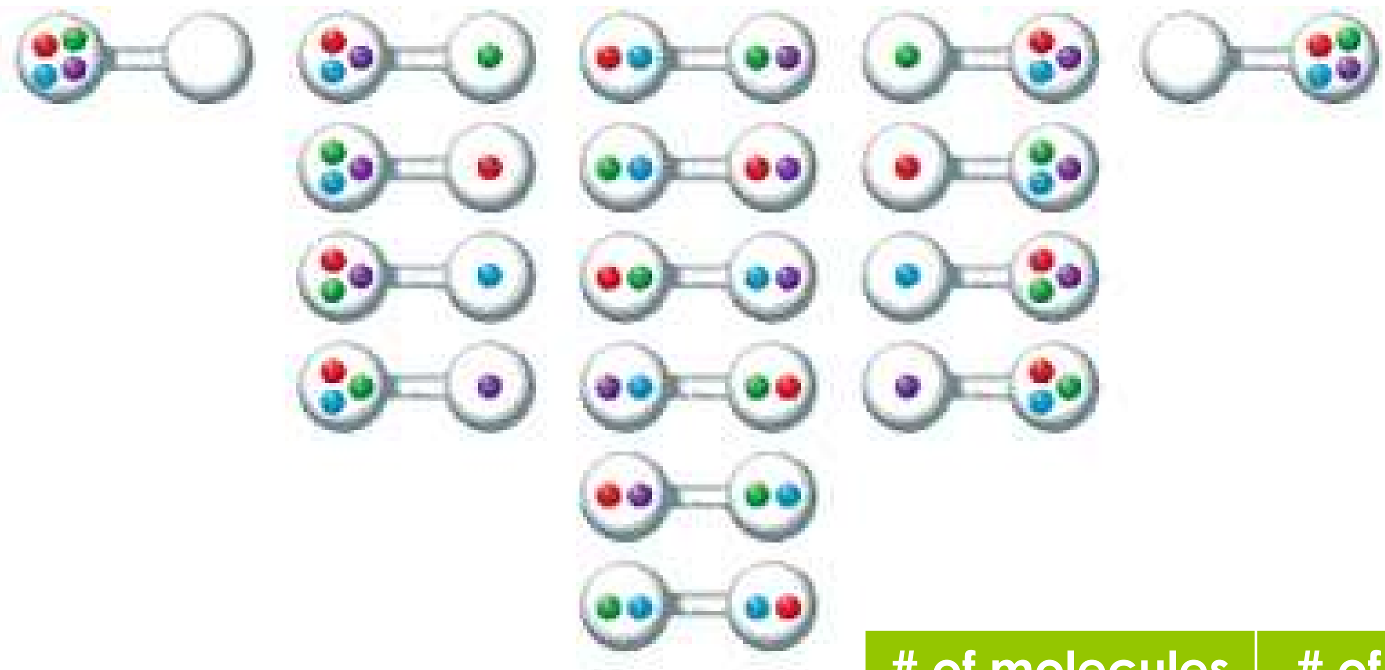
Chapter 10 Spontaneity, Entropy, & Free Energy

- Entropy
- ΔS of Physical Reactions
- Isothermal Processes
- 2nd Law of Thermo
- Free Energy
- Hess's Law/ 3rd Law of Thermo
- Equilibrium

Big Idea: The change in free energy of a reaction indicates whether a reaction is spontaneous. In any spontaneous process there is always an increase in the entropy of the universe.

Entropy



- **Entropy (*S*):** Entropy is a measure of how energy and matter can be distributed in a chemical system.

# of molecules of left side	# of ways of arranging (microstates)
4	1
3	4
2	6
1	4
0	1

Entropy

In General:

- **Entropy** increases from solid to liquid to gas corresponding to an increase in positional probability.
- **Entropy** increases when you dissolve a solid in liquid corresponding to an increase in positional probability.
- The larger the **volume** the larger the positional probability and the greater the entropy (n constant).
- The larger the **pressure** the smaller the positional probability and the lower the entropy (n constant).
- The larger the **molecule** the larger the number of relative positions of the atoms resulting in a greater positional probability and a greater entropy.
- The higher the **temperature** the greater the range of energies, therefore the larger the entropy.

Entropy

Student Question

Predict which of the following reactions has a negative entropy change.

I. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

II. $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

III. $2KClO_4(s) \rightarrow 2KClO_3(s) + O_2(g)$

a) II and III
b) III
c) II
d) I
e) I and II

Entropy

- **Phase Change:** The condition (for a given pressure, and temperature) at which two different phases are in dynamic equilibrium.

Melting/Freezing	Liquid/Solid
Evaporation/Condensation	Liquid/Gas
Sublimation/Deposition	Solid/Gas

ΔS of Physical Reactions

Calculating ΔS for physical reaction

$X(s, T_i) \rightarrow X(g, T_f)$

- **Step 1:** Calculate ΔS to bring to melting point

$$\Delta S = mC_{solid} ln\left(\frac{T_M}{T_i}\right)$$

- **Step 2:** Calculate ΔS involved in fusion

$$\Delta S = \frac{n\Delta H_{fus}}{T}$$

- **Step 3:** Calculate ΔS to bring to boiling point

$$\Delta S = mC_{liquid} ln\left(\frac{T_B}{T_M}\right)$$

- **Step 4:** Calculate ΔS involved in vaporization

$$\Delta S = \frac{n\Delta H_{vap}}{T}$$

- **Step 5:** Calculate ΔS to bring to final temperature

$$\Delta S = nC_{P_{gas}} ln\left(\frac{T_f}{T_B}\right)$$

ΔS of Physical Reactions

Student Question

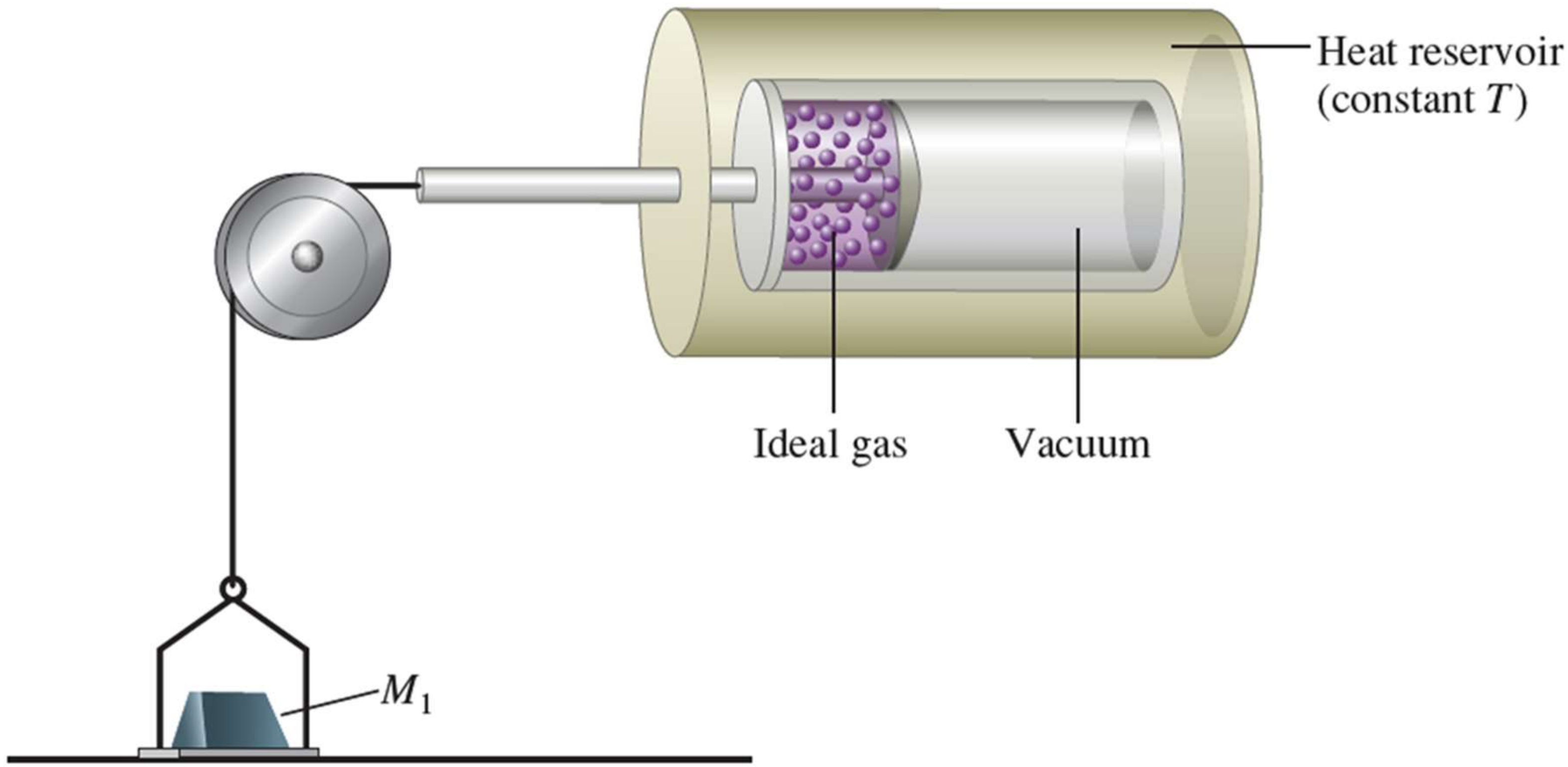
What is ΔS for 88.0 g of CO_2 undergoing the following reaction at constant pressure?

