## Final Review KEY

 In each pair of compounds, pick the one with the higher vapor pressure at a given temperature. Explain your reasoning. (Tro 2nd Ed, Ch 11, #43) The stronger the intermolecular forces (IMFs) of a compound are, the lower its vapor

pressure and the higher its boiling point will be.

a)  $Br_2$  or  $I_2$ 

Both compounds are nonpolar so they will only have london dispersion forces (LDFs). Since Br is less massive than I, it will have weaker LDFs (IMFs) and thus a higher vapor pressure and lower boiling point.

b)  $H_2S$  or  $H_2O$ 

Both compounds are polar so they will have LDFs and dipole-dipole forces (DDFs). Since  $H_2S$  doesn't exhibit hydrogen bonding like  $H_2O$ , it will have weaker IMFs and thus a higher vapor pressure and lower boiling point.

c)  $NH_3$  or  $PH_3$ 

Both compounds are polar so they will have LDFs and dipole-dipole forces (DDFs). Since  $PH_3$  doesn't exhibit hydrogen bonding like  $NH_3$ , it will have weaker IMFs and thus a higher vapor pressure and lower boiling point.

- Determine if each pair of compounds forms a homogeneous solution when combined. For those that form homogeneous solutions, indicate the type of forces that are involved. (Tro 2nd Ed, Ch 11, #45)
  - a) CCl<sub>4</sub> and  $H_2O$

 $\text{CCl}_4$  is a nonpolar molecule while  $\text{H}_2\text{O}$  is a polar molecule so the two will NOT form a homogenous solution.

b) KCI and  $H_2O$ 

KCl is an ionic compound while  $H_2O$  is a polar molecule so the two WILL form a homogenous solution due to the ion-dipole forces. LDFs, DDFs, and hydrogen bonding will also be involved.

c)  $Br_2$  and  $CCI_4$ 

 $Br_2$  is a nonpolar molecule while  $CCl_4$  is a nonpolar molecule so the two WILL form a homogenous solution due to the LDFs.

d) CH<sub>3</sub>CH<sub>2</sub>OH and H<sub>2</sub>O

 $CH_3CH_2OH$  is a polar molecule while  $H_2O$  is a polar molecule so the two WILL form a homogenous solution due to the hydrogen bonding. LDFs and DDFs will also be involved.

 Identify the states present at points a through g in the phase diagram shown here. (Tro 2nd Ed, Ch 11, #71)



a = solid, b = liquid, c = gas, d = supercritical fluid, e = solid/liquid equilibrium, f = liquid/gas equilibrium, g = solid/liquid/gas equilibrium

- Rank each set of substances in order of increasing standard molar entropy (S°). Explain your reasoning. (Tro 2nd Ed, Ch 18, #53)
  - a) NH<sub>3</sub>(g); Ne(g); SO<sub>2</sub>(g); CH<sub>3</sub>CH<sub>2</sub>OH(g); He(g)

All substances are gases and atomic substances have lower entropies than molecular substances so He(g) and Ne(g) will have the lowest entropies. Further, He(g) has a lower molar mass than Ne(g) so it will have the lowest entropy and Ne(g) has the second lowest entropy. Meanwhile, the molecular substances will have lower entropies if they have lower molecular complexity. Therefore, SO<sub>2</sub>(g) will have the middle entropy, NH<sub>3</sub>(g) will have the second highest entropy and CH<sub>3</sub>CH<sub>2</sub>OH(g) will have the highest entropy.

 $He(g) < Ne(g) < SO_2(g) < NH_3(g) < CH_3CH_2OH(g)$ 

b)  $H_2O(s); H_2O(l); H_2O(g)$ 

All substances are different phases of water molecules and gases have higher entropy than liquids which have higher entropy than solids. Therefore,  $H_2O(s)$  will have the lowest entropy,  $H_2O(I)$  will have the middle entropy, and  $H_2O(g)$  will have the highest entropy.

