

Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.

1. (10 points) A cylinder of compressed nitrogen gas contains 2.74×10^3 grams of nitrogen. The tank is held at a temperature of 18.7°C and the pressure is 3.75×10^7 Pa. The cylinder is opened and gas is allowed to escape into the atmosphere where the pressure is 1 bar. At the end of the process, the pressure in the tank has dropped to 1.80×10^5 Pa. Assuming that the gas is ideal and that the temperature remains unchanged, what volume of nitrogen has been released into the external environment?

First, calculate the number of moles of nitrogen in the tank to start:

$$n_{init} = \frac{2.74 \times 10^3 \text{ g}}{28.00134 \text{ g/mol}} = 97.85 \text{ mol}$$

The number of moles that are left after the process is

$$n_{final} = \frac{1.80 \times 10^5 \text{ Pa}}{3.75 \times 10^7 \text{ Pa}} 97.85 \text{ mol} = 0.47 \text{ mol}$$

Therefore, one must have allowed into the atmosphere, $\Delta n = 97.85 \text{ mol} - 0.47 \text{ mol} = 97.38 \text{ mol}$

Because we know the temperature and the atmospheric pressure, we can determine the volume to which this number of moles corresponds:

$$V = \frac{\Delta n RT}{P} = \frac{97.38 \text{ mol} (8.3144349 \text{ J K}^{-1} \text{ mol}^{-1}) (291.85 \text{ K})}{100,000 \text{ Pa}} = 2.36 \text{ m}^3$$

**DO NOT WRITE
IN THIS SPACE**

p. 1 _____/10

p. 2 _____/10

p. 3 _____/15

p. 4 _____/10

p. 5 _____/10

p. 6 _____/15

p. 7 _____/10

p. 8 _____/10

p. 9 _____/10

p. 10 _____/10

p. 11 _____/10

p. 12 _____/15

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 p. 13 _____/10
 (Extra credit)

=====
 TOTAL PTS

/135

2. (10 points) Match the best ending of the phrase from the right column with the beginning of the phrase from the left column:

1) An adiabatic process occurs with no (g) heat transfer	a) Anharmonic corrections
2) U and V are the examples of (q) state functions	b) Boyle temperature
3) A process the direction of which can be changed by an infinitesimal change in the driving force is (o) reversible	c) Compression factor
4) The Joule-Thompson experiment is an example of a process that is (i) isenthalpic	d) Entropy
5) An energy change in a system that does not involve the flow of heat across the boundary must involve (s) work	e) First law of thermodynamics
6) The condition at which a real gas tends to have P-V behavior like an ideal gas is characterized by the (b) Boyle temperature	f) Heat capacity
7) The conditions for which a table of properties is given define the (p) standard state	g) Heat transfer
8) A description of the equation of state of a gas in terms of the reduced variables suggests the hypothesis of the (l) law of corresponding states	h) Irreversible
9) "Two objects in thermal equilibrium with a third object are in thermal equilibrium with each other" is a statement of the (t) zeroth law of thermodynamics	i) Isenthalpic
10) In the Carnot cycle, there are two steps that are adiabatic and two steps that are (k) isothermal	j) Isochoric
	k) Isothermal
	l) Law of corresponding states
	m) Path functions
	n) Random functions
	o) Reversible
	p) Standard state
	q) State functions
	r) Third law of thermodynamics
	s) Work
	t) Zeroth law of thermodynamics

3. (15 points) Solid copper is used in many applications where heat transfer is needed, such as a heating block because it transmits heat well. This question is about how much it absorbs. The NIST compilation reports that the standard heat capacity of copper is

$$C_p^\theta(T) = \left(17.72891 + 28.09870 T - 31.25289 T^2 + 13.97243 T^3 + \frac{0.068611}{T^2} \right) \frac{J}{K \text{ mol}}$$

With this information, determine the change in the standard molar enthalpy of copper when it is heated from 300 K to 400 K.

