

## THE SECOND LAW

### Chapter 3 Outline

**HW:** Questions are below. Solutions are in separate file on the course web site.

Sect.	Title and Comments	Required?
1.	The Dispersal of Energy	YES
2.	Entropy We won't be covering the Boltzmann Formula (Sect. 2.b).	YES
3.	Entropy Changes Accompanying Specific Processes The text concentrates on <b>reversible</b> processes only. We will also show the calculation of entropy changes for <b>irreversible</b> processes.	YES
4.	The Third Law of Thermodynamics	YES
5.	The Helmholtz and Gibbs Energies We will just comment briefly on the relation of $\Delta A$ to maximum work and of $\Delta G$ to non-PV work (Sects. 3.5.c and 3.5.d). You are not responsible for this.	YES
6.	Standard Reaction Gibbs Energies	YES
7.	The Fundamental Equation We will add additional examples of applications of the thermodynamic equations, which are not in the text. We will also show how one can calculate thermodynamic properties of systems with non-PV work.	YES
8.	Properties of the Internal Energy	YES
9.	Property of the Gibbs Energy	YES

### Chapter 3 Homework Questions

- 3.1** Calculate  $\Delta S$  (for the system) when the state of 3. moles of a perfect gas at 25 °C and 1. atm is changed to 125 °C and 5. atm.  
**Note:** The constant pressure molar heat capacity of this gas is  $C_{p,m} = (5/2)R$ ,
- 3.2** A sample consisting of 3. moles of a diatomic perfect gas at -73 °C is compressed reversibly and adiabatically until the temperature reaches -23. °C. For this gas,  $C_{V,m} = 27.5 \text{ J/mol}\cdot\text{K}$ . Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  for this process.
- 3.3** Calculate the changes in entropy of the system and the surroundings when a 14. g sample of  $\text{N}_2(\text{g})$  [ $M=28$ ] at 1. bar and 25 °C doubles its volume in  
(a) a reversible isothermal expansion  
(b) an irreversible isothermal expansion against  $p_{\text{ex}} = 0$ .  
(c) a reversible adiabatic expansion
- 3.4** The enthalpy of vaporization of chloroform ( $\text{CHCl}_3$ ,  $M=119.4$ ) is 29.4 kJ/mol at its normal boiling point of 62 °C. For the vaporization of 240. grams of  $\text{CHCl}_3$  at its normal boiling point, calculate (a)  $\Delta S$  of the system and (b)  $\Delta S$  of the surroundings.
- 3.5** The normal boiling point of ethanol,  $\text{C}_2\text{H}_5\text{OH}$  [ $M=46$ ], is 78 °C. The Enthalpy of Vaporization of ethanol is 38.6 kJ/mol.  
  
Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  when 150 grams of ethanol vapor is condensed to the liquid at 78 °C and 1 bar pressure.
- 3.6** The normal melting point of ethanol,  $\text{C}_2\text{H}_5\text{OH}$  [ $M=46$ ], is -114 °C. The Enthalpy of Fusion of ethanol is 9.45 kJ/mol.  
  
Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  when 150 grams of ethanol liquid crystallizes to the solid at -114 °C and 1 bar pressure.
- 3.7** The normal boiling point of benzene is 80 °C = 353 K. The enthalpy of vaporization of benzene at its normal boiling point is  $\Delta_{\text{vap}}H = 35.7 \text{ kJ/mol}$ . The constant pressure molar heat capacities of the liquid and vapor are:  $C_{p,m}(\text{l}) = 138.7 \text{ J/mol}\cdot\text{K}$  and  $C_{p,m}(\text{g}) = 35.1 \text{ J/mol}\cdot\text{K}$   
  
Consider the vaporization of one mole of superheated benzene at 100 oC. Calculate  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{univ}}$  for this process.