 $H_2O(s) \le H_2O(l) \le H_2O(g)$ 

## c) $CH_4(g); CF_4(g); CCI_4(g)$

All substances are gases and have the same molecular structure so they will have lower entropies if they have lower molar masses. Therefore,  $CH_4(g)$  will

have the lowest entropy,  $CF_4(g)$  will have the middle entropy, and  $CCI_4(g)$  will have the highest entropy.

 $CH_4(g) < CF_4(g) < CCI_4(g)$ 

- 5) Use data from Appendix IIB to calculate  $\Delta S^{\circ}_{rxn}$  for each of the reactions. In each case, try to rationalize the sign of  $\Delta S^{\circ}_{rxn}$ . (Tro 2nd Ed, Ch 18, #55)
  - a)  $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$   $\Delta S^{\circ}_{rxn} = 1(229.2 \text{ J/K}) - 1(219.3 \text{ J/K}) - 1(130.7 \text{ J/K}) = -120.8 \text{ J/K}$  $\Delta S^{\circ}_{rxn}$  is **negative** since the number of moles of gas **decreases** in the rxn
  - b)  $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$   $\Delta S^{\circ}_{rxn} = 1(197.7 \text{ J/K}) + 1(130.7 \text{ J/K}) - 1(5.7 \text{ J/K}) - 1(188.8 \text{ J/K}) = 133.9 \text{ J/K}$  $\Delta S^{\circ}_{rxn}$  is **positive** since the number of moles of gas **increases** in the rxn
  - c)  $CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$   $\Delta S^{\circ}_{rxn} = 1(130.7 \text{ J/K}) + 1(213.8 \text{ J/K}) - 1(197.7 \text{ J/K}) - 1(188.8 \text{ J/K}) = -42.0 \text{ J/K}$  $\Delta S^{\circ}_{rxn}$  is **negative** since the molecules become **simpler** in the rxn (H<sub>2</sub>O to H<sub>2</sub>)
  - d)  $2 H_2S(g) + 3 O_2(g) \rightarrow 2 H_2O(I) + 2 SO_2(g)$   $\Delta S^{\circ}_{rxn} = 2(70.0 J/K) + 2(248.2 J/K) - 2(205.8 J/K) - 3(205.2 J/K) = -390.8 J/K$  $\Delta S^{\circ}_{rxn}$  is **negative** since the number of moles of gas **decreases** in the rxn
- 6) Without doing any calculations, determine the sign of  $\Delta S_{sys}$  and  $\Delta S_{surr}$  for each chemical reaction. (Tro 2nd Ed, Ch 18, #37)

Recall that if the entropy of the system increases then  $\Delta S_{sys} > 0$  and if it decreases then  $\Delta S_{sys} < 0$ . Also, recall that  $\Delta S_{surr} = (-\Delta H^{\circ} / T)$ .

- a)  $C_3H_8(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O(g)$   $\Delta H^\circ rxn = -2044 \text{ kJ}$  $\Delta S_{sys} > 0 \text{ and } \Delta S_{surr} > 0$
- b)  $N_2(g) + O_2(g) \rightarrow 2 \text{ NO}(g)$   $\Delta S_{sys} < 0 \text{ and } \Delta S_{surr} < 0$  $\Delta H^\circ rxn = +182.6 \text{ kJ}$
- c)  $2 N_2(g) + O_2(g) \rightarrow 2 N_2O(g)$   $\Delta B^{\circ}rxn = +163.2 \text{ kJ}$  $\Delta S_{sys} < 0 \text{ and } \Delta S_{surr} < 0$
- d) 4 NH<sub>3</sub>(g) + 5 O<sub>2</sub>(g)  $\rightarrow$  4 NO(g) + 6 H<sub>2</sub>O(g)  $\Delta$ H°rxn = -906 kJ  $\Delta$ S<sub>sys</sub> > 0 and  $\Delta$ S<sub>surr</sub> > 0
- 7) Given the values of ΔH°<sub>rxn</sub>, ΔS°<sub>rxn</sub>, and T, determine ΔS<sub>univ</sub> and predict whether each reaction is spontaneous. (Assume that all reactants and products are in their standard states.) (Tro 2nd Ed, Ch 18, #41)

