Taking another look at Enthalpy vs. Entropy

1) Tell whether each of the following chemical reactions is endothermic or exothermic and state whether the reactants or the products are favoured by minimum enthalpy.
YOU MUST BALANCE THE EQUATIONS YOURSELF!!!!

a) $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g) \qquad \Delta H = 92.5\ kJ$

Endothermic
Reactants have the minimum enthalpy

b) $Cl_2\ (g) \rightleftharpoons Cl_2\ (aq) \qquad \Delta H = -25\ kJ$

Exothermic
Products have the minimum enthalpy

c) $2NH_3\ (g) + 92.4\ kJ \rightleftharpoons N_2\ (g) + 3H_2\ (g)$

Endothermic
Minimum enthalpy favours reactants

d) $CO\ (g) + 3H_2\ (g) \rightleftharpoons CH_4\ (g) + H_2O\ (g) + 49.3\ kJ$

Exothermic
Minimum enthalpy favours products

2) For each of the above reactions, state whether enthalpy is increasing or decreasing ***in the forward direction***, and if this is favourable.

a) Enthalpy increases to the right. This IS NOT favourable.
b) Enthalpy DEcreases to the right. This IS favourable.
c) Enthalpy increases to the right. This IS NOT favourable.
d) Enthalpy DEcreases to the right. This IS favourable.

3) Tell whether reactants or products show maximum entropy. Give as many reasons as apply, to justify your choice.

YOU MUST BALANCE THE EQUATIONS YOURSELF!!!!

a) $I_2\,(s) \rightleftharpoons I_2\,(aq)$

Product has greater entropy.
(aq vs. s: dissolved ions have more entropy than solids)

b) $2NH_3\,(g) \rightleftharpoons N_2\,(g) + 3H_2\,(g)$

Products have greater entropy.
(There are more moles of gas in the products (4 moles total)
vs. only 2 moles of gas in the reactants.
Also the products have more variety of molecules.)

c) $NH_3\,(g) \rightleftharpoons NH_3\,(aq)$

Reactant has greater entropy.
(g vs aq : gas particles are much farther apart, and moving faster,
than aqueous particles – molecules dissolved in a water solution)

d) $CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g)$

Reactants have greater entropy.
(2 moles of gas on left side vs. 1 mole of gas in products on the right side,
more variety of molecules in reactants)

e) $MgCO_3\,(s) + 2HCl\,(aq) \rightleftharpoons MgCl_2\,(aq) + H_2O\,(l) + CO_2\,(g)$

Products have greater entropy.
(Moles are EQUAL on both sides, so you can NOT use the reason
that there are more moles.
But there is more VARIETY of molecules.
Also there are more random phases
on the products side: aq, liq and g **vs.** sol and aq)

4) Based on your answers to #3, if all of those 5 reactions are to be in DYNAMIC EQUILIBRIUM (also called CHEMICAL EQUILIBRIUM), ***meaning that they are reversible,*** then state whether the reaction must be endothermic or exothermic to facilitate the reversibility of the reaction. Remember that the drive for enthalpy and entropy must oppose each other for a reversible reaction.

Also, add a sentence justifying why this would make sense.
(Why would the energy have to be on **this** side of the reaction for it to occur?)

a) I_2 (s) **+ kJ** $\rightleftharpoons$ I_2 (aq)

Since products have greater entropy, then this reaction must be ENDOTHERMIC to achieve reversibility.
That is, Enthalpy must favour the reactants and Entropy would favour the products.
This makes senses because if you add energy to a solid, it will help it dissolve in aqueous solution.

b) $2NH_3$ (g) **+ kJ** $\rightleftharpoons$ N_2 (g) + $3H_2$ (g)

Since the Products have greater entropy, then this reaction must be ENDOTHERMIC to achieve reversibility.
That is, Enthalpy must favour the reactants and Entropy would favour the products.
This makes sense, since you have to add energy for a decomposition reaction to occur.

c) NH_3 (g) $\rightleftharpoons$ NH_3 (aq) **+ kJ**

Since the Reactant has greater entropy, the energy term would have to be on the products side, for this reaction to be reversible.
This makes sense because gases are faster moving particles, so heating the aqueous ammonia would increase the kinetic energy of the particles and make them move faster, eventually allowing some of the molecules to escape into the gas phase.

d) CO (g) + Cl_2 (g) $\rightleftharpoons$ $COCl_2$ (g) **+ kJ**

Since the Reactants have greater entropy, the energy term would have to be on the products side, for this reaction to be reversible.
This makes sense because essentially this would be a decomposition reaction if you read it in reverse.