- 3.8** The standard molar entropy of  $\text{NH}_3(\text{g})$  is  $192.45 \text{ J/mol}\cdot\text{K}$  at  $25^\circ\text{C}$ . The constant pressure heat capacity is temperature dependent and is given by:

$$C_{p,m} = a + bT + \frac{c}{T^2} \quad a = 29.8 \quad , \quad b = 2.5 \times 10^{-2} \quad , \quad c = -1.6 \times 10^5$$

Calculate the entropy of 3. moles of  $\text{NH}_3(\text{g})$  at:

- (a)  $100^\circ\text{C}$   
 (b)  $500^\circ\text{C}$
- 3.9** The constant pressure heat capacity of  $\text{F}_2(\text{g})$  is temperature dependent and given by:

$$C_{p,m} = a - \frac{b}{T} \quad a = 39.6 \text{ J/mol}\cdot\text{K} \quad \text{and} \quad b = 2.5 \times 10^3 \text{ J/mol}$$

Consider 100 grams of  $\text{F}_2(\text{g})$  [ $M = 38.$ ] initially at a pressure of 2. bar and temperature of  $600^\circ\text{C}$ . Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$  for each of the following processes.

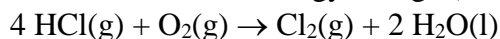
- (a) The gas is cooled to  $300^\circ\text{C}$  at constant pressure.  
 (b) The gas is cooled to  $300^\circ\text{C}$  at constant volume
- 3.10** Use the standard molar entropies (at 298 K) in the table below to calculate the reaction entropies,  $\Delta_r S^\circ$ , for the following reactions.
- (a)  $2 \text{CH}_3\text{CHO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CH}_3\text{COOH}(\text{l})$   
 (b)  $\text{Hg}(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow \text{HgCl}_2(\text{s})$ .

<b>Compound</b>	<b><math>S_m^\circ</math></b>
$\text{CH}_3\text{CHO}(\text{g})$	$250.3 \text{ J/mol}\cdot\text{K}$
$\text{O}_2(\text{g})$	$205.1$
$\text{CH}_3\text{COOH}(\text{l})$	$159.8$
$\text{Hg}(\text{l})$	$76.0$
$\text{Cl}_2(\text{g})$	$223.1$
$\text{HgCl}_2(\text{s})$	$146.0$

- 3.11** Use the standard Gibbs Energies of Formation (at 298 K) in the table below to calculate the **reaction** entropies,  $\Delta_r S^\circ$ , for the following reactions.
- (a)  $2 \text{CH}_3\text{CHO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CH}_3\text{COOH}(\text{l})$   
 (b)  $\text{Hg}(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow \text{HgCl}_2(\text{s})$ .

<b>Compound</b>	<b><math>\Delta_f G_m^\circ</math></b>
$\text{CH}_3\text{CHO}(\text{g})$	$-128.9 \text{ kJ/mol}$
$\text{CH}_3\text{COOH}(\text{l})$	$-389.9$
$\text{HgCl}_2(\text{s})$	$-178.6$

- 3.12** Use the standard molar entropies and the enthalpies of formation in the table below to calculate the standard Gibbs energy change (at 298 K) for the reaction:



<b>Compound</b>	<b><math>S_m^\circ</math></b>	<b><math>\Delta_f H_m^\circ</math></b>
HCl(g)	186.9 J/mol•K	-92.3 kJ/mol
O <sub>2</sub> (g)	205.1	
Cl <sub>2</sub> (g)	69.9	
H <sub>2</sub> O(l)	223.1	-285.8

