Ch. 18 Thermodynamics: Direction of Reactions

18.1 Product Favored Processes

ex

$2Na + Cl_2 \longrightarrow 2NaCl +$ heat

$H_2O(s) \longrightarrow H_2O(l)$ at 50°C

$gas + O_2 \longrightarrow CO_2 + H_2O +$ heat

$NaCl(s) \xrightarrow{water} NaCl(aq)$

Others
Drop something
Desk getting messy

Reactant Favored

$2H_2O \longrightarrow 2H_2 + O_2$

① Product-favored may be slow at room temp, but catalyst a spark can initiate so it proceeds on its own (activation barrier)

② Reactant-favored can proceed only if energy is continuously supplied from outside

③ most product-favored process are exothermic

18.2 Probability & Reaction

Facts

① exothermic processes usually product favored

② some processes are favored but not exo:

ΔH=0 { – expansion of gas into vacuum
– heat (energy) transfer hot → cold
– mix colored solns

endo – NaCl dissolve in water
– desk gets messy, chem knowledge disordered

Common: Increase in **disorder**

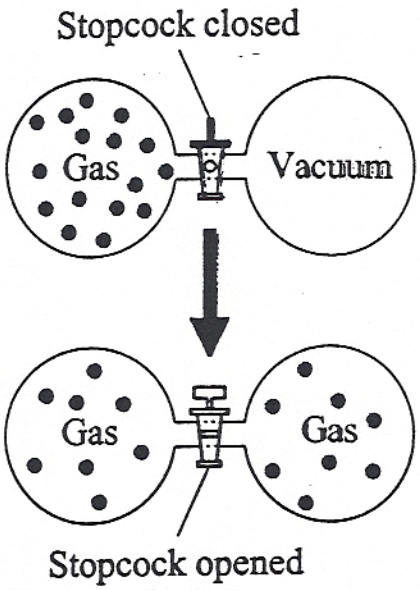
① Dispersal of energy
– exothermic process disperses energy to surroundings, favorable
– chemicals ⟶ surroundings
(small # particles) (large # particles)

– more probable for energy to be dispersed than concentrated in small # particles

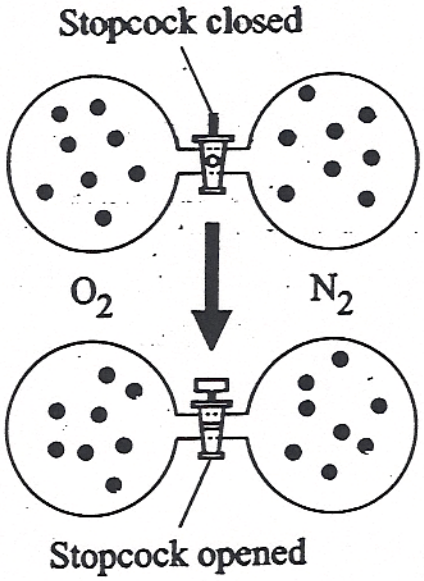
② Dispersal of matter
– concentrated matter tends to disperse (gases, dissolving ---)
– more probable for matter to be dispersed

