Spontaneity and Free Energy DCI

Name _____	Section _____

1. Summarize the signs (+ or –) of ΔH°_{rxn} and ΔS°_{rxn} for each of the following reactions (refer to the previous DCI activities on page 91 and 95).

a) $H_2O(l) \rightarrow H_2O(g)$ at 25 °C	**+ΔH**	**[+ΔS°]**	**+ΔG°**
b) $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$	**[–ΔH°]**	**–ΔS**	**–ΔG°**
c) $Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(aq) + 2NH_3(g) + 10H_2O(l)$	**+ΔH**	**[+ΔS°]**	**–ΔG°**
d) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ or (g)	**[–ΔH°]**	**–ΔS**	**–ΔG°**
e) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$	**[–ΔH°]**	**–ΔS**	**–ΔG°**
f) $Al(s) + \frac{3}{2} Br_2(l) \rightarrow AlBr_3(s)$	**[–ΔH°]**	**–ΔS**	**–ΔG°**

2. Circle which driving forces account for the spontaneity of each of the previous reactions

   The driving force has a box around it in Q1.

3. In which reactions do the driving forces oppose each other?

   Reaction a), b) c), d), e) and f)

4. The net driving force for a chemical reaction is called the free energy (ΔG°_{rxn}) for the reaction. It is the energy that is free to drive the reaction rather than oppose another driving force. It can be calculated from free energies of formation (ΔG°_f) in the same way as enthalpies of formation. Calculate (ΔG°_{rxn}) for the reactions in Q1.
   a) $H_2O(l) \rightarrow H_2O(g)$

   $\Delta G^\circ_{rxn} = \Sigma m \Delta G^\circ_f$(products)- $\Sigma n \Delta G^\circ_f$(reactants)
   $\Delta G^\circ_{rxn} = \Delta G^\circ_f(H_2O(g)) - \Delta G^\circ_f(H_2O(l))$
   $\Delta G^\circ_{rxn} = -229\ kJ\ mol^{-1} - (-237\ kJ\ mol^{-1}) = +8\ kJ\ mol^{-1}$

b) $2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$

$\mathbf{\Delta G^\circ_{rxn} = \Sigma m\Delta G^\circ_f(products) - \Sigma n\Delta G^\circ_f(reactants)}$

$\mathbf{\Delta G^\circ_{rxn} = 2\Delta G^\circ_f(MgO_{(s)}) - [2\Delta G^\circ_f(Mg_{(s)}) + \Delta G^\circ_f(O_{2(g)})]}$

$\mathbf{\Delta G^\circ_{rxn} = 2 \cdot -569\ kJ\ mol^{-1} - [2 \cdot 0\ kJ\ mol^{-1} + 0\ kJ\ mol^{-1}] = -1038\ kJ\ mol^{-1}}$

c) $Ba(OH)_2 \cdot 8H_2O_{(s)} + 2NH_4Cl_{(s)} \rightarrow BaCl_{2(aq)} + 2NH_{3(g)} + 10H_2O_{(l)}$

$\mathbf{\Delta G^\circ_{rxn} = \Sigma m\Delta G^\circ_f(products) - \Sigma n\Delta G^\circ_f(reactants)}$

$\mathbf{\Delta G^\circ_{rxn} = [\Delta G^\circ_f(BaCl_{2(aq)}) + 2\Delta G^\circ_f(NH_{3(g)}) + 10\Delta G^\circ_f(H_2O_{(l)})] - [\Delta G^\circ_f(Ba(OH)_2 \cdot 8H_2O_{(s)}) - 2\Delta G^\circ_f(NH_4Cl_{(g)})]}$

$\mathbf{\Delta G^\circ_{rxn} = -823\ kJ\ mol^{-1} + 2 \cdot -17\ kJ\ mol^{-1} + 10 \cdot -237\ kJ\ mol^{-1} - [-2793\ kJ\ mol^{-1} + 2 \cdot -201\ kJ\ mol^{-1}] = -32\ kJ\ mol^{-1}}$

d) $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$

$\mathbf{\Delta G^\circ_{rxn} = \Sigma(mS^\circ(products)) - \Sigma(nS^\circ(reactants))}$