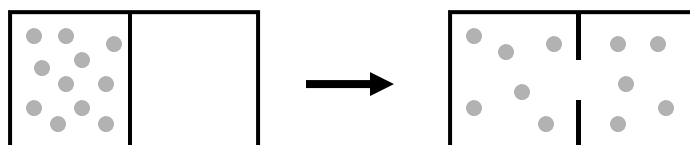
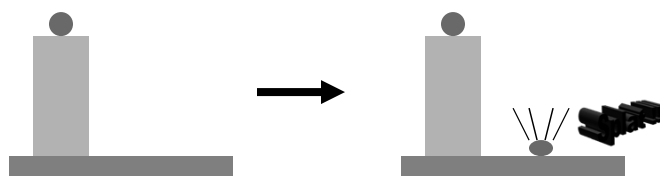
- 3.13** Consider 70. grams of N<sub>2</sub>(g) [M=28] initially at 40 °C and 25 L. The gas is compressed isothermally to a final volume of 500 mL. Calculate  $\Delta G$  for this process.
- 3.14** The change in the Gibbs Energy for a certain constant pressure process is given by:  
 $\Delta G = a + bT^2$  ,  $a = +5620 \text{ J}$  ,  $b = 8.0 \times 10^{-2} \text{ J/K}^2$ .  
Calculate  $\Delta S$  for this process at 30 °C (in J/K)
- 3.15** Calculate the change in Gibbs Energy (in J) of 20. moles of liquid benzene (C<sub>6</sub>H<sub>6</sub>, M = 78 g/mol, d = 0.88 g/mL) when the pressure on the sample is increased from 1.0 atm to 100 atm.
- 3.16** Calculate the change in Gibbs Energy (in J) of 20. moles of H<sub>2</sub>(g) when the pressure on the sample is increased from 1.0 atm to 100 atm at 25 °C.
- 3.17** A solid has two crystalline forms, A(s) and B(s). For the transition A(s) → B(s),  $\Delta G^\circ = +6.0 \text{ kJ/mol}$  (i.e. at 1 bar pressure). The difference in molar volumes of the two forms is  
 $V_m(\text{B}) - V_m(\text{A}) = \Delta V_m = -15 \text{ mL/mol}$ .  
Calculate the pressure, in bar, at which the two forms will be in equilibrium.

# Chapter 3

## The Second Law

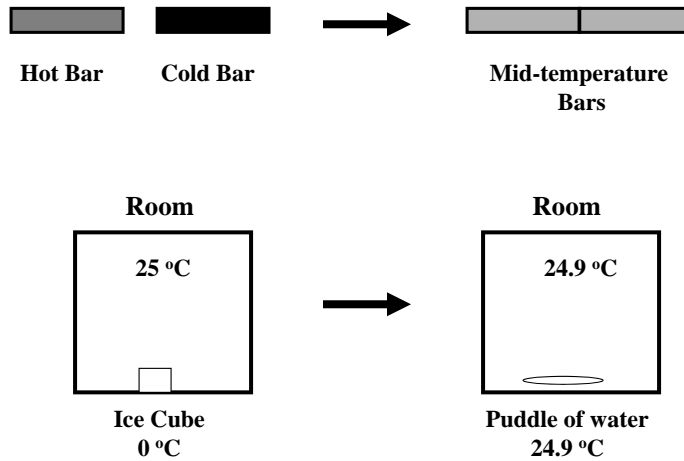
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### Spontaneous Processes



2

## Spontaneous Processes



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## Observations

- All four processes are spontaneous only in the direction shown (left to right)
- The First Law (energy conservation) is obeyed regardless of the direction
- The disorder (randomness) increases in the spontaneous direction.
- A dispersal of energy accompanies the process.

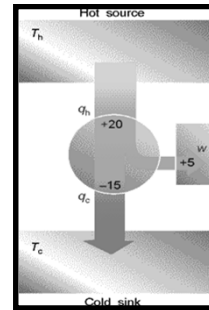
**Conclusion:** In order to predict the direction in which a process is spontaneous, we require a function which is a measure of the amount of disorder and energy dispersal.

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## Heat Engines

A Heat Engine:

1. Removes heat from a high temperature source ( $T_h$ )
2. Performs work on the surroundings
3. Expels the remaining heat into a cold temperature sink ( $T_c$ )



In the next section, we will analyze an idealized engine, called the Carnot Engine (or Carnot Cycle).