If both energy & atoms are more dispersed ⇒ product favored
neither ⇒ reactants

T 64 Fig. 9.10 Spontaneous Processes



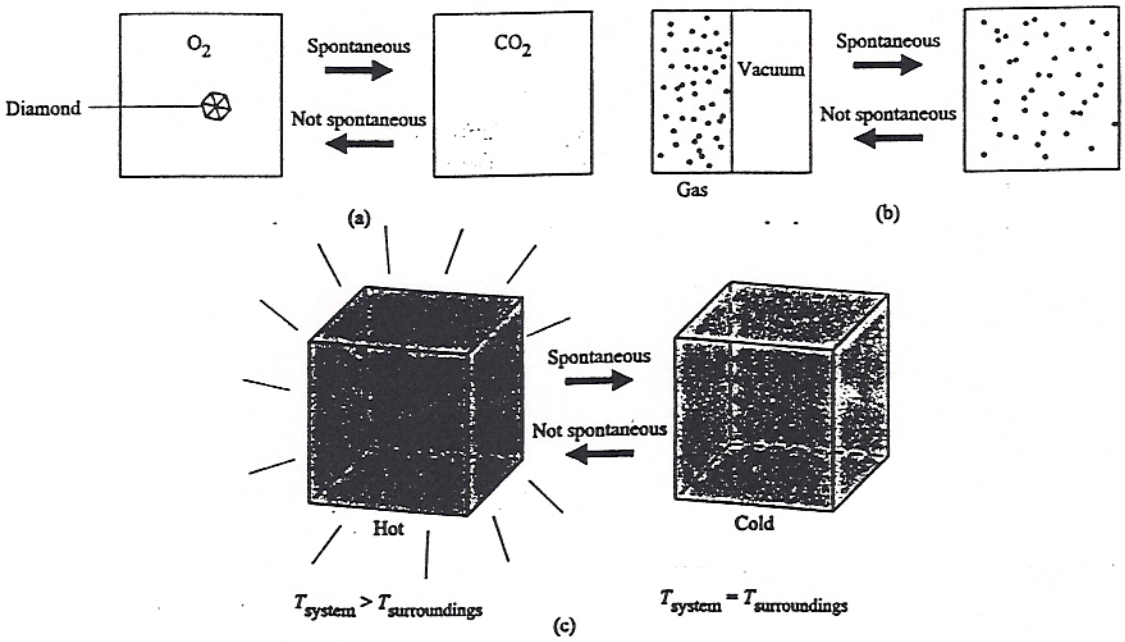
(a)



(b)

ATOMS MOLECULES
AND REACTIONS
Gillespie/Eaton/
Humphreys/Robinson

T 63 Fig. 9.9 Spontaneous and Nonspontaneous Processes



ATOMS MOLECULES
AND REACTIONS
Gillespie/Eaton/
Humphreys/Robinson

18.3 "Entropy" = S = Amount of Disorder
- each chemical has a finite "S" S° (Brown, T-150)

- factors in size, motion
  - more motion, more disorder
    - translational, rotational, vibrational motion

- higher S, higher entropy (+ movement)
- even elements have $S \neq 0$ (unlike ΔH_f°)
- standard: 25°C, 1 atm, per mole

