CH353 – Physical Chemistry I
Spring 2015, Unique 51170

Exam 2 – March 3, 2015

Name: Key

Always assume ideal gas unless directed otherwise.

You may use any material that does not have a heartbeat and does not connect to the internet or cellular network. Calculators may be used for computing arithmetic only.

Honor Code:

"The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community."

I certify that the work on this exam is entirely my own.

Signature **Date**

1. (15 points) Determine if the following statements are true or false.

a. [✓ True] False For a reversible process, $\Delta S_{tot} = 0$ always.

b. True [✓ False] Volume and entropy are properties that are natural variables of Gibbs free energy.

c. True [✓ False] The second law of thermodynamics defines $\Delta G < 0$ as a spontaneous process.

d. [✓ True] False A system will move spontaneously in the direction of increasing number of microstates.

e. True [✓ False] A reversible process is one in which the final state is equal to the initial state.

2. (20 points) Recall the weather balloon described in Quizzes 1 and 3. To remind you, this weather balloon is filled with hydrogen gas and released from a ground-based weather station, then slowly rises through the atmosphere recording and relaying weather conditions. It eventually reaches an altitude of 60,000 ft (~18 km); at this altitude, the weather balloon is 15 m in diameter, the pressure of the atmosphere is 1% of the value at the earth's surface, and the ambient temperature is -60°C. How many microstates are available to the system when the balloon reaches its final altitude? Assume the balloon is spherical and that it is a closed system.

W = degeneracy of a space = $\left(\frac{V}{b}\right)^N$ where V = volume of balloon = $\left(\frac{4}{3}\right)\pi(7.5\,m)^3$ $= 1.8\times10^3\,m^3$

estimate $d(H_2) = 1\times10^{-10}\,m$

$b = \left(\frac{4}{3}\right)\pi\left(\frac{1\times10^{-10}\,m}{2}\right)^3 = 5.2\times10^{-31}\,m^3$ b = volume of individual H_2 molecule

N = number of molecules of N_2.

recall from Quiz 1 that the balloon holds $n = \underline{1034 \text{ moles of } H_2}\left|\frac{6.022\times10^{23}\text{ molecules } H_2}{1\text{ mol } H_2}\right|$

(or you can recalculate this from the given information)

$N = 6.22\times10^{26}$ molecules of H_2

$$W = \left(\frac{V}{b}\right)^N = \left(\frac{1.8\times10^3\,m^3}{5.2\times10^{-31}\,m^3}\right)^{6.22\times10^{26}} = \boxed{\left(3.5\times10^{33}\right)^{6.22\times10^{26}} = W}$$

This is a huge number.

3. (30 points) Here are a series of ranking questions. Please read each question carefully.

a. Rank the following in order of *increasing intermolecular interactions*:

3 2 1
Solid, liquid, gas i.e. gas < liquid < Solid

b. Rank the following in order of *increasing intermolecular interactions*:

Ethane (C_2H_6), ethanoic acid (CH_3COOH), ethanol (CH_3CH_2OH)
1 3 2

c. Rank the following in order of *increasing molar entropy*:

1 2 3
Solid, liquid, gas

d. Rank the following in order of *increasing molar entropy*:

3 2 1
Hexane (C_6H_{14}), cyclohexane (C_6H_{12}), benzene (C_6H_6)

e. Rank the following in order of *increasing work performed by the system*:

Expansion against an external pressure of 1 atm 2
Expansion against an external pressure of 10 atm 3
Expansion against an external pressure of 0 atm 1

f. Rank the following in order of *increasing* ΔS_{sys}:

2 Reversible adiabatic expansion of an ideal gas $\Delta S_{sys} = 0$
3 Irreversible adiabatic expansion of an ideal gas $\Delta S_{sys} > 0$
1 Reversible isothermal compression of an ideal gas $\Delta S_{sys} < 0$

4. (15 points) Consider the reversible expansion of an ideal gas. Explain, using clear and concise English and any equations and symbols you need, why PV^{γ} = constant if the expansion is adiabatic, but PV = constant if the expansion is isothermal.

In an isothermal expansion, energy flows into the system as heat to maintain a constant temperature, despite the fact that energy is being lost as work. In the adiabatic case, no heat flows into the system, and the temperature of the system must fall as work is done. This means that pressure must fall faster in an adiabatic case than in an isothermal case. $\left(\frac{1}{V^{\gamma}} < \frac{1}{V}\right)$

5. (20 points) A 20 L vessel containing 1.0 mol of an ideal gas with $C_{V,m} = (5/2)R$ initially at 298 K is subjected to the following three-step cycle. Determine q, w, ΔU, ΔH, and ΔS_{sys} for each step, and for the overall cycle.

a) The system is heated at constant volume to twice its initial pressure.
b) The system expands reversibly and adiabatically to its initial temperature.
c) The system is compressed reversibly and isothermally back to its original pressure.
d) Remember to determine q, w, ΔU, ΔH, and ΔS_{sys} for the entire cycle.

a) $V_i = 20\ L$

$\Delta V = 0$

$V_f = 20\ L$

$n = 1.0\ mol$

$T_i = 298\ K$

$C_{v,m} = \frac{5}{2} R$

$$P_i = \frac{nRT_i}{V_i} = \frac{(1.0\ mol)(0.082\ L\,atm/mol\,K)(298\ K)}{20\ L}$$