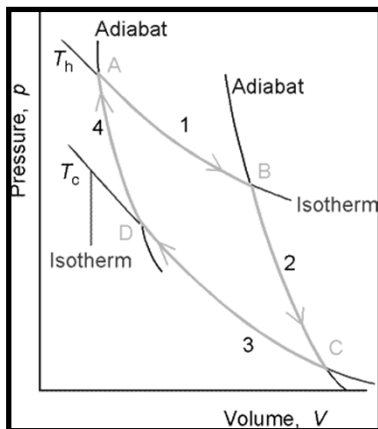
We will use the Carnot Cycle to:

- (a) Develop an expression for the maximum efficiency of a heat engine
- (b) Introduce Entropy ( $S$ ) as a State Function (needed to characterize spontaneous processes)

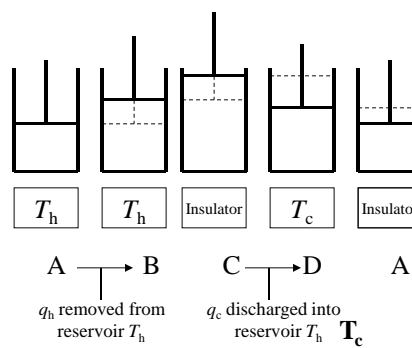
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## The Carnot Cycle (Reversible)

**System:** 1 mole of Perfect Gas



1. Rev. Isothermal Expansion from  $V_A$  to  $V_B$
2. Rev. Adiabatic Expansion from  $V_B$  to  $V_C$
3. Rev. Isothermal Compression from  $V_C$  to  $V_D$
4. Rev. Adiabatic Compression from  $V_D$  to  $V_A$



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1. Rev. Isothermal Expansion from  $V_A$  to  $V_B$  ( $T = T_h$ )

$$\Delta U_1 = C_{V,m} \Delta T = 0 \quad w_1 = -RT_h \ln\left(\frac{V_B}{V_A}\right) < 0$$

$$q_1 = -w_1 = +RT_h \ln\left(\frac{V_B}{V_A}\right) > 0$$

2. Rev. Adiabatic Expansion from  $V_B$  to  $V_C$  ( $T_h \rightarrow T_c$ )

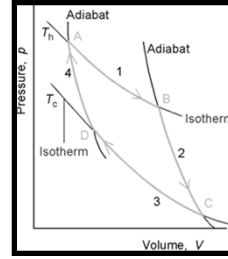
$$\Delta U_2 = C_{V,m} (T_c - T_h) < 0 \quad q_2 = 0 \quad w_2 = \Delta U_2 = C_{V,m} (T_c - T_h) < 0$$

3. Rev. Isothermal Compression from  $V_C$  to  $V_D$  ( $T = T_c$ )

$$\Delta U_3 = C_{V,m} \Delta T = 0 \quad w_3 = -RT_c \ln\left(\frac{V_D}{V_C}\right) > 0 \quad q_3 = -w_3 = +RT_c \ln\left(\frac{V_D}{V_C}\right) < 0$$

4. Rev. Adiabatic Compression from  $V_D$  to  $V_A$  ( $T_c \rightarrow T_h$ )

$$\Delta U_4 = C_{V,m} (T_h - T_c) > 0 \quad q_4 = 0 \quad w_4 = \Delta U_4 = C_{V,m} (T_h - T_c) > 0$$



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**Timeout:** Relation of  $V_D/V_C$  to  $V_B/V_A$

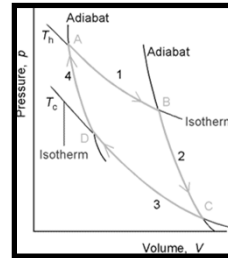
Steps 2 and 4 are adiabatic. In Chapter 2, we learned that, for an adiabatic expansion or compression:

$$\left(\frac{T_{fin}}{T_{init}}\right) = \left(\frac{V_{init}}{V_{fin}}\right)^{\frac{R}{C_{V,m}}} \quad \text{or} \quad \frac{V_{init}}{V_{fin}} = \left(\frac{T_{fin}}{T_{init}}\right)^{\frac{C_{V,m}}{R}}$$