a.	$\Delta H_{\rm rxn}^{\rm o} = +115 \text{ kJ};$	$\Delta S_{\rm rxn}^{\rm o} = -263  {\rm J/K};$	T = 298  K
b.	$\Delta H_{\rm rxn}^{\rm o} = -115 \text{ kJ};$	$\Delta S_{\rm rxn}^{\rm o} = +263  {\rm J/K};$	T = 298  K
c.	$\Delta H_{\rm rxn}^{\rm o} = -115 \text{ kJ};$	$\Delta S_{\rm rxn}^{\rm o} = -263  {\rm J/K};$	T = 298  K
d.	$\Delta H_{\rm rxn}^{\rm o} = -115 \text{ kJ};$	$\Delta S_{\rm rxn}^{\rm o} = -263  {\rm J/K};$	T = 615  K

DSuni = DSsystem + DSuniverse
$\Delta S_{nniv} = \left(-\Delta H_{SNV}\right) + \Delta S(SVS)$
SSND o for spontaneous provenes
a) $\Delta S_{u,v} = (-\Delta H S_{3}) + \Delta S_{System}$
= (-115,000 5 + (-263 3/2) + (-263 3/2)
= -648.9 20
-> Non Spontanear J
b) Farran process a
$A_{nsumer}$ : $648.9 > 0$
-> Sporteneous
c) failus pracess a
Answer: [122.31] >0
Sphifuncan
d) Follows place a
Answer: -76.0120
- Non spontaneous

8) For each reaction, calculate △H°rxn, △S°rxn, and △G°rxn at 25°C and state whether the reaction is spontaneous. If the reaction is not spontaneous, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from 25 °C? (Tro 2nd Ed, Ch 18, #61)

a. 
$$N_2O_4(g) \longrightarrow 2 NO_2(g)$$
  
b.  $NH_4Cl(s) \longrightarrow HCl(g) + NH_3(g)$   
c.  $3 H_2(g) + Fe_2O_3(s) \longrightarrow 2 Fe(s) + 3 H_2O(g)$   
d.  $N_2(g) + 3 H_2(g) \longrightarrow 2 NH_3(g)$ 

dru: 1) 
$$N_2O_4(g) \rightarrow 2NO_2(g)$$
  

$$\Delta H^*_{TXA} = E\Delta H_{fpreduct} - E\Delta H_{f}reactaut - = 2(33.2kJ/mol) - (9.2kJ/mol) = 57.2kJ/mol$$

$$= 2(33.2kJ/mol) - (9.2kJ/mol) = 57.2kJ/mol$$

$$= 2(240.1) - (504.3) = 0.175 kJ/mol$$

$$= 175.9J/kmol = 0.175 kJ/mol$$

$$\Delta Q^\circ = \Delta H^\circ - T\Delta S^\circ]$$

$$= 57.2 - (298 k) (0.175 kJ/kmol)$$

$$= 4.752 kJ/mol (two hence non-spontaneous)$$

$$\Delta Q < o \quad \therefore [\Delta H^\circ - T\Delta S^\circ < 0]$$

$$-T\Delta S^\circ < -\Delta H^\circ$$

$$T > \Delta H^\circ$$

$$T > \Delta H^\circ$$

$$T > 326.85 k$$

$$Interevalue: above 326.85 k$$

$$\frac{(2)}{(2)} = (AY_{HU} + AH^{2}NH_{3}) - (DH_{NHUU}) = (-92kJ/mol) + (-461kJ/mol) - (-314.4 kJ/mol) = + 17.6.3 kJ/mol$$

$$\begin{aligned} \Delta S_{KKR} &= (186.7 \ \text{J} [Kmol]) + (192.77\ \text{F} [Kmol]) - (94.85\ \text{F} [Kmol]) \\ &= 284.6 \ \text{J} [Kmol] = 0.285 \ \text{KJ} [Kmol] \\ \Delta G_{9}^{\circ} \text{rm} &= \Delta H^{\circ} - T \Delta S^{\circ} \\ &= 176.3 - (298)(0.285) = 91.46 \ \text{KJ} [mol] \\ \text{two haves twe neaction is men-spentaneous} = 5.0 \\ \text{for spentanisty} \quad \Delta H - T\Delta S < 0 \\ T > \Delta H \\ \Delta S \Rightarrow T > 618.6 \ \text{K} \end{aligned}$$

