CHEM 3423 001 Spring 2016

Name: KEY
ID:

Midterm Exam # 1

Answer Sheet: (All problems are multiple choice. List the letter that corresponds to the correct answer. Maximum number of points you can get is 25 pts!)

Conceptual questions (each **1.0 pts**):

1) d
2) e
3) c
4) a
5) b
6) a
7) b
8) b
9) b
10) c
11) a
12) c
13) b

Problems and Calculations (each **2.0 pts**):

1) i
2) i
3) a
4) e
5) F
6) g

Conceptual Questions:

1. Which of the following properties is intensive?

   a. Mass
   b. Volume
   c. Particle number
   [✓ d.] Density
   e. None of a) - d)

2. Suppose we decrease the temperature of a gas by a factor 3 ($T_2 = T_1/3$). What is the relationship between the kinetic energies?

   a. $E_2 = 9 E_1$
   b. $E_2 = E_1$
   c. $E_2 = 3 E_1$
   d. $E_2 = E_1/\sqrt{3}$
   [✓ e.] $E_2 = E_1/3$
   f. None of a)-e)

3. If N_2 and H_2 behave as an ideal gas, and are at the same temperature, the average kinetic energy

   a. of N_2 is smaller than that of H_2
   b. of N_2 is larger than that of H_2
   [✓ c.] of the molecules in both gases is the same

4. The Maxwell distribution law gives the probability distribution of the speed of gas molecules. When temperature increases,

   [✓ a.] the distribution curve becomes flatter
   b. the distribution curve becomes more peaked
   c. the area under the distribution becomes smaller
   d. the average speed of the molecules decreases
   e. none of a)-d)

5. Atmospheric pressure

   a. does not depend on temperature
   [✓ b.] decreases exponentially with altitude
   c. increases exponentially with altitude
   d. None of a) – c)

6. Let P_W be the pressure resulting from a 2 m column of water, and P_{Hg} be the pressure resulting from a 2 m column of mercury. Which statement is true?

   [✓ a.] $P_w < P_{Hg}$
   b. $P_w = P_{Hg}$
   c. $P_w > P_{Hg}$

7. Which of the following statements is correct about the Joule-Thomson experiment?
    a. $\Delta U = 0$
    [✓ b.] $\Delta H= 0$
    c. $W = 0$
    d. None of a) – c)

8. During reversible isothermal compression of an ideal gas,
    a. $\Delta U = 0$ and $\Delta H > 0$
    [✓ b.] $\Delta U = 0$ and $\Delta H = 0$
    c. $\Delta U = 0$ and $\Delta H < 0$
    d. None of a) – c)

9. The first law of thermodynamic states that
    a. The energy of an isolated system increases as it approaches equilibrium
    [✓ b.] The energy is conserved in an isolated system
    c. The energy of an isolated system decreases as it approaches equilibrium
    d. The entropy of all perfectly crystalline substances is zero at T = 0 K.
    e. External work is needed to pump heat from a system at low temperature to one at a higher temperature.
    f. None of a) - e)

10. The second law of thermodynamic states that
    a. The energy is conserved in an isolated system
    b. The entropy of all perfectly crystalline substances is zero at T = 0 K.
    [✓ c.] External work is needed to pump heat from a system at low temperature to one at a higher temperature.
    d. None of a)-c)

11. Which of the following statements is true for a Carnot cycle?
    [✓ a)] The efficiency of a Carnot Cycle depends on the ratio of temperatures $T_L/T_{H,}$, where T_H is the higher temperature
    b. Not all Carnot engines have the same efficiency.
    c. A Carnot engine cannot be used as a refrigerator
    d. None of a)-c)

12. The entropy change in a Carnot cycle is
    a. positive
    b. negative
    [✓ c.] zero

13. For a reversible adiabatic expansion of a real gas, the entropy changes as
    a. $\Delta S > 0$
    [✓ b.] $\Delta S = 0$
    c. $\Delta S < 0$

Problems and Calculations:

1. An ideal gas occupies a volume V of 1.25 dm^3 at a pressure P of 5.0×10^5 Pa. What is the new volume of the gas maintained at the same temperature T if the pressure P is reduced to 1.0×10^5 Pa?
    - a. 0.25 dm^3
    - b. 0.32 dm^3
    - c. 0.42 dm^3
    - d. 0.63 dm^3
    - e. 1.25 dm^3
    - f. 2.50 dm^3
    - g. 3.75 dm^3
    - h. 5.00 dm^3
    - [✓ i.] 6.25 dm^3
    - j. none of a) – i)