CO_2(s, 150. K) → CO_2(g, 195. K)

Helpful Information: $T_{sub} = 195K$, $\Delta H_{sub} = 25.2\,\frac{kJ}{mol}$, $C_{CO_2(s)} = 1.07\frac{J}{g \cdot K}$

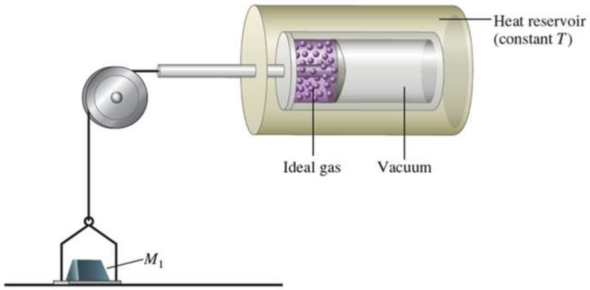
a) $24.9\,\frac{J}{K}$
b) $154\,\frac{J}{K}$
c) $233\,\frac{J}{K}$
d) $283\,\frac{J}{K}$
e) None of the above

Isothermal Processes



Isothermal Process

- **Isothermal Expansion of Ideal Gas**



Remove the weight

How much work is done?

$$w = -P_{ex}\Delta V$$

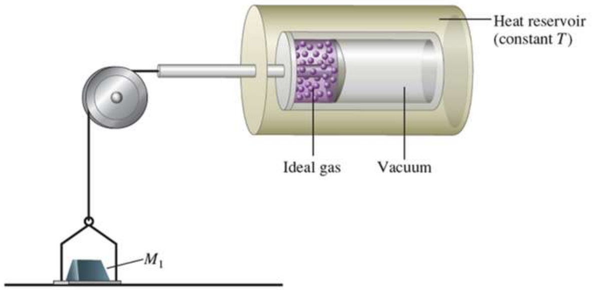
What is P_{ex}?

P_{ex} =

This is known as:

Isothermal Process

- **Isothermal Expansion of Ideal Gas**



Other ways to expand the gas

For all other cases

Initial: V_i, P_i

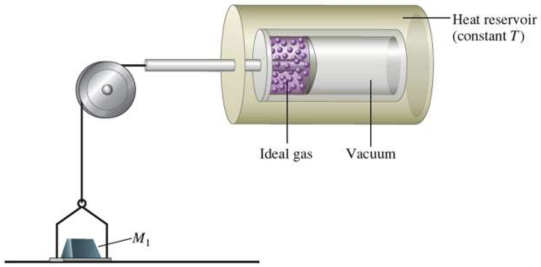
$$P = \frac{force}{area} = \frac{mg}{A}$$ Changing mass changes pressure

$$P_i = \frac{m_i g}{A}$$

Final: $V_f = 4V_i$, $P_f =$ therefore mass final =

Isothermal Process

- **Isothermal Expansion of Ideal Gas (1 - Step)**



Expand $V_i \rightarrow V_f(4V_i)$; $P_i \rightarrow P_f\left(\frac{P_i}{4}\right)$