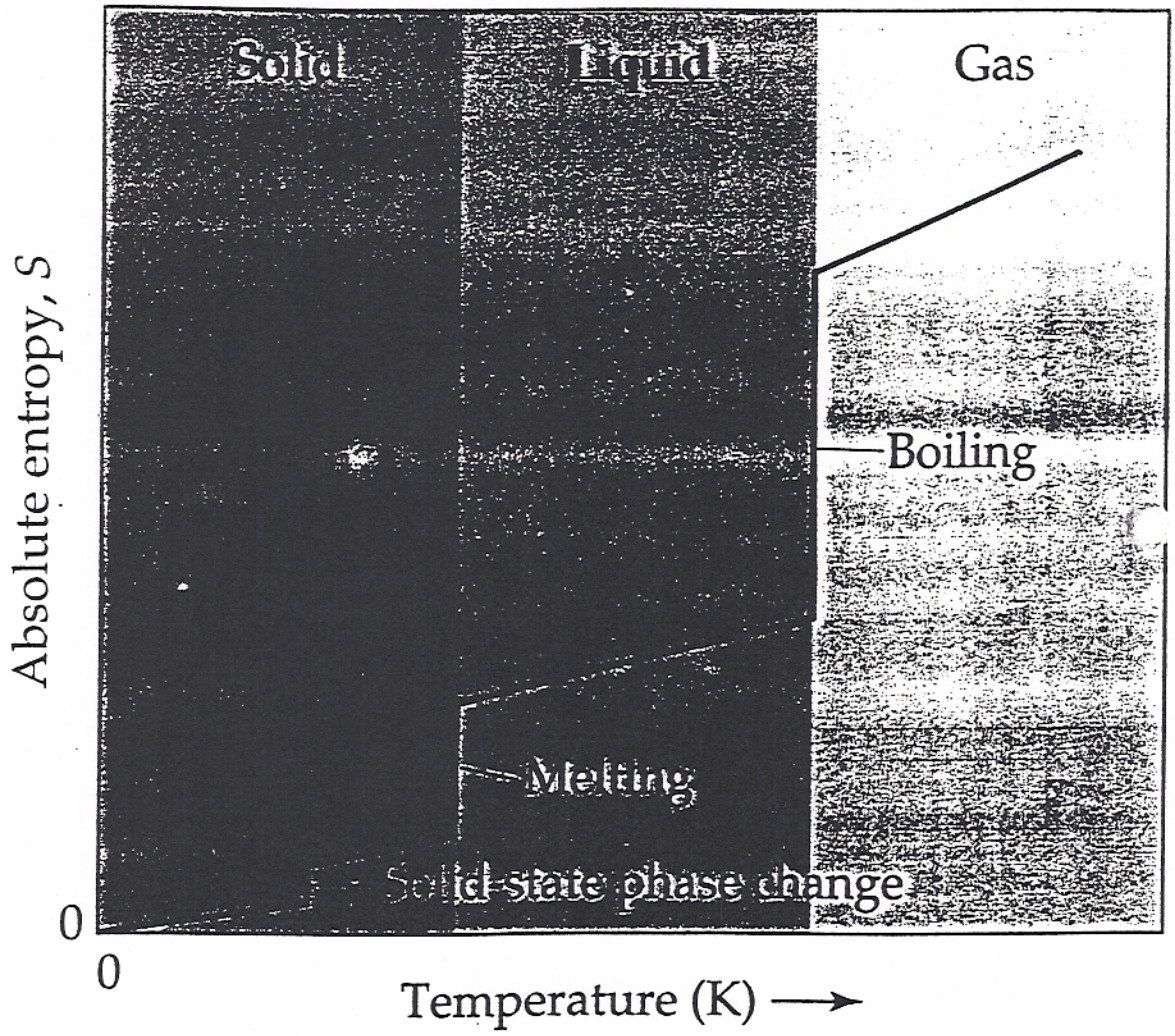
Qualitative Guidelines for Entropy

(#1) Phases: Gases >>> Liquids > Solids (Brown T-149)
- big difference for gases
- related to movement/disorder

For an rxn., if one side has more gas, always has more entropy

- phase changes ⇒ predictable ΔS

T–149 **Fig. 19.10 Entropy Changes as a Function of Temperature**



② Else equal, larger molecule > smaller

$C_5H_{12} > C_4H_{10} > C_3H_8 > C_2H_6$

③ Else equal, more molecules/particles > less

$\underbrace{NC + 2C_3}_{3,\ more} \longrightarrow \underbrace{2\,NC_2}_{2,\ less}$

→ combination reaction ΔS neg
→ fragmentation reaction ΔS pos

④ Entropy increases when a solid ~~is liquid~~ is dissolved in a solvent
– gets more disorganized
– more motion (translational, rotational,
– especially for ionics, which dissociate

$MgCl_2(s) \xrightarrow{water} 1\,Mg^{2+}(aq) + 2Cl^-(aq)$
("special fragmentation reaction")

⑤ Higher temp, higher entropy (Brown, T-149)

Skill: Predict Entropy Changes

$\Delta S = S_{products} - S_{reactants}$

– if products have more entropy, ΔS positive
(Brown, T-C) less ΔS negative

TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

Substance	$S°$, J/mol-K
Gases	
$H_2(g)$	130.6
$H_2O(g)$	188.8
$N_2(g)$	191.5
$NH_3(g)$	192.5
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$C_6H_6(l)$	172.8
Solids	
$Fe(s)$	27.2
$Ca(OH)_2(s)$	83.4