$P_i = 1.2\ atm$, $P_f = 2P_i$

$$\frac{P_i}{T_i} = \frac{P_f}{T_f} \qquad T_f = \frac{P_f T_i}{P_i} = \frac{(2\cancel{P_i})(298\ K)}{\cancel{P_i}}$$

$$\boxed{T_f = 596\ K}$$

$\Delta V = 0 \Rightarrow \boxed{w = 0}$

$\Delta U = n C_{v,m} \Delta T = (1.0\ mol)(5/2)(8.31\ J/K\,mol)(298\ K)$

$\boxed{\Delta U = 6.2\ kJ}$

$\Delta S = n C_v \ln(T_f/T_i) = (5/2)(8.314\ J/mol\,K)\ln\left(\frac{596}{298}\right)$

$\Delta U = q + \cancel{w}^{0}$ $\boxed{q = 6.2\ kJ}$ $\boxed{\Delta S = 14.3\ J/K}$

$\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_f V_f - P_i V_i)$

$\Delta H = 6.2\ kJ + ((2)(1.2\ atm)(20\ L) - (1.2\ atm)(20\ L))\left(\frac{1.01\times10^5\ Pa}{1\ atm}\right)\left(\frac{1\ dm^3}{1\ L}\right) \cdot \left(\frac{1\ m}{10\ dm}\right)^3$

$\Delta H = 6.2\ kJ + 2.4\ kJ$

$\boxed{\Delta H = 8.6\ kJ}$

Scratch Paper

b) $T_i = 596\,\text{K}$

$P_i = 2(1.2\,\text{atm}) = 2.4\,\text{atm}$

$V_i = 20\,\text{L}$

$T_f = 298\,\text{K}$

$\cancel{P}\ V_f = V_i\left(\frac{T_i}{T_f}\right)^c \qquad c = \frac{C_{v,m}}{R} = \frac{5}{2}$

$V_f = (20\,\text{L})\left(\frac{596\,\text{K}}{298\,\text{K}}\right)^{5/2}$

$\underline{V_f = 113\,\text{L}}$

$$P_f = \frac{nRT_f}{V_f} = \frac{(1.0\,\text{mol})(0.082\,\frac{\text{L atm}}{\text{mol K}})(298\,\text{K})}{113\,\text{L}} = \underline{0.22\,\text{atm} = P_f}$$

$\boxed{q = 0}$

$\Delta U = nC_{v,m}\Delta T = (1.0\,\text{mol})(5/2)(8.31\,\text{J/K mol})(298\,\text{K} - 596\,\text{K})$

$\boxed{\Delta U = -6.2\,\text{kJ}}$ (makes sense is ΔT is equal + opposite to part a)

$w = \Delta U - q = \boxed{-6.2\,\text{kJ} = w}$ (makes sense since $V_f > V_i$)

$\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_f V_f - P_i V_i)$

$\Delta H = -6.2\,\text{kJ} + \left[(0.22\,\text{atm})(113\,\text{L}) - (2.4\,\text{atm})(20\,\text{L})\right]\left(\frac{1.01\times10^5\,\text{Pa}}{1\,\text{atm}}\right)\left(\frac{1\,\text{m}}{10\,\text{dm}}\right)^3 \cdot \left(\frac{1\,\text{L}}{1\,\text{dm}^3}\right)$

$\boxed{\Delta H = -8.5\,\text{kJ}}$

$\Delta S_{tot} = \Delta S_{sys} + \overset{0}{\cancel{\Delta S_{surr}}} \overset{\swarrow}{=} 0$ ← b/c reversible

$\uparrow$ b/c adiabatic

$\Rightarrow \boxed{\Delta S = 0}$

c) $T_f = T_i = 298\,K$ $(\Delta T = 0)$

$P_i = 0.22\,atm$

$P_f = P_i$ (part a) $= 1.2\,atm$

$V_i = 113\,L$

$V_f = \frac{nRT_f}{P_f} = 20\,L$ (by inspection)

$$\boxed{\Delta U = n C_{v,m} \Delta T = 0}$$

$$w = -nRT \ln\left(\frac{V_f}{V_i}\right) = -(1.0\,mol)(298\,K)(8.314\,J/K\,mol) \ln\left(\frac{20\,L}{113\,L}\right)$$

$\boxed{w = +4.3\,kJ}$ (makes sense since $V_f < V_i$

$q = \Delta U - w = -w = \boxed{4.3\,kJ = q}$

$\Delta S = nR\ln(V_f/V_i)$

$\Delta S = (1.0\,mol)(8.314\,J/mol\,K)\ln\left(\frac{20\,L}{113\,L}\right)$

$\boxed{\Delta S = -14.3\,J/K}$

$$\boxed{\Delta H = \Delta U + \Delta(PV) = 0}$$

d) Overall : $\Delta U_{TOT} = \Delta U(a) + \Delta U(b) + \Delta U(c) = 0$

$\Delta H_{TOT} = \Delta H(a) + \Delta H(b) + \Delta H(c) = 0$

$\Delta S_{tot} = \Delta S(a) + \Delta S(b) + \Delta S(c) = 0$

These ~~two~~ 3 we could have figured out by inspection

$w_{TOT} = w(a) + w(b) + w(c) = 0 + -6.2\,kJ + 4.3\,kJ = \underline{-1.9\,kJ}$

$q_{TOT} = q(a) + q(b) + q(c) = 6.2\,kJ + 0 \mp 4.3\,kJ = \underline{1.9\,kJ}$