This is a straightforward integration:

$$\begin{aligned} \Delta H &= \int_{300 \text{ K}}^{400 \text{ K}} \left(\frac{\partial H}{\partial T} \right)_P dT = \int_{300 \text{ K}}^{400 \text{ K}} C_p dT = \int_{300 \text{ K}}^{400 \text{ K}} a + bT - cT^2 + dT^3 + \frac{e}{T^2} dT \\ &= a(400 - 300) + \frac{b}{2}(400^2 - 300^2) - \frac{c}{3}(400^3 - 300^3) + \frac{d}{4}(400^4 - 300^4) - e \left(\frac{1}{400} - \frac{1}{300} \right) \end{aligned}$$

where the coefficients are those in the equation above. Doing the calculation, term by term, gives

$$\Delta H = (1773 + 983,454.5 - 3.855 \times 10^8 + 6.113 \times 10^{10} + 5.7176 \times 10^{-5}) J = 6.075 \times 10^{10} J$$

4. (10 points) For a gas that obeys the Berthelot equation of state, derive a formula (showing all work) for the derivative of the entropy with respect to volume at constant temperature. (Use the constants in the equation as defined in the Handbook.)

The Berthelot equation of state is

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

By an equation in the handbook:

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

Substitution gives:

$$\begin{aligned}\left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial}{\partial T} \left(\frac{RT}{V_m - b} - \frac{a}{TV_m^2}\right)\right)_V \\ &= \frac{R}{V_m - b} + \frac{a}{T^2 V_m^2}\end{aligned}$$

5. (10 points) For each reaction on the left side of the Table, give the numerical value (along with proper units) of the quantity indicated in the right-hand box, at 298.15 K. Show work below the box, but put your answer in the box.

Reaction	Quantity
(a) $2H_2(g) + O_2(g) \rightarrow 2H_2O(liq)$	$\Delta H^\theta = -571.6 kJ$
(b) $I_2(g) \rightarrow 2 I(g)$	$\Delta S^\theta = 100.9 J K^{-1}$
(c) $HCl(g) + HBr(g) \rightarrow BrCl(g) + H_2(g)$	$\Delta G^\theta = 147.7 kJ$
(d) $K(s) \rightarrow K(g)$	$P_K^\bullet = 2.52 \times 10^{-11} bar = 2.52 \times 10^{-6} Pa$
(e) $CaCO_3(s, ara) \rightarrow CaCO_3(s, cal)$	$K_a = 1.44$

(a) This is just twice the molar enthalpy of formation of liquid water, found in Table 5.8.

(b) This is the difference between the standard entropies of the materials found on Table 5.8.

$$\Delta S^\theta = 2 \times 180.8 J K^{-1} - 260.7 J K^{-1} = 100.9 J K^{-1}$$

(c) This is found by sum and difference of the free energies of formation of the various components.

$$\Delta G^\theta = -1.0 kJ + 0.0 kJ - (-95.3 kJ) - (-53.4 kJ) = 147.7 kJ$$

(d) One has to calculate the equilibrium constant for this reaction from the free-energy change. The free-energy change is just the free energy of formation of the gaseous atom, which is given in Table 5.8.

$$K = \exp\left(-\frac{\Delta G^\theta}{RT}\right) = \exp\left(-\frac{60.5 \times 10^3 J}{8.3144349 J K^{-1} (298.15 K)}\right) = \exp(-24.405) = 2.52 \times 10^{-11}$$

So, the equilibrium constant is very small. Since the activity of the solid is 1, the equilibrium constant is simply the pressure of the gas phase expressed in the units of the standard pressure (which is 1 bar = 0.1 MPa).

(e) This is identical to the calculation in (d):

$$\Delta G^\theta = -1129.1 kJ - (-1128.2 kJ) = -0.90 kJ$$

$$K = \exp\left(-\frac{\Delta G^\theta}{RT}\right) = \exp\left(-\frac{-0.90 \times 10^3 J}{8.3144349 J K^{-1} (298.15 K)}\right) = \exp(0.363) = 1.44$$

6. (15 points) Sulfur transforms from the rhombic form to the monoclinic form under a pressure of 1 bar at 95.4°C. Its reported enthalpy of transition is 0.38 kJ mol⁻¹. (a) What is the entropy of transition?