$PV = nRT \Rightarrow V = nRT/P$

$P_{new} = P_{old}/5 \Rightarrow V_{new} = 5 \times V_{old} = 6.25\ dm^3$

2. For O_2 gas at 600 K, calculate the ratio of the fraction of molecules that have the speed $u_2 = 3\,u_1$ to the fraction that have speed u_1. Assume that $u_1 = \bar{u}$ (the average speed of molecules at this temperature).
    - a. 1.42 x 10^{-9}
    - b. 4.26 x 10^{-9}
    - c. 1.28 x 10^{-8}
    - d. 1.06 x 10^{-5}
    - e. 3.17 x 10^{-5}
    - f. 9.50 x 10^{-5}
    - g. 3.77 x 10^{-5}
    - h. 1.13 x 10^{-4}
    - [✓ i.] 3.39 x 10^{-4}
    - j. none of a) –i)

$$\frac{N(u)}{N} = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mu^2/k_B T} \cdot u^2\,du$$

$$\frac{N(u_2)}{N(u_1)} = \frac{u_2^2}{u_1^2} \cdot exp\left(-\frac{m}{2k_B T}\left(u_2^2 - u_1^2\right)\right)$$

$$= 9 \cdot exp\left(-\frac{m}{2k_B T}(9-1)u_1^2\right)$$

$$= 9 \cdot exp\left(-8u_1^2 \frac{m}{2k_B T}\right) \qquad u_1 = \bar{u} = \sqrt{\frac{8k_B T}{\pi m}}$$

$$\Rightarrow u_1^2 = \frac{8k_B T}{\pi m}$$

$$= 9\, exp\left(-\frac{32}{\pi}\right)$$

$$= 9 \cdot exp(-10.186)$$

$$= 9 \cdot 3.77 \cdot 10^{-5}$$

$$= 3.39 + 10^{-4}$$

3. Calculate the pressure of 2.5 dm³ of a gas weighing 60.0 g at 700 K using the van der Waal's equation (use a = 0.85 Pa m⁶ /mol²; b= 0.00007 m³/mol). The molar mass of the gas is M = 15.0 g/mol

   [✓ a)] 83.11 bar
   b. 8.311 bar
   c. 0.8311 bar
   d. 1.049 bar
   e. 10.49 bar
   f. 104.9 bar
   g. 126.6 bar
   h. 12.66 bar
   i. 1.266 bar
   j. none of a) – i)

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\Rightarrow P = \frac{nRT}{V-nb} - \frac{an^2}{V^2} \qquad n = \frac{m}{M} = \frac{60}{15}\,mol = 4\,mol$$

$$= \frac{4 \cdot 8.3145 \cdot 700}{2.5\times10^{-3} - 4 \cdot 0.00007}\,Pa - \frac{0.85 \cdot 4^2}{2.5^2 \cdot 10^{-6}}\,Pa$$

$$= \frac{23280.6}{2.5\times10^{-3} - 2.8\cdot10^{-4}}\,Pa - \frac{13.6}{6.25\cdot10^{-6}}\,Pa$$

$$= \frac{23280.6}{2.22\times10^{-3}}\,Pa - \frac{2.176}{10^{-6}}\,Pa$$

$$= 10486.5 \cdot 10^{3}\,Pa - 2.176 \cdot 10^{6}\,Pa$$

$$= 10.487 \cdot 10^{6}\,Pa - 2.176 \cdot 10^{6}\,Pa$$

$$= 8.311 \times 10^{6}\,Pa$$

$$= 83.11\ bar$$

4. Two mol of an ideal gas is reversibly expanded at a constant temperature until $V_2 = 8\ V_1$. If the gas performed W = -24 kJ of work, what is its temperature T?

a. 2670 K
b. 1441 K
c. 1388 K
d. 720 K
[✓ e.] 694 K
f. 612 K
g. 413 K
h. 223 K
i. 103 K
j. none of a) – i)

$$W = nRT \ln \frac{V_1}{V_2} \Rightarrow T = \frac{W}{nR \ln V_2/V_1}$$

$$T = \frac{-24 \cdot 10^3}{-2 \cdot 8.3145 \cdot \ln 8} \cdot 10^3\ K$$

$$= \frac{12}{8.3145 \cdot 2,0794} \cdot 10^3\ K$$

$$= \frac{12}{17.2895} \cdot 10^3\ K$$

$$= 0.6941 \cdot 10^3 K$$

$$= 694.1\ K$$

5. A Carnot engine operates between temperatures T_H=3000 K and T_C=75 K. How much heat (absolute value) needs to be put into the engine at T_H in order to obtain W=-6000 J of work from the engine?
   a. 1625.0 kJ
   b. 162.50 kJ
   c. 16.250 kJ
   d. 1.6250 kJ
   e. 5.8537 kJ
   [✓ f.] 6.1538 kJ
   g. 61.538 kJ
   h. 615.38 kJ
   i. 6153.8 kJ
   j. none of a) – i)

$$\eta = 1 - \frac{T_C}{T_H} = 1 - \frac{75}{3000} = 1 - 0.025 = 0.975$$

$$= -\frac{W_{rev}}{Q_H} \Rightarrow Q_H = \frac{-W_{rev}}{\eta} = \frac{6000 J}{0.975} = 6153.8 J$$