1. From each pair, which has more entropy?

a. $H_2O(\ell)$ vs. $H_2O(g)$

b. $H_2O(\ell)$ at 80°C vs. $H_2O(\ell)$ at 20°C

c. $Ca_3(PO_4)_2(s)$ vs. $FeO(s)$

d. $CaBr_2(s)$ vs. $CaBr_2(aq)$

e. $C_3H_8O(\ell)$ vs. $C_3H_6(\ell) + H_2O(\ell)$

2. Will ΔS be Positive or Negative?

a. $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$ $\quad \underline{\Delta S}$

b. $NaNO_3(s) \xrightarrow{water} NaNO_3(aq)$

c. $2C_2H_6(\ell) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(g)$

d. $C_4H_8Br_2(\ell) \longrightarrow C_4H_8(\ell) + Br_2(\ell)$

e. $AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$

f. $C_7H_{14}(s) \longrightarrow C_7H_4(\ell)$

g. $CO_2(g) \longrightarrow CO_2(s)$

h. $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

Jasperse - Chem 160 Ch. 18 Class Problems

18-5

1. From each pair, which has more entropy? Answer

a. $H_2O(l)$ vs. $H_2O(g)$ — gas

b. $H_2O(l)$ at 80°C vs. $H_2O(l)$ at 20°C — temp

c. $Ca_3(PO_4)_2(s)$ vs. $FeO(s)$ — size

d. $CaBr_2(s)$ vs. $CaBr_2(aq)$ — dissolved

e. $C_3H_8O(l)$ vs. $C_3H_6(l) + H_2O(l)$ — dissociated

2. Will ΔS be Positive or Negative?

		ΔS	Why
a.	$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$	Neg	Gas
b.	$NaNO_3(s) \xrightarrow{water} NaNO_3(aq)$	Pos	Dissolved
c.	$2C_2H_6(l) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$	Pos	Gas
d.	$C_4H_8Br_2(l) \rightarrow C_4H_8(l) + Br_2(l)$	Pos	Dissociated
e.	$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$	Neg	Aque dissol
f.	$C_7H_{14}(s) \rightarrow C_7H_{14}(l)$	Pos	Phase
g.	$CO_2(g) \rightarrow CO_2(s)$	Neg	Gas, Phase
h.	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	Pos	Gas

18.4 Calculating ΔS

$$\Delta S^\circ = S^\circ(\text{products}) - S^\circ(\text{reactants})$$

Units: $\frac{J}{mol \cdot K}$ (not kJ)

- same as for ΔH° but:
  1) units (J not kJ)
  2) elements $\Delta H_f^\circ = 0$ $\quad S^\circ \neq 0$

* Remember to factor in # of moles

Problem 18-7

18.5 2nd Law of Thermodynamics: the Total Entropy of Universe is Increasing

1st Law: energy neither created nor destroyed

3rd Law: Entropy at Absolute Zero is Zero

Notes

① unlike energy, entropy is not conserved
- constantly getting more messy!
- increasing disorder a fundamental law of nature

② Product-favored $\quad \Delta S_{univ} > 0$

Reactant-favored $\quad < 0$

** Equilibrium $\quad \Delta S_{univ} = 0$

① Find ΔS° for $C_2H_6(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

$S^\circ =$ 161 205 214 70

② $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

$S^\circ =$ 92.9 38.1 213.7

Calculate overall ΔS when 2.3 moles of $CaCO_3$ decomposes.

① Find ΔS° for $C_2H_6(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$

$S^\circ =$ 161 205 214 70

$\Delta S^\circ = S^\circ(prod) - S^\circ(react)$

$= [(214 \times 2) + (70 \times 3)] - [161 + (205 \times 3)]$

$= 638 - 776$

$= \boxed{-138 \text{ J/K·mol}}$

Note Coefficients

Note coefficients!
Qual: Product-favored
Not due to entropy, but enthalpy

② $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

$S^\circ =$ 92.9 38.1 213.7

Calculate overall ΔS when 2.3 moles of $CaCO_3$ decomposes.

$\Delta S^\circ = (38.1 + 213.7) - 92.9 = +293 \text{ J/K·mol}$

$\boxed{\Delta S^\circ \text{ on a per mole basis}}$

$\Delta S = \frac{2.3 \text{ mol} \mid 293 \text{ J}}{1 \text{ mol}} = \boxed{675 \text{ J}}$

③ $\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings}$

- surroundings count !!

$$\Delta S_{surroundings} = -\frac{\Delta H_{system}}{T}$$

so $$\boxed{\Delta S_{univ} = \Delta S_{system} - \frac{\Delta H_{system}}{T}}$$

④ A system can gain order, but if so surroundings must lose order

⑤ Product favored associated with:
a. dispersal of matter (ΔS_{system} positive)
* b. dispersal of energy $\Rightarrow \Delta S_{surroundings}$ positive !!