Step 2:  $V_B \rightarrow V_C$  and  $T_h \rightarrow T_c$ :  $\frac{V_B}{V_C} = \left(\frac{T_c}{T_h}\right)^{\frac{C_{V,m}}{R}}$

Step 4:  $V_D \rightarrow V_A$  and  $T_c \rightarrow T_h$ :  $\frac{V_D}{V_A} = \left(\frac{T_h}{T_c}\right)^{\frac{C_{V,m}}{R}} \rightarrow \frac{V_A}{V_D} = \left(\frac{T_c}{T_h}\right)^{\frac{C_{V,m}}{R}}$

Therefore:  $\frac{V_B}{V_C} = \frac{V_A}{V_D} \rightarrow \frac{V_D}{V_C} = \frac{V_A}{V_B} = \left(\frac{V_B}{V_A}\right)^{-1}$



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## Totals around the Cycle

### Internal Energy

$$\Delta U_{tot} = \Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4$$

$$\Delta U_{tot} = 0 + C_{V,m}(T_c - T_h) + 0 + C_{V,m}(T_h - T_c) = 0$$

Expected for a State Function

### Work

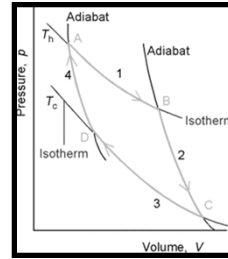
$$w_{tot} = w_1 + w_2 + w_3 + w_4$$

$$w_{tot} = -RT_h \ln(V_B/V_A) + C_{V,m}(T_c - T_h) - RT_c \ln(V_D/V_C) + C_{V,m}(T_h - T_c)$$

$$w_{tot} = -RT_h \ln(V_B/V_A) - RT_c \ln(V_D/V_C) = -RT_h \ln(V_B/V_A) - RT_c \ln(V_B/V_A)^{-1}$$

$$w_{tot} = R \ln(V_B/V_A)(T_c - T_h) < 0$$

Not surprising that  $w_{tot} \neq 0$  because  $w$  is not a State Function



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## Totals around the Cycle

### Heat

$$q_{tot} = q_1 + q_2 + q_3 + q_4$$

$$q_{tot} = +RT_h \ln(V_B/V_A) + 0 + RT_c \ln(V_D/V_C) + 0$$

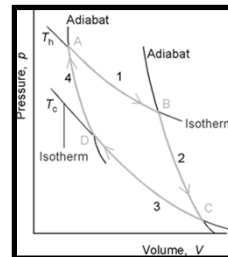
$$q_{tot} = +RT_h \ln(V_B/V_A) + RT_c \ln(V_B/V_A)^{-1}$$

$$q_{tot} = R \ln(V_B/V_A)(T_h - T_c) > 0$$

Not surprising that  $q_{tot} \neq 0$  because  $q$  is not a State Function

$$\text{However, note that: } w_{tot} + q_{tot} = R \ln(V_B/V_A)(T_c - T_h) + R \ln(V_B/V_A)(T_h - T_c) = 0$$

Expected because:  $q_{tot} + w_{tot} = \Delta U_{tot} = 0$

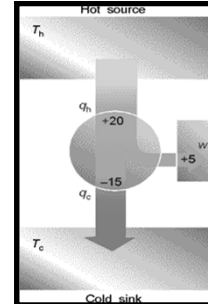


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## Thermodynamic Efficiency of the Carnot Cycle (Engine)

The idealized Carnot Cycle is similar to real heat engines in that it:

1. Removes heat from a high temperature source ( $T_h$ )  
( $q_h = q_1$  in the Isothermal Expansion at  $T_h$ )
2. Performs work on the surroundings  
(Work performed is  $-w_{tot}$ )
3. Expels the remaining heat into a cold temperature sink ( $q_c = q_3$  in the Isothermal Compression at  $T_c$ )



The Thermodynamic Efficiency ( $\epsilon$ ) is defined as:

$$\epsilon = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{-w_{tot}}{q_h}$$