Initial have on m_i, replace with $m_f\left(\frac{m_i}{4}\right)$

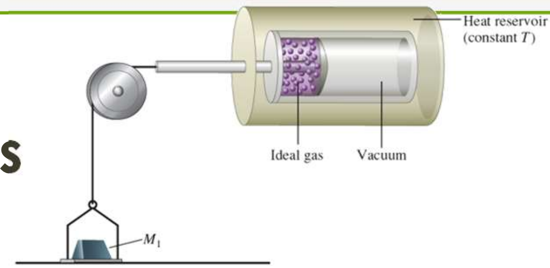
Calculate the work

$$w = -P_{ex}\Delta V = -P_{ex}\left(V_f - V_i\right)$$

What is P_{ex}? P_{ex} =

w=

Isothermal Process



- **Isothermal Expansion of Ideal Gas (2 - Step)**

Expand $V_i \rightarrow V_2\ (2V_i) \rightarrow V_f$; $P_i \rightarrow P_2 \left(\frac{P_i}{2}\right) \rightarrow P_f$

Initial have on m_i, replace with $m_2 \left(\frac{m_i}{2}\right)$, then replace m_2 with $m_f \left(\frac{m_i}{4}\right)$

Calculate the work in step 1

$$w = -P_{ex}\Delta V =$$

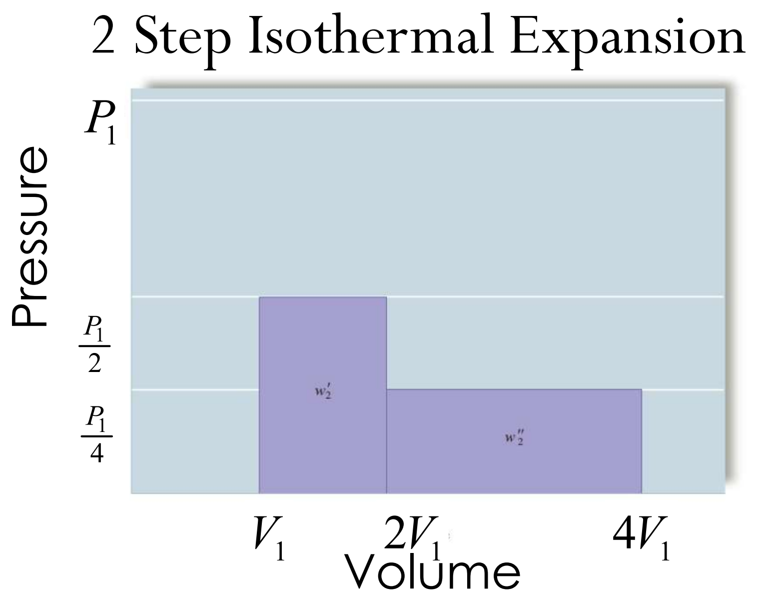
Calculate the work in step 2

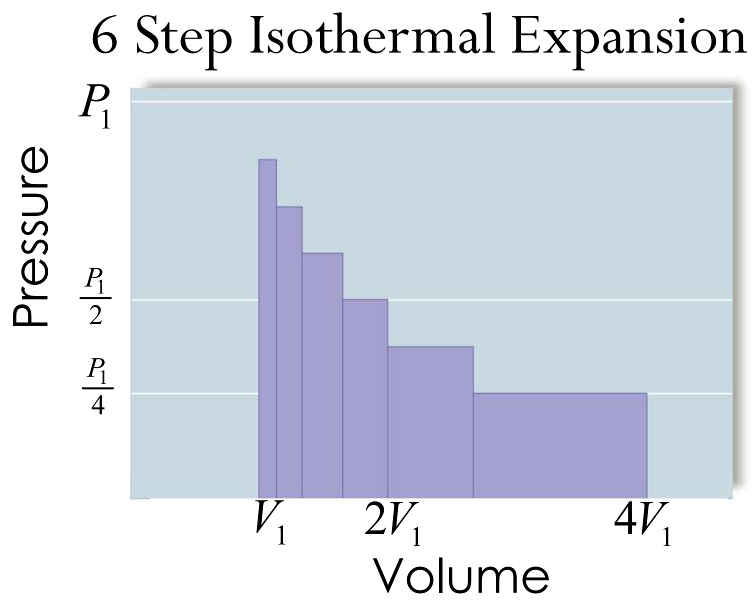
$$w =$$

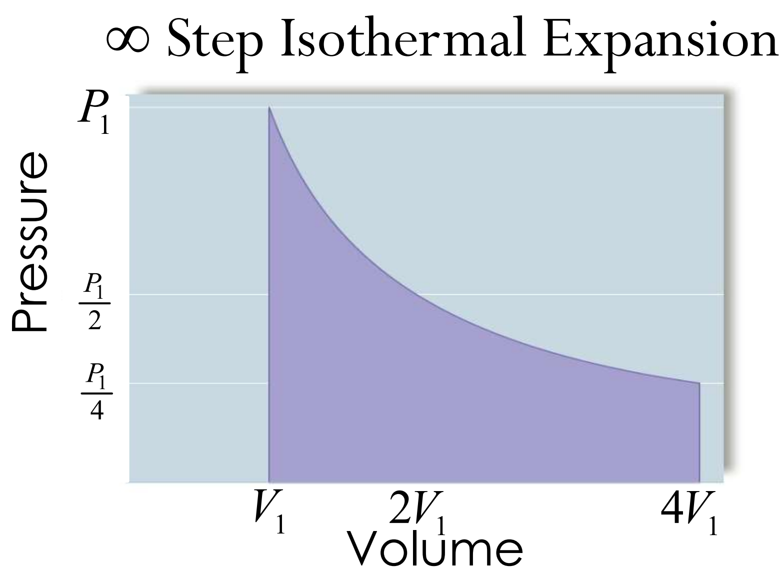
Calulate the work total

$$w_{tot} =$$

Isothermal Processes







- Reversible Process: A process that can be reversed by an infinitesimal change in a variable.

Note: In order for a reversible process to occur the system must be at equilibrium during the entire process.

Isothermal Processes

Student Question

Calculate the ΔS associated with a process in which 5.00 mol of gas expands reversibly at constant temperature T = 25°C from a pressure of 10.0 atm to 1.00 atm.

a) $28{,}500\frac{J}{K}$
b) $95.7\frac{J}{K}$
c) $-95.7\frac{J}{K}$
d) $-28{,}500\frac{J}{K}$
e) None of the above

2nd Law of Thermo

2nd Law of Thermodynamics: A spontaneous change is accompanied by an increase in the total entropy of the system and its surroundings.

- $\Delta S_{uni} = \Delta S_{sys} + \Delta S_{sur}$

Note: The second law of thermodynamics applies to ΔS_{uni} and not ΔS_{sys}. So far we have only discussed ΔS_{sys}.

Free Energy