$\mathbf{\Delta G^\circ_{rxn} = -237\ kJ\ mol^{-1}}$

e) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

$\mathbf{\Delta G^\circ_{rxn} = \Sigma(mS^\circ(products)) - \Sigma(nS^\circ(reactants))}$

$\mathbf{\Delta G^\circ_{rxn} = -817\ kJ\ mol^{-1}}$

f) $Al_{(s)} + \frac{3}{2} Br_{2(l)} \rightarrow AlBr_{3(s)}$

$\mathbf{\Delta G^\circ_{rxn} = \Sigma(mS^\circ(products)) - \Sigma(nS^\circ(reactants))}$

$\mathbf{\Delta G^\circ_{rxn} = -505\ kJ\ mol^{-1}}$

5. Another way to calculate the free energy is to combine the two driving forces of enthalpy and entropy to recognize contribution of each to compensate for any way the oppose each other. The equation for doing this (called the Gibbs free energy equation) is: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Calculate the free energy of the equations in Question 1 using this equation, and compare your results with the values you determined from free energies of formation.

a) $H_2O_{(l)} \rightarrow H_2O_{(g)}$

$\mathbf{\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}}$

$\mathbf{\Delta G^\circ_{rxn} = \Delta G^\circ_f (H_2O_{(g)}) - \Delta G^\circ_f (H_2O_{(l)})}$

$\mathbf{\Delta G^\circ_{rxn} = -229\ kJ\ mol^{-1} - (-237\ kJ\ mol^{-1}) = +8\ kJ\ mol^{-1}}$

b) $2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$

$\mathbf{\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}}$

$\mathbf{\Delta G^\circ_{rxn} = 2\Delta G^\circ_f (MgO_{(s)}) - [2\Delta G^\circ_f (Mg_{(s)}) + \Delta G^\circ_f (O_{2(g)})]}$

$\mathbf{\Delta G^\circ_{rxn} = 2 \cdot -569\ kJ\ mol^{-1} - [2 \cdot 0\ kJ\ mol^{-1} + 0\ kJ\ mol^{-1}] = -1038\ kJ\ mol^{-1}}$

c) $Ba(OH)_2 \cdot 8H_2O_{(s)} + 2NH_4Cl_{(s)} \rightarrow BaCl_{2(aq)} + 2NH_{3(g)} + 10H_2O_{(l)}$

$\mathbf{\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}}$

$\mathbf{\Delta G^\circ_{rxn} = [\Delta G^\circ_f (BaCl_{2(aq)}) + 2\Delta G^\circ_f (NH_{3(g)}) + 10\Delta G^\circ_f (H_2O_{(l)})] - [\Delta G^\circ_f (Ba(OH)_2 \cdot 8H_2O_{(s)}) - 2\Delta G^\circ_f (NH_4Cl_{(g)})]}$

$\mathbf{\Delta G^\circ_{rxn} = -823\ kJ\ mol^{-1} + 2 \cdot -17\ kJ\ mol^{-1} + 10 \cdot -237\ kJ\ mol^{-1} - [-2793\ kJ\ mol^{-1} + 2 \cdot -201\ kJ\ mol^{-1}] = -32\ kJ\ mol^{-1}}$

d) $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$

$\mathbf{\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}}$

$\mathbf{\Delta G^\circ_{rxn} = -237\ kJ\ mol^{-1}}$

e) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

$\mathbf{\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}}$

$\mathbf{\Delta G^\circ_{rxn} = -817\ kJ\ mol^{-1}}$

f) $Al_{(s)} + \frac{3}{2} Br_{2(l)} \rightarrow AlBr_{3(s)}$

$\mathbf{\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}}$

$\mathbf{\Delta G^\circ_{rxn} = -505\ kJ\ mol^{-1}}$

6. Use your data from question 1 to complete the blank cells for DG˚ rxn when the driving forces drive in the same direction. What does the sign for DG˚ rxn signify for the spontaneity of the reaction?

