^{-23}$ J K^{-1} = R/N$_A$. $N_A = 6.022 \times 10^{23}$ mol^{-1}. R = 8.314 J K^{-1} mol^{-1}.
$p^{\ominus} = 10^5$ Pa.

(1) *20 points*
At 1000 K, consider the reaction: $C_2H_5Br_{(g)} \rightarrow C_2H_{4\,(g)} + HBr_{(g)}$
These species can be treated as ideal gases. $\Delta G^{\ominus}_{1000}$ = -5 kJ mol^{-1} and $\Delta H^{\ominus}_{1000}$ = +120 kJ mol^{-1} for this reaction.

a) A vessel initially contains the following partial pressures: $p(C_2H_5Br) = 6 \times 10^4$ Pa, $p(C_2H_4) = 2 \times 10^4$ Pa, $p(HBr) = 5 \times 10^4$ Pa. Decide whether the mixture will spontaneously react to form more or less C_2H_5Br. *No credit unless your answer is supported by a calculation.*

b) Derive the equilibrium constant K and hence find the equilibrium partial pressures of the reactant and products.

c) Find $\Delta S^{\ominus}_{1000}$.

d) Do you expect K to increase or decrease as the temperature is raised? *No credit unless supported by a brief but detailed, reasoned argument.*

(2) *10 points*
For a sample of an ideal gas, it can be shown that $pV = (1/3)mNc^2$
where m is the molecular mass, N is the number of molecules in the sample and c^2 is the mean square velocity.

a) Use this result together with the ideal gas law to show that the average kinetic energy ϵ of the molecules is given by $\epsilon = (3/2)k_BT$.

b) Consider two bulbs, containing He and SF_6 respectively, under identical conditions. The molar masses are in the ratio 1:36. For the molecules in the two bulbs, (i) deduce the ratios of the average kinetic energy of the molecules, and (ii) decide which gas will effuse faster, given equal sized holes, and why? Estimate the relative rates of effusion through identical holes for the two gases.

(3) *20 points*

a) Starting with the definitions of H and G and the information that dU = -pdV + TdS, derive an expression for the differential dG in terms of p, V, T and S.

b) By also considering G as function of p and T, prove that
$(\partial G/\partial p)_T = V$ and $(\partial G/\partial T)_p = -S$.

c) Use the results given in (b) to prove that $(\partial V/\partial T)_p = -(\partial S/\partial p)_T$.

d) Hence determine $(\partial S/\partial p)_T$ for 1 mole of a non-ideal gas whose equation of state is $pV/(RT) = 1 + x$ where x is a constant.

Exam 4, 11-20-92

1 a) $a = P/p^\ominus$ ∴ $Q = \dfrac{0.5\times0.2}{0.6} = 0.1667$.

$\Delta G_r = \Delta G^\ominus + RT\ln Q = -5000 - 14895 = -19895 \text{ J mol}^{-1} < 0$

∴ products favored and C_2H_5Br lost spontaneously

b) $\Delta G^\ominus = -RT\ln K$ ∴ $K = e^{-\frac{\Delta G^\ominus}{RT}} = e^{+\frac{5000}{8.314\times1000}} = 1.825$.

	C_2H_5Br ⇌	C_2H_4 +	HBr
Initial activity	0.6	0.2	0.5
Eq. activity	0.6 − x	0.2 + x	0.5 + x

$$K = \frac{(0.2+x)(0.5+x)}{0.6-x} \quad \therefore \quad x^2 + 2.525x - 0.995 = 0$$

$$\therefore \quad x = \frac{-2.525 \pm \sqrt{10.36}}{2} = 0.347 \text{ or } -2.872.$$

2nd result is physically unreasonable ∴ $a_{C_2H_5Br} = 0.254$ i.e. $p_{C_2H_5Br} = 2.54\times10^4$ Pa.

At equilibrium, $p_{C_2H_4} = (0.2+x)\times10^5 \text{ Pa} = 5.47\times10^4 \text{ Pa}$. $p_{HBr} = 8.47\times10^4$ Pa.

c) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ ∴ $\Delta S^\ominus = \dfrac{\Delta G^\ominus - \Delta H^\ominus}{-T}$

$$= \frac{-5000 - 120\,000 \text{ J mol}^{-1}}{-1000 \text{ K}} = +125 \text{ J K}^{-1}\text{ mol}^{-1}.$$

d) Le Chatelier's principle tells us that a system tends to move spontaneously to oppose an external change. Here heat is added so reaction moves in the endothermic direction. Here, that means more HBr is formed i.e. K increases.

2 a) $pV = \frac{1}{3} m N c^2 = nRT$

$$\therefore \frac{1}{3} m c^2 = \frac{nRT}{N} = \frac{RT}{N_A} = k_B T$$

$$\therefore \epsilon = \frac{1}{2} m c^2 = \frac{3}{2} k_B T .$$

b i) ϵ independent of m $\therefore$ both He and SF_6 have equal ϵ.

ii) Effusion rate $\propto$ average velocity. Since $\epsilon_{SF_6} = \epsilon_{He}$, but $m_{SF_6} > m_{He}$, average velocity is greater for He and so is its effusion rate.

rate $\propto \sqrt{c^2} \propto \frac{1}{\sqrt{m}}$ (Graham's law) $\therefore$ 6 times faster for He.

3 a) $H = U + pV$; $G = H - TS$.

$$dG = dH - TdS - SdT = dU - TdS - SdT + pdV + Vdp$$

$$= \cancel{TdS} - \cancel{pdV} - \cancel{TdS} - SdT + \cancel{pdV} + Vdp$$

$$= Vdp - SdT.$$

b) $dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT$ $\therefore$ $\left(\frac{\partial G}{\partial p}\right)_T = V$ and $\left(\frac{\partial G}{\partial T}\right)_p = -S$.

c) $\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)\right)_p = \frac{\partial^2 G}{\partial T \partial p} = \left(\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right)\right)_T = -\left(\frac{\partial S}{\partial p}\right)_T .$

d) $\frac{pV}{RT} = 1 + x$ $\therefore$ $V = (1+x) \cdot \frac{RT}{p}$ $\therefore$ $\left(\frac{\partial V}{\partial T}\right)_p = (1+x)\frac{R}{p}$

$= -\left(\frac{\partial S}{\partial p}\right)_T$ $\therefore$ $\left(\frac{\partial S}{\partial p}\right)_T = -\frac{(1+x)R}{p}$.