Can we relate spontaneity to a change in the system instead of the universe assuming we are at constant temperature and pressure?

- $\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$
- Divide Through by T
- $\dfrac{\Delta G_{sys}}{T} = \dfrac{\Delta H_{sys}}{T} - \dfrac{T\Delta S_{sys}}{T}$
- $\dfrac{\Delta G_{sys}}{T} = -\Delta S_{sur} - \Delta S_{sys}$
- $-\dfrac{\Delta G_{sys}}{T} = \Delta S_{univ}$

$\Delta S_{univ} > 0$ then $\Delta G_{sys} < 0$
spontaneous process

$\Delta s_{univ} < 0$ then $\Delta G_{sys} > 0$
non spontaneous process

Free Energy

Student Question

Hold the rubber band a short distance from your lips. Quickly stretch it and press it against your lips carefully (don't hurt those delicate lips). Do you experience a warming or cooling sensation? Carefully release the rubber band and experience the sensation. Is stretching a spontaneous or a non-spontaneous process? What are the correct signs for ΔG, ΔH, and ΔS when you allow the rubber band to relax?

	ΔG	ΔH	ΔS
a)	–	+	+
b)	–	–	+
c)	+	+	–
d)	+	–	–

Hess's Law / 3rd Law of Thermo

Hess's Law: A reaction enthalpy/free energy/entropy is the sum of the enthalpies/free energies/entropies of any sequence of reactions (at the same temperature and pressure) into which the overall reaction can be divided.

Things to remember:

- If you add reactions together, add $\Delta H/\Delta G/\Delta S$.
- If you flip a reaction, flip the sign of $\Delta H/\Delta G/\Delta S$.
- If you multiply a reaction by a constant, multiply $\Delta H/\Delta G/\Delta S$ by the same constant.

Student Question

What is $\Delta G°$ for $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$ given the following information?

