#### Thermo Notes # 4 Entropy & the Free Energy

Friday, February 3 CHEM 102H T. Hughbanks

# Problem

- The "Mond Process" is used commercially to produce pure nickel. Ni(s) + 4 CO(g) → Ni(CO)<sub>4</sub>(g)
- First, try to <u>predict</u> the signs of  $\Delta S^{\circ}$  and  $\Delta H^{\circ}$ .
- Then use data on next slide to calculate values.

#### Data for Problem $Ni(s) + 4 CO(g) \rightarrow Ni(CO)_4(g)$ $\diamond \Delta S^{\circ}, \Delta H^{\circ} = ??$ $Ni(CO)_4(g)$ Ni(s) CO(g) $\Delta H_{f}^{\circ}$ 0 -602.9 -110.52 $S_{298}^{\circ}$ 29.87 197.56 410.6 $\Delta H_{\rm f}{}^{\rm o}$ in kJ mol-1, $S_{298}{}^{\rm o}$ in J K-1 mol-1. Watch units!



# Free Energy

- One more state function ....
- We know  $\Delta S_{universe} > 0$  for a spontaneous change, but  $\Delta S_{univ} = \Delta S_{(sys)} + \Delta S_{surr}$  and keeping track of the surroundings is inconvenient, to say the least.
- We are still looking for a state function of the *system* that will predict spontaneity.
- Define a new function that satisfies this need. Call it "free energy." (sometimes "Gibbs free energy")

#### Free Energy: Definition

- Define the free energy by:
   G = H TS
- ◆ G is a state function, since H, T, & S are. If <u>T</u> <u>& P are variables we control</u>, G is the function that predicts spontaneity.
- Consider a process that occurs at <u>constant</u> <u>temperature</u>.

 $\Delta G = \Delta H - T\Delta S$ 

 This is the central equation in chemical thermodynamics!







#### $\Delta G \ \mathcal{E} \ Spontaneity$

- ΔG is thus the function we have been seeking:
  - a state function of the system
  - sign tells us whether a process (reaction or phase change) is spontaneous
- ΔG is generally the most useful thermodynamic function for a chemist.

# $\Delta G$ - Change in Free Energy

- Predictor of spontaneity. A spontaneous reaction has  $\Delta G < 0$ .
- Also tells us the maximum amount of energy which can be produced and used to do work. So ΔG is useful in determining amounts of fuel needed, etc.
- We saw that when ΔS<sub>univ</sub> = 0, the system and surrounding are at <u>equilibrium</u>. Likewise, when ΔG = 0, the system is at <u>equilibrium</u> – a concept we will emphasize for the next several weeks!



## Spontaneity: Role of T

• ΔG tells us whether or not a reaction will occur spontaneously.

 $\Delta G = \Delta H - T \Delta S$ 

- Usually, we assume that  $\Delta H$  and  $\Delta S$  do not depend on T. This means that only the T $\Delta S$  term varies with T.
- Effect of temperature depends on signs.

Spontaneity: Role of $\Delta H$ , $\Delta S$ , T						
$\Delta H$	$\Delta S$					
	+	Always Spontaneous				
+	_	Never Spontaneous				
+	+	Spontaneous at sufficiently high T				
I	I	Spontaneous at sufficiently low T				
_	-	sufficiently low T				



### $\Delta G$ : Using Tabulated Data

- Thermodynamic tables (Appendix E) usually include  $\Delta G_{f}^{\circ}$  values.
- $\bullet$  These are defined and used just like  $\Delta H_{f}^{\,\,o's}.$ 
  - refer to formation reactions
    same standard state convention
- $\Delta G^{\circ}_{rxn} = \Sigma n \Delta G_{f}^{\circ}_{products} \Sigma n \Delta G_{f}^{\circ}_{reactants}$
- Can also use  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$  to find  $\Delta G^{\circ}$

#### Tabulated Data

- For N<sub>2</sub>(g):  $\Delta H_f^{\circ} = 0$ ,  $\Delta G_f^{\circ} = 0$ , S° = 191.61 J K<sup>-1</sup> mol<sup>-1</sup>
- Note that the data give S° and **NOT** $\Delta S_{f}^{\circ}$
- $\bullet$  Also, note that  $\Delta G_f^\circ\,$  IS  $\underline{NOT}$  EQUAL TO  $\Delta H_f^\circ T\,S^\circ$



# Mond Process Ni(s) + 4 CO(g) → Ni(CO)<sub>4</sub>(g) • $\Delta$ H° and $\Delta$ S° are both negative, so at low T the reaction is spontaneous.

 At high T, ΔG° becomes positive, so reaction proceeds spontaneously to the left. At high T, Ni(CO)<sub>4</sub> decomposes.

### \_\_\_\_\_

Mond Process

 $Ni(s) + 4 CO(g) \rightarrow Ni(CO)_4(g)$ 

- ◆ For Ni purification: First react impure Ni with pure CO to form Ni(CO)<sub>4</sub>. (This works only for Ni, other metals are not as reactive with CO.)
- ♦ Need "low" T for reaction to go to right. Run at 50°C. (T<sub>boil</sub> = 42°C for Ni(CO)<sub>4</sub>.)





## • Example (prob. 751): Use data in Appendix 2A to calculate $\Delta G^{\circ}$ for each of the following reactions under standard conditions (at 25 K): (a) $2 \operatorname{SO}_2(g) + \operatorname{O}_2(g) \rightarrow 2 \operatorname{SO}_3(g)$ (b) $2 \operatorname{CaCO}_3(s) \rightarrow \operatorname{CaO}(s) + \operatorname{CO}_2(g)$ (c) $2 \operatorname{C}_8 \operatorname{H}_{18}(l) + 25 \operatorname{O}_2(g) \rightarrow 16 \operatorname{CO}_2(g) + 18 \operatorname{H}_2 O(l)$

Data						
	$\Delta H_{\rm f}^{\circ}(\rm kJ/mol^{-1})$	$\Delta G_{\rm f}^{\circ}$ (kJ/mol <sup>-1</sup> )	S <sub>m</sub> ° (J/mol <sup>-1</sup> K <sup>-1</sup> )			
$SO_2(g)$	-296.83	-300.19	248.22			
$O_2(g)$			205.14			
$SO_3(g)$	-395.72	-371.06	256.76			
$CaCO_3(s)$	-1206.9	-1128.8	92.9			
CaO(s)	-635.09	-604.03	39.75			
$CO_2(g)$	-393.51	-394.36	213.74			
$H_2O(l)$	-285.83	-237.13	69.91			
$C_{e}H_{1e}(l)$	-249.9	+6.4	358			

 $\checkmark$ ΔH, ΔS, & ΔG vs. T

 The <u>most important</u> temp. dependence in ΔG can be seen directly: ΔG = ΔH - TΔS
 ΔH and ΔS actually do depend on T:

 $(\Delta X = X_{\text{final}}(T) - X_{\text{initial}}(T); X = H \text{ or } S)$ 

For infinitesimal changes for a single substance:

 $dH = C_P dT \quad ; \quad dS = \frac{dq}{T} = \frac{C_P dT}{T}$ 

# $\Delta H, \Delta S, \mathcal{E} \Delta G vs. T$

 ΔH and ΔS at temperatures other than 298 K can be obtained by integration, provided we know the heat capacities:

$$H(T) = \int_{298}^{T} C_P dT' \quad ; \quad S(T) = \int_{298}^{T} \frac{C_P dT'}{T'}$$

• We then account for the changes in H's and S's for all the substances in the "reactants" and "products" and plug into  $\Delta G = \Delta H - T\Delta S$ .