Exothermic usually favorable because results in positive $\Delta S_{surroundings}$!!

- energy causes heat, faster motion, etc (explain)

⑥ Nothing is ever spontaneously "ordered"
- only as effect of something else
- outside work/energy (effort call of which disorder surroundings) needed
(clean desk, comb hair, study/organize knowledge ...)

(7) Qualitative Prediction for ΔS_{univ}, Favorability
- consider ΔS, ΔH for system

	ΔS	ΔH	ΔS_{univ}
Agree	Pos (good)	Neg (exc, good)	Pos (good)
	Neg (bad)	Pos (endo, bad)	Neg (bad)
Disagree	Pos (good)	Pos (bad)	Depends on numbers, temp
	Neg (bad)	Neg (good)	" "

When they disagree, depends on magnitudes, and temp

If products favored, may be entropy driven, enthalpy driven, or driven by both

(18-10)

Classify as Product-Favored or Reactant-Favored.

1. $A \rightarrow B$ $\Delta S^\circ = +52$ J/K $\Delta H^\circ = -32$ kJ/mol

2. $A \rightarrow B$ $\Delta S^\circ = -116$ J/K $\Delta H^\circ = +12$ kJ/mol

3. $A \rightarrow B$ $\Delta S^\circ = +76$ J/K $\Delta H^\circ = +4$ kJ/mol

The following Reactions are Product-Favored. Which are enthalpy favored, entropy favored, or both?

4. $C \rightarrow D$ $\Delta S^\circ = -28$ J/K $\Delta H^\circ = -112$ kJ/mol

5. $E \rightarrow F$ $\Delta S^\circ = +563$ J/K $\Delta H^\circ = +7.3$ kJ/mol

6. $G \rightarrow H$ $\Delta S^\circ = +89$ J/K $\Delta H^\circ = -42$ kJ/mol

(18-10)

Classify as Product-Favored or Reactant-Favored

1. $A \rightarrow B$ $\Delta S^\circ = +52$ J/K (Yes) $\Delta H^\circ = -32$ kJ/mol (Yes)

Product Favored both enthalpy + entropy agree, favor product

2. $A \rightarrow B$ $\Delta S^\circ = -116$ J/K (bad) $\Delta H^\circ = +12$ kJ/mol (bad)

Reactant Favored Enthalpy + entropy both favor reactant

3. $A \rightarrow B$ $\Delta S^\circ = +76$ J/K (Good) $\Delta H^\circ = +4$ kJ/mol (bad)

Can't tell: entropy favors, enthalpy disfavors Later: product favored at high Temp, reactant favored at low temp.

The following Reactions are **Product-Favored.** Which are enthalpy favored, entropy favored, or both?

4. $C \rightarrow D$ $\Delta S^\circ = -28$ J/K (bad) $\Delta H^\circ = -112$ kJ/mol (good)

Enthalpy favored (must overcome entropy)

5. $E \rightarrow F$ $\Delta S^\circ = +563$ J/K (good) $\Delta H^\circ = +7.3$ kJ/mol (bad)

Entropy favored (overcomes enthalpy)

6. $G \rightarrow H$ $\Delta S^\circ = +89$ J/K (good) $\Delta H^\circ = -42$ kJ/mol (good)

Both

18.6 Gibbs "Free Energy" = G

A. $\boxed{\Delta G = \Delta H - T\Delta S}$ $\quad \Delta G = -T\Delta S_{universe}$

– show derivation

① Since ΔG factors $\Delta S_{universe}$, it tells whether any process is product favored

② Value: by measuring ΔH, ΔS for system, can find $\Delta H / \Delta G$ for universe
– need not measure surroundings!!