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$$\epsilon = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{-w_{tot}}{q_h} = \frac{+q_{tot}}{q_h} = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h}$$

$\uparrow$   
 Since  $q_{tot} + w_{tot} = 0$

The ratio of heats can be related to the temperatures of the two reservoirs.

$$q_h = q_1 = RT_h \ln\left(\frac{V_B}{V_A}\right) \quad q_c = q_3 = RT_c \ln\left(\frac{V_D}{V_C}\right) = RT_c \ln\left(\frac{V_B}{V_A}\right)^{-1} = -RT_c \ln\left(\frac{V_B}{V_A}\right)$$

Therefore: 
$$\frac{q_c}{q_h} = \frac{-RT_c \ln\left(\frac{V_B}{V_A}\right)}{RT_h \ln\left(\frac{V_B}{V_A}\right)} = -\frac{T_c}{T_h}$$

Thus, the efficiency of a Carnot engine is:

$$\epsilon = \epsilon_{rev} = 1 - \frac{T_c}{T_h}$$

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**Notes:**

$$\varepsilon = \varepsilon_{rev} = 1 - \frac{T_c}{T_h}$$

Although this result was derived for the idealized Carnot cycle, it can be proven that the efficiency of all reversible engines are the same.

(The explanation is given in the text, but you are not responsible for it)

The efficiency of a real (i.e. irreversible) engine is lower than for reversible engines.

$$\varepsilon_{irrev} < 1 - \frac{T_c}{T_h}$$

$\varepsilon = 1$  ??

It is obvious from the expression that the only way one can achieve perfect efficiency is if either:

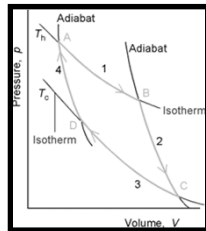
- (a)  $T_h = \infty$ . Obviously not possible.
- (b)  $T_c = 0$  K. The Third Law of Thermodynamics is that one cannot reach 0 K

Thus, one of the statements of the Second Law of Thermodynamics (due to Lord Kelvin) is that the efficiency of an engine cannot be unity; i.e. it is not possible to convert 100% of the heat taken from a thermal reservoir to useful work.

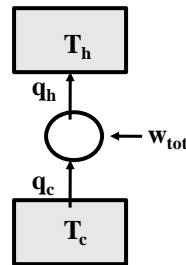
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## Refrigeration

If a heat engine is operated in reverse, it becomes a refrigerator.



Reverse all steps



**Coefficient of Performance (c)**

$$c = \frac{\text{Heat removed from } T_c}{\text{Work input required}} = \frac{q_c}{w_{tot}} = \frac{q_c}{-q_{tot}} = \frac{q_c}{-q_c - q_h} = \frac{q_c/q_h}{-q_c/q_h - 1}$$

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## Refrigeration

### Coefficient of Performance (c)

$$c = \frac{\text{Heat removed from } T_c}{\text{Work input required}} = \frac{q_c}{w_{\text{tot}}} = \frac{q_c}{-q_{\text{tot}}} = \frac{q_c}{-q_c - q_h} = \frac{q_c/q_h}{-q_c/q_h - 1}$$

Remember that we showed:  $\frac{q_c}{q_h} = -\frac{T_c}{T_h}$

Therefore:  $c = \frac{q_c}{w_{\text{tot}}} = \frac{q_c/q_h}{-q_c/q_h - 1} = \frac{-T_c/T_h}{+T_c/T_h - 1} = -\frac{-T_c}{T_c - T_h} = \frac{T_c}{T_h - T_c}$

$$c = \frac{q_c}{w_{\text{tot}}} = \frac{T_c}{T_h - T_c}$$

A "perfect" refrigerator would have  $c \rightarrow \infty$

For a Carnot refrigerator with  $T_h = 298 \text{ K}$  and  $T_c = 273 \text{ K}$ ,  $c = 11$ .