The entropy of transition is easily calculated from these two quantities.

$$\Delta S^\theta = \frac{\Delta H^\theta}{T_i} = \frac{380 \text{ J mol}^{-1}}{(95.43 + 273.15) \text{ K}} = 1.03 \text{ J K}^{-1} \text{ mol}^{-1}$$

(b) Assume that the heat capacity at constant pressure of rhombic sulfur is independent of temperature between 25°C and 95.4°C. What is the standard entropy of monoclinic sulfur at 95.4°C?

First calculate the standard entropy of rhombic sulfur at 95.4°C.

$$S_{rhomb,T}^\theta = S_{rhomb,298.15}^\theta + \int_{298.15}^T \frac{C_P^\theta}{T} dT = S_{rhomb,298.15}^\theta + C_P^\theta \ln\left(\frac{T}{298.15}\right)$$

The information at 298.15 K is given in Table 5.8. Substitution gives:

$$S_{rhomb,368.55}^\theta = 32.1 \text{ J K}^{-1} \text{ mol}^{-1} + 22.6 \text{ J K}^{-1} \text{ mol}^{-1} \ln\left(\frac{368.55}{298.15}\right) = 36.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

Finally, since the difference in the standard entropies of the two forms has been found in part (a), all one has to do is add that to the value just found to give the standard entropy of the monoclinic form at this temperature.

$$S_{mono,368.55}^\theta = S_{rhomb,368.55}^\theta + \Delta S^\theta = 36.9 \text{ J K}^{-1} \text{ mol}^{-1} + 1.03 \text{ J K}^{-1} \text{ mol}^{-1} = 37.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

7. (10 points) Consider a heat pump that removes heat from a cold reservoir (such as the external ambient air) and deposits it into a hotter reservoir (such as your living room). Let's suppose that the outside air is at a temperature of 5°C, typical of a cool day here in Delaware. Let's also suppose that your living room is at 20°C. (a) What is the maximum efficiency of a heat pump operating between these two temperatures.

The maximum efficiency of such a heat pump is given by the equation:

$$\epsilon = \frac{T_{hot}}{T_{hot} - T_{cold}}$$

The temperatures are: $T_{hot} = 293.15\text{ K}$ and $T_{cold} = 278.15\text{ K}$

The efficiency is therefore

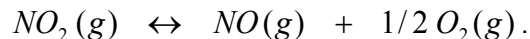
$$\epsilon = \frac{293.15}{293.15 - 278.15} = 19.543$$

(b) How much work (in joules) must be done by such a heat pump to supply 100 joules of heat to the living room?

The efficiency is defined in terms of the amount of heat deposited at the high temperature to the work, and therefore one can find the amount of work for deposition of a particular amount of heat:

$$w = \frac{q_{hot}}{\epsilon} = \frac{100\text{ joules}}{19.543} = 5.12\text{ joules}$$

8. (10 points) Consider the equilibrium of nitrogen dioxide and nitric oxide by the following chemical reaction:



Initially exactly one mole of nitrogen dioxide is placed in a vessel. At equilibrium, the volume of the vessel is adjusted so that the total pressure is exactly 1 bar. The gas is analyzed, and $P_{\text{NO}}/P_{\text{NO}_2} = 0.872$ at a temperature of 426.85°C. (a) Calculate K_P for this reaction at this set of conditions.

Since the gases all arise from the original material, let us create a table.

Time	NO ₂	NO	O ₂	Total pressure
0	P ₀	0	0	P ₀
Equilibrium	P ₀ -p	p	p/2	P ₀ +p/2
Ratio	1	x = p/(P ₀ -p)	x/2	

One can calculate the pressure of NO₂ from Dalton's law:

$$P_{\text{NO}_2} + P_{\text{NO}} + P_{\text{O}_2} = 1$$

Substitution gives

$$P_{\text{NO}_2} + xP_{\text{NO}_2} + \frac{x}{2}P_{\text{NO}_2} = 1$$

$$\left(1 + x + \frac{x}{2}\right)P_{\text{NO}_2} = 1 = \left(1 + 0.872 + \frac{0.872}{2}\right)P_{\text{NO}_2}$$

which gives $P_{\text{NO}_2} = 0.433 \text{ bar}$. With this, one can estimate $P_{\text{NO}} = 0.378 \text{ bar}$ and $P_{\text{O}_2} = 0.189 \text{ bar}$