③ Value 2: Each chem has a standard "free energy" G, so can easily calculate ΔG_{rxn}

④ Sign Meaning: $\Delta G < 0$ product-favored
$\Delta G > 0$ reactant-favored
** $\Delta G = 0$ equilibrium

– opposite to ΔS_{univ}!! Given $\Delta G \Rightarrow$ predict
Given what really happens $\Rightarrow$ predict ΔG

⑤ Sign Review

	Neg	Positive
ΔG	Good	Bad
ΔH	Good	Bad
ΔS	Bad	Good

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

Derivation from

$$\Delta S_{universe} = \Delta S_{surroundings} + \Delta S_{system}$$

Recall: $\Delta S_{surroundings} = -\frac{\Delta H_{system}}{T}$

So $\Delta S_{universe} = -\frac{\Delta H}{T} + \Delta S$

Multiply by $-T$

So $-T\Delta S_{universe} = \Delta H - T\Delta S$

By definition, $-T\Delta S_{universe} = \Delta G$

So $\boxed{\Delta G = \Delta H - T\Delta S}$

Note: ΔG reflects $\Delta S_{universe}$, but ΔH, ΔS are both for system only. Easy to measure

Note: ΔG and $\Delta S_{universe}$ have opposite sign

B. Calculations $\Delta G = \Delta H - T\Delta S$

1. - given any 3, solve for 4th

Units: ΔG kJ/mol
ΔH kJ/mol
T Kelvin (not °C)
ΔS J/mol·K (not kJ!)

2. $\Delta G^\circ_{rxn} = \Delta G^\circ_f$ (products) $- \Delta G^\circ_f$ (reactants)

- same format as ΔH, ΔS

ΔG°_f = standard free energy of formation from elements in standard state

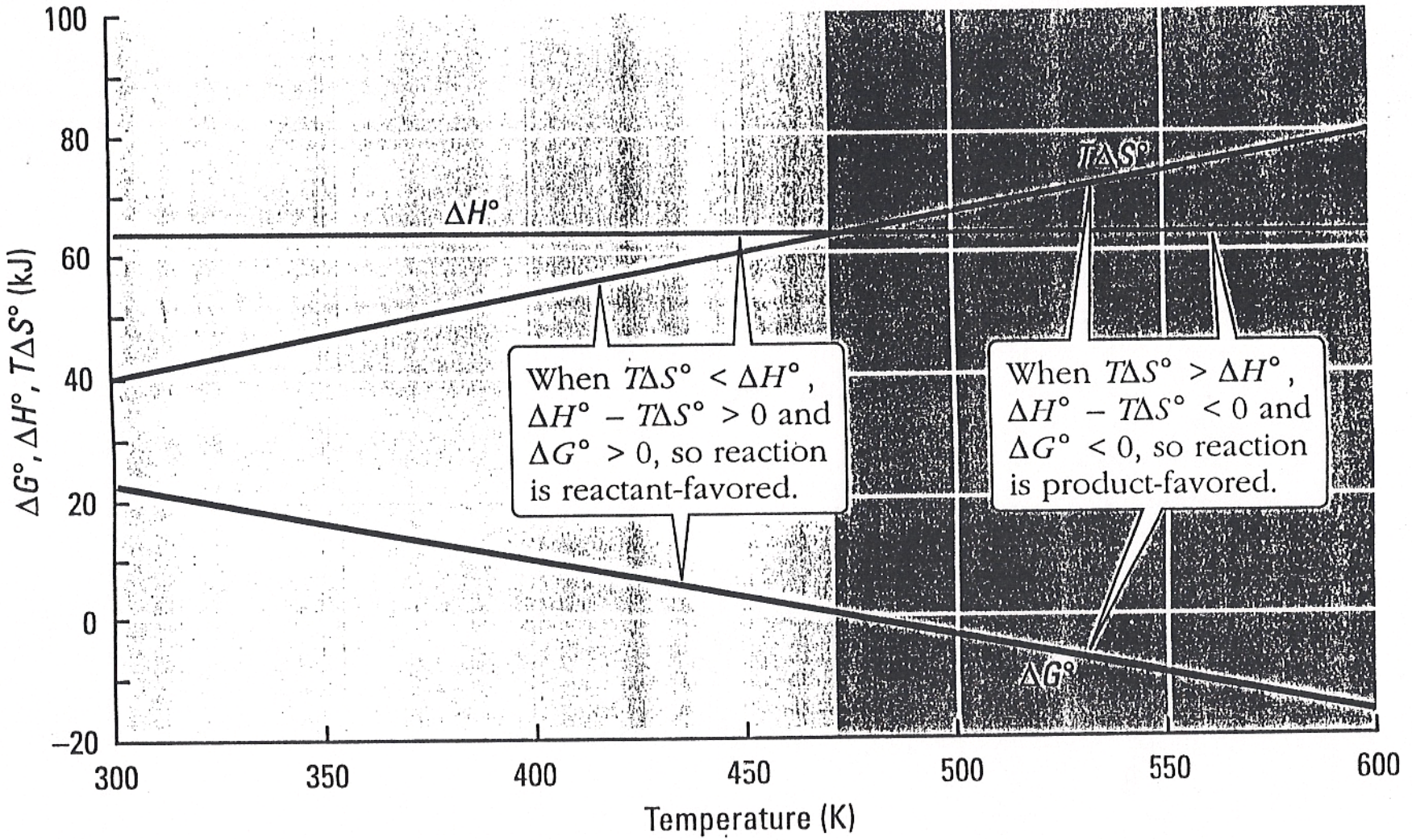
elements: ΔG°_f, $\Delta H^\circ_f = 0$
$S^\circ \neq 0$