Sign of ΔH°_{rxn} (25 ˚C)	Sign of ΔS°_{rxn} (25 ˚C)	Sign of ΔG°_{rxn} (25 ˚C)	Sign of ΔG°_{rxn} at high T	Sign of ΔG°_{rxn} at low T
–	+	–	–	–
+	–	+	+	+
–	–	**– or +**	+	–
+	+	**+ or –**	–	+

7. Predict whether the entropy of the system increases, remains constant or decreases when the following processes occur. Explain your reasoning.

a. Ice melts at 0 ˚C.
$H_2O_{(s)} \rightarrow H_2O_{(l)}$ Since the products are more random compared to the reactant, because a liquid phase is more random compared to a solid phase, the phase change leads to greater randomness and ΔS is positive.

b. A precipitate forms in aqueous solution.
$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$ The products are less random compared to the reactant, because a solid phase is less random compared to ions dissolved and distributed in water, a precipitation leads to lower randomness and ΔS is negative.

c. A solid dissolves in water.
$C_6H_{12}O_{6(s)} \rightarrow C_6H_{12}O_{6(aq)}$ When a solid dissolves in water the substance is distributed through out the solution so there is much greater randomness when the solid has dissolved compared to the solid phase where particles can not move.

d. A gas condenses to a liquid.
$N_{2(g)} \rightarrow N_{2(l)}$ The products are less random compared to the reactant, because a liquid phase is less random compared to the gas phase, the phase change leads to lower randomness and ΔS is negative.

Substance and State	ΔH_f° (kJ/mol)	Substance and State	ΔH_f° (kJ/mol)
C(*s*) (graphite)	0	HCl(*g*)	-92.3
C(*s*) (diamond)	2	HBr(*g*)	-36.4
CO(*g*)	-110.5	HI(*g*)	26.5
CO_2(*g*)	–393.5	$I_{2(g)}$	62.25
CH_4(*g*)	–75	O_2(*g*)	0
CH_3OH(*g*)	-201	O(*g*)	249
CH_3OH(*l*)	-239	O_3(*g*)	143
H_2CO(*g*)	-116		
CCl_4(*l*)	-135.4	N_2(*g*)	0
HCOOH(*g*)	-363	NH_3(*g*)	-46
HCN(*g*)	135.1	$NH_{3(aq)}$	-80
CS_2(*g*)	117.4	NH_4^+*(aq)*	-132
CS_2(*l*)	89.7	NH_4Cl(*s*)	-314.4
C_2H_2(*g*)	227	$N_2H_{4(l)}$	50.6
C_2H_4(*g*)	52	NO(*g*)	90.25
CH_3CHO(*g*)	-166	NO_2(*g*)	33.18
C_2H_5OH(*l*)	-278	N_2O(*g*)	82.0
$C_2H_5O_2N_{(g)}$	-533	N_2O_4(*g*)	9.16
C_2H_6(*g*)	-84.7	N_2O_4(*l*)	20
C_3H_6(*g*)	20.9	HNO_3(*aq*)	-207.36
C_3H_8(*g*)	-104	HNO_3(*l*)	-174.10
C_4H_{10}(*g*)	-126	NH_4ClO_4(*s*)	-295
C_8H_{18}(*l*)	-208		
$CH_2 = CHCN$(*l*)	152		
CH_3COOH(*l*)	-484	$S_2Cl_{2(g)}$	-18
$C_6H_{12}O_6$(*s*)	-1275	$SO_{2(g)}$	-296.83
		$H_2S_{(g)}$	-20.6
Cl_2(*g*)	0	$SOCl_{2(g)}$	-213
Cl_2(*aq*)	-23		
Cl^-(*aq*)	-167.5	$SiCl_{4(g)}$	-657
		$SiO_{2(s)}$	-910.94
		$SiF_{4(g)}$	-1614.9
$H_{2(g)}$	0		
$H_{(g)}$	217	$Ba(OH)_2 \cdot 8H_2O$(*s*)	-3342
H^+(*aq*)	0	$BaCl_{2(aq)}$	-872
$OH^-_{(aq)}$	-230	$AlBr_{3(s)}$	-526
$H_2O_{(l)}$	-286		
$H_2O_{(g)}$	-242	ZnS(*s*)	-206