$$\begin{aligned} \textbf{(3)} \ 3H_{2}(\textbf{g}) + \text{Fe}_{2}\textbf{O}_{3}(\textbf{s}) &= 2\text{Fecs} + 3H_{2}\textbf{O}(\textbf{g}) \\ \Delta H^{\circ}_{MR} = (2144 (\text{Fe}) + 3\ \Delta H_{H_{2}0}) - (2044H_{H_{2}0}) + \Delta H_{4} \ R_{2}0_{3}) \\ &= 2(0) + 3(-2418 \ \text{KJ} [mol]) - (0)3 + (-322.1 \ \text{KJ} [mol]) \\ &= [96.7 \ \text{KJ} [mol] \\ \Delta S_{0RM} = 2(0) + 3(-228.59 \ \text{J} [Kmol]) - (0) + (-741.3 \ \text{J} [Kmol]) \\ \Delta S_{0RM} = 2(20.1 + 3(198.83) - ((130.6)3 + (90.5) \\ &= 138.7 \ \text{J} [Kmol] \\ &= 0.(39 \ \text{KJ} / \text{Kmol} \\ &= 55.27 \ \text{KJ} [mol] = + \text{vs bases non-spontaneous} \\ T > \Delta M = 96.7 \\ &= 0.(39 \ \text{KJ} / \text{Kmol} \\ \Delta S_{0RM} = 2(-46.1) - (0 + 3(0)) = -92.2 \ \text{KJ} [mol] \\ \Delta H^{\circ}_{0RM} = 2(-46.1) - (0 + 3(0)) = -92.2 \ \text{KJ} [mol] \\ \Delta H^{\circ}_{0RM} = 2(-46.1) - (0 + 3(0)) = -92.2 \ \text{KJ} [mol] \\ \Delta S_{0RM} = 2(-92.2 + 298 (0.199) = -32.9 \ \text{KJ} [mol] \\ = -92.2 \ \text{KJ} [mol] \\ \Delta S_{0RM} = 2(-92.2 + 298 (0.199) = -32.9 \ \text{KJ} [mol] \\ = -92.2 \ \text{KJ} [mol] \\ \Delta S_{0RM} = 2 \ \text{KJ} [mol] \\ \Delta S_{0RM} = 2 \ \text{KJ} [mol] = -32.9 \ \text{KJ} [mol] \\ = -92.2 \ \text{KJ} [mol] \\ = -92.9 \ \text$$

9) Consider the reaction: 2 NO(g) +  $O_2(g) \rightarrow 2 NO_2(g)$ 

Estimate  $\Delta G^{\circ}$  for this reaction at each temperature and predict whether the reaction is spontaneous. (Assume that  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  do not change too much within the given temperature range.) (Tro 2nd Ed, Ch 18, #65)

- a) 298 K
- b) 715 K
- c) 855 K
- 10) Determine  $\Delta G^{\circ}$  for the reaction: Fe<sub>2</sub>O<sub>3</sub> (s) + 3 CO(g)  $\rightarrow$  2 Fe(s) + 3 CO (g)

Use the following reactions with known  $\Delta G^{\circ}rxn$  values: (Tro 2nd Ed, Ch 18, #67)

$$2 \operatorname{Fe}(s) + \frac{3}{2} \operatorname{O}_2(g) \longrightarrow \operatorname{Fe}_2 \operatorname{O}_3(s) \quad \Delta G^{\circ}_{\operatorname{rxn}} = -742.2 \text{ kJ}$$
$$\operatorname{CO}(g) + \frac{1}{2} \operatorname{O}_2(g) \longrightarrow \operatorname{CO}_2(g) \quad \Delta G^{\circ}_{\operatorname{rxn}} = -257.2 \text{ kJ}$$