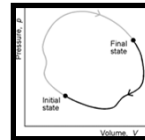
Real refrigerators would have a lower coefficient of performance

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## Entropy (S): A new State Function

The definition of a State Function is that its cyclic integral vanishes.

$$\oint df = 0 \longrightarrow \left[ \int_{\text{init}}^{\text{fin}} df \right]_{\text{Path A}} = \left[ \int_{\text{init}}^{\text{fin}} df \right]_{\text{Path B}}$$



For the Carnot Cycle, we saw that:

$$q_{\text{tot}} = \sum_{\text{cycle}} q_i = RT_h \ln(V_B/V_A) + RT_c \ln(V_D/V_C) = RT_h \ln(V_B/V_A) - RT_c \ln(V_B/V_A) \neq 0$$

Not surprising because  $q$  is not a State Function

However, let's consider summing  $q_i/T_i$

$$\sum_{\text{cycle}} \frac{q_i}{T_i} = \frac{RT_h \ln(V_B/V_A)}{T_h} + \frac{RT_c \ln(V_D/V_C)}{T_c} = R \ln(V_B/V_A) - R \ln(V_B/V_A) = 0$$

So:  $\sum_{\text{cycle}} \frac{q_i}{T_i} = 0$  for the Carnot Cycle

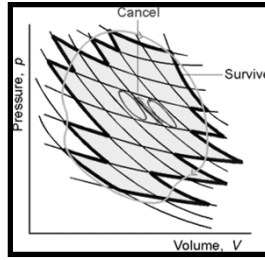
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So:  $\sum_{\text{cycle}} \frac{q_i}{T_i} = 0$  for the Carnot Cycle

Using this result for the Carnot Cycle, it can be shown that:

$$\sum_{\text{cycle}} \frac{q_{i,rev}}{T_i} = 0 \quad \text{for any reversible cycle}$$

and in the limiting case:  $\oint \frac{dq_{rev}}{T} = 0$



This permits us to define a new State Function Entropy (S) by its differential:

$$dS \equiv \frac{dq_{rev}}{T} \longrightarrow \Delta S = S_{fin} - S_{init} = \int_{init}^{fin} \frac{dq_{rev}}{T}$$

It is critically important to note that if a process is **irreversible**, one cannot use the above expression to compute the entropy change.

As a matter of fact, it can be shown that:  $\Delta S > \int_{init}^{fin} \frac{dq_{irrev}}{T}$

i.e. if you use the formula incorrectly (i.e. for an irreversible process, the only thing you will know is that your answer is too low, but not by how much.

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i.e. if you use the formula incorrectly (i.e. for an irreversible process, the only thing you will know is that your answer is too low, but not by how much.

i.e. S is a State Function, but its change can be calculated from the defining formula only if the process is reversible

However, if one can devise a reversible path to go from the same initial to the same final state, then the entropy change can be calculated from the formula:

$$\Delta S_{irrev} = \Delta S_{rev} = \int_{init}^{fin} \frac{dq_{rev}}{T}$$

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## Interpretation of $\Delta S$

$\Delta S$  is a measure of the amount of increase OR decrease in the degree of disorder (randomness)\*\* during a process.

<p><b>T</b></p> <div style="border: 1px solid gray; background-color: #e0e0e0; padding: 5px; display: inline-block; margin: 5px;">System</div> <p style="margin: 5px 0;">↑</p> <p><b>q<sub>rev</sub></b></p>	<p><b>General</b></p> $\Delta S = \int \frac{dq_{rev}}{T}$	<p><b>Isothermal</b></p> $\Delta S = \frac{q_{rev}}{T}$
	<p><b>Units</b></p> <p><math>\Delta S</math>: J/K</p> <p><math>\Delta S_m</math>: J/mol-K</p>	<p><b>Trends</b></p> <p><math>\Delta S \propto q_{rev}</math></p> <p><math>\Delta S \propto 1 / T</math></p> <p>If <math>q_{rev} &lt; 0</math>, <math>\Delta S &lt; 0</math></p>

\*\*Some texts refers to this as "energy dispersal", which is basically the same thing.