Using these values in the equilibrium equation, one may calculate

$$K_P = \frac{P_{\text{NO}}P_{\text{O}_2}^{1/2}}{P_{\text{NO}_2}} = \frac{(0.378 \text{ bar})(0.189 \text{ bar})^{1/2}}{0.433 \text{ bar}} = 0.380 \text{ bar}^{1/2}$$

(b) Calculate the standard free energy of reaction under these conditions, assuming the gases are ideal.

Assuming that the standard pressure is 1 bar, and that the pressures are low enough that the gases may be treated as ideal, the value of K_P is also K_a . Then, one may use the standard expression to determine the free energy change.

$$\Delta G^\theta = -RT \ln K_a = -8.3144349 \text{ J K}^{-1}((273.15 + 426.85)\text{K}) \ln(0.380) = 5631 \text{ J}$$

9. (10 points) Indicate the number of phases and the number of components for each system. [Graded right minus 0.5 wrong. Do not guess.]

System	Number of phases	Number of components
1. an unsaturated solution of sodium chloride in water	1	2
2. a saturated solution of sodium chloride in water with excess sodium chloride present	2	2
3. an unsaturated solution of sodium chloride and sucrose in water	1	3
4. a system containing a water phase and an organic phase in which iodine is present	2	3
5. water at its triple point	3	1

10. (10 points) The equilibrium constant for the dissolution of the sparingly soluble salt, TiCl , at 298.15 is $K_a = 1.855 \times 10^{-4}$. What is the solubility of TiCl in water at 298.15 K?

One must set up the equilibrium equation.

$$K_a = a_{\text{Ti}^+} a_{\text{Cl}^-} = \gamma_{\pm}^2 m^2 \quad \text{or} \quad m = \sqrt{\frac{K_a}{\gamma_{\pm}^2}}$$

One must also simultaneously satisfy the DHG equation:

$$\ln \gamma_{\pm} = -\alpha_{DH} |z_+ z_-| \left(\frac{\sqrt{I}}{1 + \sqrt{I}} \right) = -1.177 \frac{\sqrt{m}}{1 + \sqrt{m}}$$

This can be solved iteratively until self-consistency is achieved. Let's start by assuming ideality: $\gamma_{\pm} = 1$

Substitution into the first equation gives an estimate of the concentration:

$$m^{(1)} = \sqrt{K_a} = 1.362 \times 10^{-2} \text{ mol/kg}$$

Putting this into the second equation gives the estimated activity coefficient:

$$\gamma_{\pm}^{(1)} = \exp \left[-\frac{1.177 \sqrt{m^{(1)}}}{1 + \sqrt{m^{(1)}}} \right] = 0.884$$

This is obviously not the same as 1, so we have to iterate again:

$$m^{(2)} = \sqrt{\frac{K_a}{\gamma_{\pm}^{(1)2}}} = 1.540 \times 10^{-2} \text{ mol/kg}$$

Check the activity coefficient:

$$\gamma_{\pm}^{(2)} = \exp \left[-\frac{1.177 \sqrt{m^{(2)}}}{1 + \sqrt{m^{(2)}}} \right] = 0.878$$

This is pretty close to the previous value, but let's iterate again:

$$m^{(3)} = \sqrt{\frac{K_a}{\gamma_{\pm}^{(2)2}}} = 1.551 \times 10^{-2} \text{ mol/kg}$$

This is even better agreement, but let's continue:

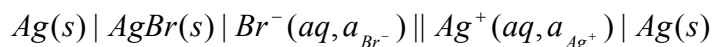
$$\gamma_{\pm}^{(3)} = \exp \left[-\frac{1.177 \sqrt{m^{(3)}}}{1 + \sqrt{m^{(3)}}} \right] = 0.878$$