$$= 6.1538 kJ$$

6. A vessel is divided by a partition into two compartments. One side contains 5 mol of O_2 at a pressure of 1 bar, the other 10 mol of N_2 at the same pressure. Assume ideal gas behavior. What is the entropy change when the partition is removed?
    a. 11.96 J
    b. 34.48 J
    c. 79.39 J
    d. 258.4 J
    e. 11.96 J/K
    f. 34.48 J/K
    [✓ g.] 79.39 J/K
    h. 258.4 J/K
    i. 108.2 J/(K mol)
    j. none of a) – i)

$$\Delta S = -R\left[n_1 \ln x_1 + n_2 \ln x_2\right]$$

$$= -R\left[n_1 \ln \frac{n_1}{n_1+n_2} + n_2 \ln \frac{n_2}{n_1+n_2}\right]$$

$$= -R\left[5 \cdot \ln \frac{5}{15} + 10 \ln \frac{10}{15}\right]$$

$$= -R\left[5 \cdot \ln \frac{1}{3} + 10 \ln \frac{2}{3}\right]$$

$$= R\left[5 \cdot \ln 3 + 10 \ln 1.5\right]$$

$$= 8.3145 \left[5 \cdot 1.0986 + 10 \cdot 0.4055\right] J/K$$

$$= 8.3145 \cdot \left[5.493 + 4.055\right] J/K$$

$$= 8.3145 \cdot 9.548 \, J/K$$

$$= 79.39 \, J/K$$

Useful Equations and Constants:

$$\overline{u^2} = \frac{3k_BT}{m}$$

$$\bar{u} = \sqrt{\frac{8k_BT}{\pi m}}$$

$$u_{mp} = \sqrt{\frac{2k_BT}{m}}$$

$$\bar{\varepsilon} = \frac{3}{2}k_BT$$

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\lambda = \frac{V}{\sqrt{2}\pi d^2 N}$$

$$\frac{dN}{N} = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-mu^2/2k_BT}u^2\,du$$

$$Z = \frac{PV}{nRT} = \frac{PV_m}{RT}$$

$$\left(P_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8}{3}T_r$$

$$P_t = \frac{RT}{V}\sum_i n_i$$

$$\Delta U = q + w$$

$$w = -\int_{V_i}^{V_f} P_{ext}\,dV$$

$$\Delta H_m(T_2) = \Delta H_m(T_1) + \int_{T_1}^{T_2} \Delta C_p\,dT$$

$$w = -P_{ext}\Delta V$$

$$w = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

$$H = U + PV$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + \Delta nRT$$

$$\Delta U = nC_{V,m}(T_2 - T_1)$$

$$\Delta H = nC_{P,m}(T_2 - T_1)$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

$$\gamma = \frac{C_{p,m}}{C_{v,m}}$$

$$C_{P,m} - C_{V,m} = R$$

$$\Delta U = -n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$w = -nRT\ln\left(\frac{V_2 - nb}{V_1 - nb}\right) - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$\eta = \frac{T_h - T_c}{T_h}$$

$$\Delta S = nR\ln\frac{V_f}{V_i}$$

$$\Delta S = nR\ln\frac{P_i}{P_f}$$

$$\Delta S = nC_{P,m}\ln\frac{T_f}{T_i}$$

$$\Delta S = nC_{V,m}\ln\frac{T_f}{T_i}$$

$$\Delta S = -R(x_1\ln x_1 + x_2\ln x_2)$$

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S \qquad \Delta S = n_1 R \ln\left(\frac{V_1 + V_2}{V_1}\right) + n_2 R \ln\left(\frac{V_1 + V_2}{V_2}\right)$$

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

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \qquad RT \ln\frac{f}{P} = \int_0^P \left(V_m - \frac{RT}{P'}\right) dP'$$

L = $6.022 \cdot 10^{23}$ mol^{-1}
R = 8.3145 J K^{-1} mol^{-1} = 0.082057 atm dm^3 K^{-1} mol^{-1} = 1.98719 cal K^{-1} mol^{-1}
k_B = $1.381 \cdot 10^{-23}$ J K^{-1}

1 atm = 101325 Pa, 1 bar = 100000 Pa
1 m^3 = 1000 liter = 1000 dm^3
1 W = 1 J s^{-1}
1 horsepower = 745.6 W

Thermodynamic data for compounds (all values are for 298.15 K and 1 bar)

	$\Delta_f H^o$ / kJ mol^{-1}	S^o / JK^{-1} mol^{-1}	$C_{P,m}$ / JK^{-1} mol^{-1}
$H_2(g)$	0	130.68	28.82
$N_2(g)$	0	191.61	29.13
$O_2(g)$	0	205.14	29.34
$CO(g)$	−110.53	197.67	29.14
$CO_2(g)$	−393.51	213.74	37.11
$H_2O(l)$	−285.83	69.91	75.29
$H_2O(g)$	−241.82	188.83	33.58
C(*graphite*)	0	5.74	8.527
$C_2H_5OH(s)$	−277.69	160.7	111.5
$C_6H_5OH(s)$	−165.47	144.0	221.2