C. Temperature + ΔG

$\Delta G = \Delta H - T\Delta S$
(enthalpy, entropy)

High temp ⇒ entropy more important
Low temp ⇒ entropy less important

ΔH	ΔS	$-T\Delta S$	ΔG	Temp	Product-Favored	
−	+	−	−	Any	Yes	
−	−	+	−	Low	Yes	enthalpy wins
			+	High	No	entropy
+	−	+	+	Any	No	
+	+	−	+	Low	No	enthalpy
			−	High	Yes	entropy



Moore/Stanitski/Jurs, Chemistry: The Molecular Science
Figure 18.8

1. $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\quad \Delta H^\circ = -394\ kJ/mol$ $\quad \Delta S^\circ = 42.9\ J/mol \cdot K$

a. What is ΔG° at 25°C?

b. What is ΔG when 0.32 mol of C reacts?

2. $C + 2H_2 \longrightarrow CH_4$ $\quad \Delta G^\circ = -50.8\ \frac{kJ}{mol}$ $\quad \Delta H^\circ = -74.5\ \frac{kJ}{mol}$

what is ΔS° (by definition, at 25°C)

3. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$\Delta G_f^\circ = -51 \qquad -394 \qquad -237$

Find ΔG°

Positive or Negative? ΔG ΔS ΔH

ΔH dominates over $-T\Delta S$

1. $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\quad \Delta H^\circ = -394\ kJ/mol$ $\quad \Delta S^\circ = 42.9\ J/mol \cdot K$

a. What is ΔG° at 25°C?

$$\Delta G = \Delta H - T\Delta S = -394\ \frac{kJ}{mol} - (273+25\ K)\left|\frac{.042\ kJ}{mol \cdot K}\right.$$

① °C → K
② Units: J vs. kJ
③ Notice ΔH dominates

$$= -394\ \frac{kJ}{mol} - 12.8\ \frac{kJ}{mol} = \boxed{-407\ kJ/mol}$$

b. What is ΔG when 0.32 mol of C reacts?

$$x\ kJ = \frac{.32\ mol\ C}{1\ mol}\left|\frac{-407\ kJ}{}\right. = \boxed{-130\ kJ}$$

2. $C + 2H_2 \longrightarrow CH_4$ $\quad \Delta G^\circ = -50.8\ \frac{kJ}{mol}$ $\quad \Delta H^\circ = -74.5\ \frac{kJ}{mol}$

What is ΔS° (by definition, at 25°C)