$2S(s) + 3O_2(g) \rightarrow 2SO_3(g)$ $\Delta G° = -742 \frac{kJ}{mol}$

$S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta G° = -300. \frac{kJ}{mol}$

a) $-71 \frac{kJ}{mol}$

b) $-442 \frac{kJ}{mol}$

c) $-671 \frac{kJ}{mol}$

d) $-1042 \frac{kJ}{mol}$

e) None of the above

Hess's Law / 3rd Law of Thermo

Thermodynamic Data at 298 K			
Substance	$\Delta H_f°$ ($\frac{kJ}{mol}$)	$\Delta G_f°$ ($\frac{kJ}{mol}$)	S° ($\frac{J}{mol \cdot K}$)
$C_2H_4(g)$	52	68	219
$CH_4(g)$	-75	-51	186
$CO_2(g)$	-393.5	-394	214
$C_2H_6(g)$	-84.7	-32.9	229.5
O(g)	-110.5	-137	198
$O_2(g)$	0	0	205.
$CH_3CO_2H(l)$	-484	-389	160.
$CH_3OH(g)$	-201	-163	240.
$CH_3CH_2OH(l)$	-278	-175	161
$C_6H_{12}O_6(s)$	-1275	-911	212
HCl(g)	-92	-95	187
$H_2(g)$	0	0	131
$H_2O(l)$	-286	-237	70
$H_2O(g)$	-242	-229	189
Fe(s)	0	0	27

Thermodynamic Data at 298 K			
Substance	$\Delta H_f°$ ($\frac{kJ}{mol}$)	$\Delta G_f°$ ($\frac{kJ}{mol}$)	S° ($\frac{J}{mol \cdot K}$)
$Fe_2O_3(s)$	-826	-740.	90.
$N_2(g)$	0	0	192
$NO_2(g)$	34	52	240.
NO(g)	90.	87	211
$N_2O_4(g)$	10.	98	304
$NH_3(g)$	-46	-17	193
$HNO_3(l)$	-174	-81	156
$NH_4Cl(s)$	-314	-203	96
$O_2(g)$	0	0	205
$P_4O_{10}(s)$	-2984	-2698	229
$H_3PO_4(s)$	-1279	-1119	110
$S_{rhombic}(s)$	0	0	32
$H_2S(g)$	-21	-34	206
$SO_2(g)$	-297	-300	248
$SO_3(g)$	-396	-371	257

* Other $\Delta H°_f$, $\Delta G°_f$, and S° can be found in appendix 4 in the back of your book.

Hess's Law / 3rd Law of Thermo

Thermodynamic Data at 298 K			
Substance	$\Delta H_f°\left(\frac{kJ}{mol}\right)$	$\Delta G_f°\left(\frac{kJ}{mol}\right)$	$S°\left(\frac{J}{mol\cdot K}\right)$
$NH_3(g)$	-46	-17	193
$O_2(g)$	0	0	205.
$NO(g)$	90.	87	211
$H_2O(l)$	-286	-237	70.

- What is ΔS_{rxn}° for

  $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$?

- $\Delta S_{rxn}^{\circ} = \sum S_{prod}^{\circ} - \sum S_{react}^{\circ}$
- $\Delta S_{rxn}^{\circ} = n_{NO}S_{NO}^{\circ} + n_{H_2O}S_{H_2O}^{\circ} - n_{NH_3}S_{NH_3}^{\circ} - n_{O_2}S_{O_2}^{\circ}$
- $\Delta S_{rxn}^{\circ} = (4)\left(211\,\frac{J}{mol\cdot K}\right) + (6)\left(70.\frac{J}{mol\cdot K}\right) - (4)\left(193\,\frac{J}{mol\cdot K}\right) - (5)\left(205\,\frac{J}{mol\cdot K}\right) = -533\,\frac{J}{mol\cdot K}$

Student Question

Consider the reaction: C(graphite) + CO_2(g) ⇌ 2CO(g)

What is ΔG ($\frac{kJ}{mol}$) at 25°C when the pressures are: $P_{CO} = 0.00050\ atm,\ P_{CO_2} = 20.\ atm.$

Thermodynamic Data at 298 K		
Substance	$\Delta H_f°\left(\frac{kJ}{mol}\right)$	$S°\left(\frac{J}{mol \cdot K}\right)$
C(graphite)	0	5.74
CO_2(g)	-393.5	214
CO(g)	-110.5	198

a) $212\ \frac{kJ}{mol}$

b) $120\ \frac{kJ}{mol}$

c) $116\ \frac{kJ}{mol}$

d) $93.7\ \frac{kJ}{mol}$

e) None of the above

Equilibrium

- For the reaction below at equilibrium there are many more products then reactants. What is the sign of ΔG°?
  - $A(g) \rightarrow B(g)$

Take Away from Chapter 10

Big Idea: The change in free energy of a reaction indicates whether a reaction is spontaneous. In any spontaneous process there is always an increase in the entropy of the universe.