(Eq. 1) I reat first Equation: Fe, 0, (s) -> 3/202(1) + 2 Fe (s) Multiply original DGran by -2: △6°1×2 = -742.2 ×3 · -2 = 742.2 +3 (Eq 2) Multiply Second Equation by 3  $30(g) + \frac{3}{2}o_{2}(g) \longrightarrow 300_{2}(g)$ Multiply Orginal Dorxn by 3 66°r×n = -257.2 kJ × 3 = - 771.6 kJ

$$\frac{lombinz}{londow} := Fe_2 O_2(s) \longrightarrow \frac{3}{2} O_2^{(q)} + 2Fe(s) = 742.2 \cdot \pi 3$$

$$\frac{300(q) + \frac{3}{2} O_2(q) \longrightarrow 300_2(q) - 771.6 \times 3}{Fe_2 O_3(s) + 300(q) \longrightarrow 2Fe(s) + 300(q)}$$

$$\frac{Add}{dp} \quad up \quad New \quad b \in 3 \times 3$$

$$\frac{142.2 \times 3}{142.2 \times 3} \times \frac{142.2 \times 3}{142.2 \times 3} \times \frac{142.2 \times 3}{142.2 \times 3}$$

11) Fill in the blanks in the table below (both  $\Delta$ H and  $\Delta$ S refer to the system). (Tro 2nd Ed, Ch 18, #47)

ΔH	Δ <i>S</i>	ΔG	Low Temperature	High Temperature
-	+	_	Spontaneous	
_	-	Temperature dependent		
+	+			Spontaneous
	-		Nonspontaneous	Nonspontaneous

## ANSWER:

ΔH	ΔS	-T∆S	∆G	Spontaneity	
+	-	+	+	Nonspontaneous	
-	+	-	-	Spontaneous	
-	-	+	+ or -	Low Temp: Spontaneous	
				High Temp: Nonspontaneous	
+	+	-	+ or -	Low Temp: Nonspontaneous	
				High Temp: Spontaneous	

12) We submerge a 32.5-g iron rod, initially at 22.7 C, into an unknown mass of water at 63.2 C, in an insulated container. The final temperature of the mixture upon reaching thermal equilibrium is 59.5 C. What is the mass of the water?

When starting off these problems, it is important to identify which substance is losing heat and which substance is gaining heat. The substance that gains heat (rise in temperature) will be the one that is on the side of the equation that does not have the negative sign (left side). The iron here is gaining heat because it starts off at 22.7 deg celsius and goes to 59.6 deg celsius. The water here is on the right side with the negative sign because it LOST heat (63.2 deg celsius to 59.5 degrees celsius).

12	Tron (g 0 L hé m CST =	at water	(loss) heat			
2	Iron m = 32.5g $C = 0.451 T/g^{\circ}$ $T_f = 59.5^{\circ}$	$ \begin{array}{c}     \text{Water } & & \\                                $	(32.5g) (0.45	$1\frac{1}{9}$ (59.5-	22.7°E) <u>-</u> -(m) -2g	(4.186 <sup>J</sup> .c.)(85-82)

13) We submerge a 2.85-g lead weight, initially at 10.3 C, in 7.55 g of water at 52.3 C in an insulated container. What is the final temperature of both substances at thermal equilibrium?



14) A 2.74-g sample of a substance suspected of being pure gold is warmed to 72.1 C and submerged into 15.2 g of water initially at 24.7 C. The final temperature of the mixture is 26.3 C. What is the heat capacity of the unknown substance? Could the substance be pure gold?



15) How much heat (in kJ) is required to warm 10.0 g of ice, initially at -10.0°C, to steam at 110.0 C? The heat capacity of ice is 2.09 J/g°C, and that of steam is 1.996 J/g°C.



16) How much heat (in kJ) is evolved in converting 1.00 mol of steam at 145°C to ice at -50°C? The heat capacity of steam is 2.01 J/g°C, and that of ice is 2.09 J/g°C The process for this will be essentially the same as the above except now you are starting in the gas state. Also remember to convert the mols to grams for the temperature change equation. In this case it will just be 1.00 mol = 18.02 grams water. The only thing to change is putting a negative sign in front of the enthalpy of fusion and vaporization equations because now we are losing heat not gaining.



## FEEDBACK FORM:

