Question

At what temperature is the following process spontaneous at 1 atm (not a number, words. What do we call this temperature)?

$Br_2(l) \rightarrow Br_2(g)$

Any temperature above the boiling point, this process becomes spontaneous. Therefore, ΔG must be negative above the boiling point.

Any temperature below the boiling point ΔG is positive, and the reverse will occur (condensation).

If you are at the boiling point, ΔG is zero.

Problem

$Br_2(l) \rightarrow Br_2(g)$

ΔH^o = 31.0 kJ/mol, and ΔS^o = 93.0 J/K*mol

Determine what is the normal boiling point of liquid Br_2? Set ΔG =0

Unit agreement!!!!!

Enthalpy is in **kilojoules**/mole, entropy is in **joules**/mole kelvin

Review

- ΔS_{univ} is positive for all spontaneous processes. 2nd Law of Thermodynamics.
- This is impractical to chemistry, **don't use it**

- ΔG is the free energy change of the system.
- This is much more practical to chemists.
- ΔG is NEGATIVE when ΔS_{univ} is positive.
- ΔG represents the usable work done by a system.
- $\Delta G^o = \Delta H^o - T\Delta S^o$

Standard Values

- In thermodynamics, the change in a certain function is usually what is important.
- Absolute values for H and G cannot be determined.
- The standard used is the formation reaction of the compound from it elements at standard conditions.
- So the reaction for water is $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
- ΔG^o_f and ΔH^o_f for any element is always 0!
- For a reaction the values of ΔH^o and ΔG^o are:
- $\Delta H^o = \Sigma \Delta H^o_f$ (products) - $\Sigma \Delta H^o_f$ (reactants)
- $\Delta G^o = \Sigma \Delta G^o_f$ (products) - $\Sigma \Delta G^o_f$ (reactants)

Standard Molar Entropies, S°

- From the **third law of thermodynamics** we find that at 0 K, the entropy of a pure crystal is 0.
- Since this provides a starting point to compare all other entropies, an absolute entropy scale has meaning.
- *Standard molar entropy, S°,* is the entropy of one mole of a substance in its standard state.
- The degree symbol means at standard state which is 25° C and 1.0 atm, 1 M concentration.
- The standard molar entropy is the change in entropy from 0 K to 298 K

Entropy Changes in Chemical Reactions.

- Predicting Relative S° Values of the System.
- Temperature changes.
- For a given substance, S° increases as the temperature increase.
- Physical states and phase changes.
- For a given substance, S° increases as the substance changes from a solid to a liquid to a gas (the change from a liquid to a gas is MUCH greater than from a solid to a liquid).

Dissolution

- Dissolving a solid or liquid solute in a liquid solvent always increases the entropy of mixture.
- The type of solute and solvent and the nature of the solution process affects the overall entropy change.
- Dissolving a gas in a liquid or solid, conversely, decreases the entropy!

Complexity

- In general, difference in entropy values for substances in the same phase are based on atomic size and molecular complexity.
- For elements, those with higher molar masses have higher entropy.
- For compounds, the chemical complexity increases as the number of atoms (ions) in a compound increases, and so does the entropy.
- The phrasing AP likes best is larger molecules have "MORE POLARIZABLE ELECTRON CLOUDS".

Entropy Changes in Chemical Reactions.

- Predicting the Sign of ΔS^o.
- Predict the sign of ΔS^o for each of the following reactions.
- The thermal decomposition of solid calcium carbonate:
- $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

- The oxidation of SO_2 in air:
- $2 SO_2(g) + O_2(g) \rightarrow 2 SO_3(g)$

Predicting Relative Entropy Values

- Choose the member with the higher entropy in each of the following pairs, and justify your choice.
  - 1 mol $SO_2(g)$ or 1 mol $SO_3(g)$
  - 1 mol $CO_2(s)$ or 1 mol $CO_2(g)$
  - 2 mol $O_2(g)$ or 2 mol $O_3(g)$
  - 1 mol $KBr(s)$ or 1 mol $KBr(aq)$
  - Sea water in winter at 2 ºC or in summer at 23 ºC
  - 1 mol $HF(g)$ or 1 mol $HI(g)$

Entropy Changes in Chemical Reactions.

- Because entropy is a state function, the property is what it is regardless of pathway, the entropy change for a given reaction can be calculated by taking the difference between the *standard entropy* values of products and those of the reactants.
- $\Delta S^o_{reaction} = \Sigma n_p \Delta S^o_{products} - \Sigma n_r \Delta S^o_{reactants}$

Entropy Changes in Chemical Reactions.

- Calculating ΔS^o.
- Calculate ΔS^o at 25º C for the reaction
  $2NiS(s) + 3O_2(g) \rightarrow 2SO_2(g) + 2NiO(s)$

Substance	S^o (J/K · mol)
$SO_2(g)$	248
$NiO(s)$	38
$O_2(g)$	205
$NiS(s)$	53

Entropy Changes II

Calculate ΔS^o for the reaction of aluminum oxide by hydrogen gas:

$Al_2O_3(s) + 3H_2(g) \rightarrow 2Al(s) + 3H_2O(g)$

Substance	S^o (J/K · mol)
$Al_2O_3(s)$	51
$H_2(g)$	131
$Al(s)$	28
$H_2O(g)$	189

Free Energy and Chemical Reactions

- *Standard free energy (ΔG^o)* is the change in the free energy that will occur if the reactants in their standard states are converted to the products in their standard states.
- The value of ΔG^o tells **nothing** about the **rate of a reaction**, only its eventual equilibrium position.
- Kinetics tells us how fast it will happen. Thermodynamics tells us if it will happen.

Free Energy and Chemical Reactions

- Calculating ΔG^o as a State Function.
- $\Delta G^o = \Delta H^o - T\Delta S^o$
- Consider the reaction

  $2 SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

- carried out at 25º C and 1 atm. Calculate ΔH^o and ΔS^o, then calculate ΔG^o.

Substance	ΔH^o_f (kJ/mol)	S^o (J/K · mol)
$SO_2(g)$	−297	248
$SO_3(g)$	−396	257
$O_2(g)$	0	205