- **Entropy**
  - Know how positional probability and energy probability effects entropy (12,19,&40)
    - *Be able to predict the sign of ΔS (7,& 43)*
  - *Be able to calculate S of a system with known number of microstates*
    - $S = k_b ln(\Omega)$
  - Be able to calculate $\Delta S = S_f - S_i$ (29,30,33,48,&49)
    - $\Delta S = \frac{q}{T}$ *(constant temperature)*
    - $\Delta S = Cln\left(\frac{T_2}{T_1}\right)$ *(changing temperature)*
- **ΔS of Physical Reactions**
  - Know how to calculate ΔS for physical reactions at constant pressure (31)
  - Know that a similar multi step process that is used to calculate ΔS during physical reactions can be used for ΔH. (32)

Problems 23 and 25 review from last chapter.

Numbers correspond to end of chapter questions.

Take Away from Chapter 10

- **Isothermal Process**
  - Know that for an isothermal expansion of an ideal gas ΔE=0
  - Know that the maximum work is done for the reversible expansion/contraction of an ideal gas. (28)
    - $w_{rev} = -nRTln\left(\frac{V_2}{V_1}\right)$
    - $q_{rev} = nRTln\left(\frac{V_2}{V_1}\right)$ (27)
- **2nd Law of Thermo**
  - A spontaneous change is accompanied by an increase in the total entropy of the universe.
    - ΔS_{uni} +, *spontaneous*
    - ΔS_{uni} −, *non spontaneous*
    - $\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr}$ *(41&50)*
      - $\Delta S_{surr} = -\frac{\Delta H}{T}$ *(at constant pressure)*

Numbers correspond to end of chapter questions.

Take Away from Chapter 10

- **Free Energy**
  - Be able to calculate the change in free energy (ΔG)
    - $\Delta G = \Delta H - T\Delta S$ *(51,56,57,& 64)*
    - *Know that ΔH and ΔS are relatively temperature independent while ΔG is temperature dependent. Therefore, the equation above can be use to calculate ΔG at different temperatures.*
  - Know implications of the sign of ΔG
    - *$\Delta G_{sys\ is}$ +, non spontaneous*
    - *ΔG_{sys} is –, spontaneous*
- **Hess's Law / 3rd Law of Thermo**
  - Know that Hess's Law can be applied to ΔG and ΔS as well as ΔH
    - Know how to get ΔG°_{rxn} and ΔS°_{rxn} from other known ΔG°_{rxn} and ΔS°_{rxn}(62)
    - Know how to get ΔG°_{rxn} and ΔS°_{rxn} from table (54,60,61)
      - $\Delta G^\circ_{rxn} = \sum \Delta G^\circ_f(prod) - \sum \Delta G^\circ_f(reac)$ (59)
      - $\Delta S^\circ_{rxn} = \sum S^\circ_{prod} - \sum S^\circ_{reac}$ (44)
  - Know that while absolute values of H and G cannot be calculated, an absolute value of S can.
    - *3rd Law Thermodynamics: The entropy of a perfect crystal is 0 K is 0*

Numbers correspond to end of chapter questions.

Take Away from Chapter 10

- **Equilibrium**
  - Know that Q and ΔG are related by
    - $\Delta G = \Delta G^{\circ} + RTln(Q)$(68,69,70,& 71)
      - This equation only changes concentration and not temperature ΔG° must be for the temperature of interest
      - ΔG is +, reverse reaction spontaneous
      - ΔG is -, forward reaction spontaneous
      - ΔG is 0, at equilibrium
  - Know that K and ΔG° are related by
    - $\Delta G^{\circ} = -RTln(K)$ (74,78,79,84,86,87,88,91,&109)
      - ΔG ° = 0, (K=1) equal amounts of products and reactants at equilibrium
      - ΔG ° > 1, (K<1) more reactants than products at equilibrium
      - ΔG ° < 1, (K>1) more products than reactants at equilibrium

Numbers correspond to end of chapter questions.