QUESTION 4 continued

e) $MgCO_3\,(s) + 2HCl\,(aq) + \mathbf{kJ} \rightleftharpoons MgCl_2\,(aq) + H_2O\,(l) + CO_2\,(g)$

Since the Products have greater entropy, this would have to be an endothermic reaction in order for this reaction to be reversible.

Let's be honest here…
If I added a "chalky" substance like magnesium carbonate to hydrochloric acid, AND heated it, to produce an aqueous solution of magnesium chloride, and water and carbonated (CO_2 gas) bubbles, is it likely that it WOULD go in reverse?

So…foreshadowing to future questions in Unit 2, you will be ASKED **if** reversibliy is feasible when looking at a reaction.

BUT For now, assume the questions we will be dealing with in the next week will STATE that they ARE reversible and you would need to justify WHY by stating which side favours minimum H and which side has maximum S.

So let's leave this reaction for future consideration.

But some of you would be ready to justify (or even argue vehemently) why this reaction is "*100% spontaneous to the right…*"

5) For each of the following reactions, decide:

- which has minimum enthalpy (reactants or products) **Give a reason to justify WHY.**
- and which has maximum entropy (reactants or products**) Give a reason to justify WHY.**

You may assume that every reaction listed BELOW is DEFINITELY reversible, and that all reactions occur in a CLOSED SYSTEM (the container has a secure lid / stopper on it).

YOU MUST BALANCE THE EQUATIONS YOURSELF!!!!

a) $PCl_3\,(g) + Cl_2\,(g) \rightleftharpoons PCl_5\,(g) \quad \Delta H = -92.5\ kJ$

Reactants have Maximum entropy (more moles, more variety)

products have minimum enthalpy
Exothermic reactions prefer the products side (the forward direction of the reaction) since this is the side with the lowest potential energy

QUESTION 5 continued

b) $2NO_2\ (g) \rightleftharpoons N_2O_4\ (g) + kJ$

Reactants have Maximum entropy (more moles)

products have minimum enthalpy Exothermic reaction

c) $2PbO\ (s) + 4\ NO_2\ (g) + O_2\ (g) \rightleftharpoons 2Pb(NO_3)_2\ (s) \quad \Delta H = -597\ kJ$

Reactants have Maximum entropy (more moles more variety, more phases)

product has minimum enthalpy Exothermic reaction

d) $HCl\ (g) + kJ \rightleftharpoons H^+\ (aq) + Cl^+\ (aq)$

Reactants have minimum enthalpy ENDOTHERMIC REACTIONS prefer the reactants side, as the lowest Potential Energy would be on the left side. Endothermic reactions favour the reverse reaction.

Products have maximum enthalpy (Aqueous ions have a more random arrangement since the ions are so reactive; also more moles on products side)

Note that this reaction is HCl gas DISSOLVING into an aqueous solution, with the addition of heat. Interesting….

e) $Na_2CO_3\ (s) + 2HCl\ (aq) \rightleftharpoons 2NaCl\ (aq) + CO_2\ (g) + H_2O\ (l) + 27.7\ kJ$

I have no choice but to state that the Reactants have Maximum entropy ***… since the*** Products have minimum enthalpy Exothermic reaction

And they are indicating that this is a reversible reaction.

The only way I can justify that the reactants side has more entropy is that:
The SECOND LAW OF THERMODYNAMICS states that the ENDOTHERMIC DIRECTION would see an increase in entropy as the energy inputted would increase the randomness / chaos of the system as we proceed in the endothermic direction (that is, starting on the right and proceeding to the left; aka the reverse direction).

We might want to argue whether entropy and enthalpy WOULD in fact oppose each other in this chemical reaction….but for now, we will operate under the constraints of the question, which dictates to me that I must justify WHY enthalpy and entropy would oppose each other in this reaction.

(Your preliminary questions / quizzes / assignments in Unit 2 will ask you to justify WHY a given reaction is reversible. Later in Unit 2 you would be asked to predict, based on entropy and enthalpy IF you think a given reaction is reversible).