It has now converged, so the answer is $m^{(3)} = 1.551 \times 10^{-2} \text{ mol/kg}$

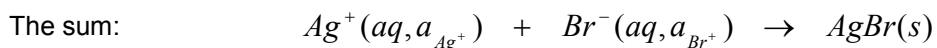
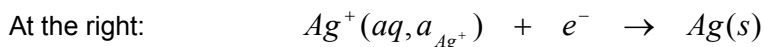
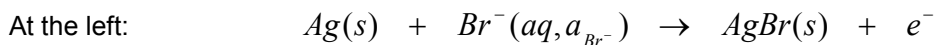
11. (10 points) Match the definitions in the right column with the words in left column by inserting the number of the definition in the space to the left of the word. **(Graded right – 0.5 wrong. Do not guess.)**

	Word	Definition
7	Amalgam	1. Decrease of volume in some highly charged salt solutions
13	Azeotrope	2. Dependence of γ_{\pm} on ionic strength
9	Colligative properties	3. Equivalent conductivity at infinite dilution
5	Conductance	4. Escaping tendency of a gas
15	Electrophoretic effect	5. Inverse of resistance
4	Fugacity	6. Measure of distillation efficiency
12	Gibbs-Duhem equation	7. Metal dissolved in mercury
11	Gibbs phase rule	8. Method of undetermined multipliers
10	Henry's law	9. Properties of dilute solutions that depend only on the number of solute molecules
6	Theoretical plates	10. Proportionality of concentration of dissolved gas to the pressure
		11. Relation for determining the number of degrees of freedom
		12. Relation of activities of components of a solution
		13. Solution that boils at a constant temperature
		14. Solution that freezes at a constant temperature
		15. Viscous effect of solvent movement around an ion on the ion of opposite charge

12. (15 points) The following cell is useful for the determination of the solubility of silver bromide.



(a) What is the overall reaction for this cell, as written?



(b) What is the standard voltage of this cell at 298.15 K, assuming no junction potential?

The standard voltage of this cell is the difference between the half-cell potential of the right half-cell minus the half-cell potential of the left half-cell.

$$\begin{aligned} \mathcal{E}^\theta &= \mathcal{E}_{right}^\theta - \mathcal{E}_{left}^\theta \\ &= 0.7996V - 0.07133V \\ &= 0.72827V \end{aligned}$$

(c) What is the standard Gibbs energy change for the cell reaction, as written, at 298.15 K?

The standard Gibbs free-energy change is determined with the Nernst equation:

$$\Delta G^\theta = -nF\mathcal{E}^\theta = -(1)(96485.3383C)(0.72827V) = -70.267 kJ$$

(d) What is K_{sp} for the AgBr at 298.15 K?

K_{sp} is the inverse of K_a for the reaction in part (a) and can be found from the standard free energy of the reverse of the equation in part (a). The result is

$$K_{sp} = \exp(-\Delta G_{reverse}^\theta / RT) = \exp\left(-\frac{-(-70267 J)}{8.3144349 J K^{-1}(298.15 K)}\right) = \exp(-28.345) = 4.895 \times 10^{-13}$$

13. (10 points, extra credit) Starting from the standard equations and definitions of thermodynamics, obtain a simple form for the following derivative:

$$\left(\frac{\partial^2 S}{\partial T^2}\right)_P =$$

An equation in Table 5.5 of the Handbook:

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

By the definition of the partial derivative, one identifies

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

Then, one takes the derivative of this while holding the pressure constant. This gives

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial T}\right)_P\right)_P = \left(\frac{\partial}{\partial T}\frac{C_P}{T}\right)_P = \frac{1}{T}\left(\frac{\partial C_P}{\partial T}\right)_P + C_P\left(\frac{\partial 1/T}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial C_P}{\partial T}\right)_P - \frac{C_P}{T^2}$$

So, the answer is

$$\left(\frac{\partial^2 S}{\partial T^2}\right)_P = \frac{1}{T}\left(\frac{\partial C_P}{\partial T}\right)_P - \frac{C_P}{T^2}$$