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

$-50.8\ \frac{kJ}{mol} = -74.5\ \frac{kJ}{mol} - 298\ K(\Delta S)$

$23.7\ \frac{kJ}{mol} = -298\ K(\Delta S^\circ)$

$\Delta S^\circ = \frac{23.7}{-298}\ \frac{kJ}{K \cdot mol} = .0795\ \frac{kJ}{K \cdot mol}$

$= \boxed{-79.5\ \frac{J}{K \cdot mol}}$

3. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$\Delta G_f^\circ = -51 \quad 0 \quad -394 \quad -237$ $\quad \Delta G^\circ = \Delta G_f^\circ(\text{prod} - \text{react})$

Find $\Delta G^\circ = [-394 + (-237 \times 2)] - [-51] = -868 - (-51) = \boxed{-817\ kJ/mol}$

Positive or Negative?

ΔG Neg → Product Favored
ΔS Neg (gas) → Not Product Favored
ΔH Must be neg, favored

$\boxed{\Delta H \text{ dominates over } -T\Delta S}$

- if enthalpy, entropy agree, sense of ΔG is same regardless of temp
- if enthalpy, entropy disagree, there is a Temp at which $\Delta G = 0$ and then changes sign
- enthalpy dominates at low temp, entropy takes over at higher temps ($T\Delta S$)

Crossover Temp: when $\Delta G = 0$, $\Delta H = T\Delta S$

Phase change: always at a crossover temp
- given ΔH, ΔS, calculate mp or bp!!

Provide Sense of ΔG, ΔH, ΔS (Given Reaction Knowledge!)

	ΔG	ΔH	ΔS

① $H_2O(\ell) \longrightarrow H_2O(g)$ at 50°C

② " at 200°C

③ $C_6H_{12}(\ell) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(\ell)$

④ $A(s) \longrightarrow A(\ell)$ $\Delta H^\circ = +132$ kJ/mol

$\Delta S^\circ = +34.3$ J/mol·K

What is the melting temp for A?

At what temp limits is process product favored?

⑤ When will the following be Product-Favored?

a. ΔH neg ΔS neg

b. ΔH neg ΔS pos

c. ΔH pos ΔS neg

d. ΔH pos ΔS pos.

⑥ $A \longrightarrow B$ $\Delta H = -14.9$ kJ/mol $\Delta S = -48$ J/mol·K

At what temp limits is process product-favored?

Provide Sense of ΔG, ΔH, ΔS (Given Reaction Knowledge!)

		ΔG	ΔH	ΔS	
①	$H_2O(l) \longrightarrow H_2O(g)$ at 50°C (heat+) (not what happens)	+	+	+	enthalpy driven
②	" at 200°C (yes, this happens)	−	+	+	entropy driven
③	$C_6H_2(l) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$ (Combustion, favorable)	−	−	+	enthalpy driven

④ $A(s) \longrightarrow A(l)$ $\quad \Delta H^\circ = +13.2$ kJ/mol

$\Delta S^\circ = +34.3$ J/mol·K

What is the melting temp for A? $\Rightarrow \Delta G = 0$ $\quad \Delta G = \Delta H - T\Delta S$

$0 = 13.2 - T(.0343)$

$13.2 = .0343T$

$T = 385$ K $= 112$ °C

At what temp limits is process product favored?

Above 112°C

⑤ When will the following be Product-Favored?

a. ΔH neg, ΔS neg — enthalpy controlled. "Low" temp

b. ΔH neg, ΔS pos — both. All temps

c. ΔH pos, ΔS neg — neither. Never

d. ΔH pos, ΔS pos. — entropy controlled. "High" temp

⑥ $A \longrightarrow B$ $\quad \Delta H = -14.9$ kJ/mol $\quad \Delta S = -48$ J/mol·K

"Crossover" $\Delta G = 0$ $\quad \Delta G = \Delta H - T\Delta S$

$\Delta H = T\Delta S$

$-14.9 = (-.048)T$

$T = 310$ K $= 37$ °C

At what temp limits is process product-favored?

Below 37°C, product favored.
Above 37°C, reactant favored.