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## The Second Law of Thermodynamics

Statement #1: Kelvin

It is impossible to convert heat completely into work in a cyclic process.  
i.e. The efficiency of a heat engine must be less than 1.

$$\varepsilon \leq 1 - \frac{T_c}{T_h} < 1$$

Statement #2: Clausius

Heat cannot flow spontaneously from a lower temperature material to a higher temperature material.

i.e. The Coefficient of Performance of a refrigerator must be finite:

$$c \leq \frac{T_c}{T_h - T_c} < \infty$$

Statement #3: Entropy

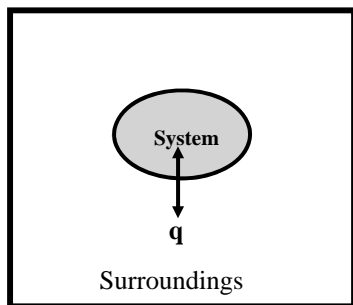
The entropy of an isolated system increases in the course of a **spontaneous** change.

Note that the Universe is an "isolated system"

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“The entropy of the Universe always increases.”

### The Universe



Heat exchange between the system and surroundings induces entropy changes in both the system ( $\Delta S_{\text{sys}}$ ) and the surroundings ( $\Delta S_{\text{surr}}$ ).

Spontaneous (Irreversible) Processes

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

Reversible (Equilibrium) Processes

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

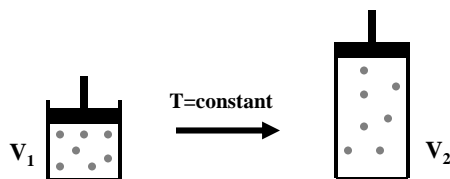
Spont. ↓  
Rev. ↑

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### Entropy Changes in Some Reversible Processes

We will first calculate the entropy changes of the system and surroundings  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  for some reversible processes.

#### Reversible Isothermal Expansion (or Compression) of a Perfect Gas



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### System

$$\Delta U = nC_{V,m}\Delta T = 0 \rightarrow q_{\text{sys}} \equiv q = -w = -[-nRT \ln(V_2/V_1)] = +nRT \ln(V_2/V_1)$$

$$\Delta S \equiv \Delta S_{\text{sys}} = \frac{q}{T} = \frac{nRT \ln(V_2/V_1)}{T} = nR \ln(V_2/V_1)$$

### Surroundings

$$q_{\text{surr}} = -q = -nRT \ln(V_2/V_1) \rightarrow \Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = \frac{-nRT \ln(V_2/V_1)}{T} = -nR \ln(V_2/V_1)$$

### Universe

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = +nR \ln(V_2/V_1) + [-nR \ln(V_2/V_1)] = 0$$

Expansion ( $V_2 > V_1$ )

$$\Delta S_{\text{sys}} > 0$$

$$\Delta S_{\text{surr}} < 0$$

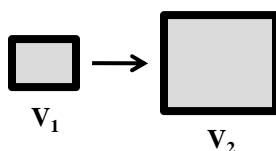
Compression ( $V_2 < V_1$ )

$$\Delta S_{\text{sys}} < 0$$

$$\Delta S_{\text{surr}} > 0$$

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### Reversible Adiabatic Expansion (or Compression) of a Perfect Gas



$$dq_{\text{sys}} = dq = 0 \quad \Delta S_{\text{sys}} = \int \frac{dq_{\text{sys}}}{T} = 0 \quad \Delta S_{\text{surr}} = \int \frac{dq_{\text{surr}}}{T} = 0$$

#### Expansion

$$\Delta U = nC_{V,m} \Delta T = w < 0. \text{ Therefore, } \Delta T < 0$$

Spatial disorder increases, but thermal order decreases

#### Compression

$$\Delta U = nC_{V,m} \Delta T = w > 0. \text{ Therefore, } \Delta T > 0$$

Spatial disorder decreases, but thermal order increases

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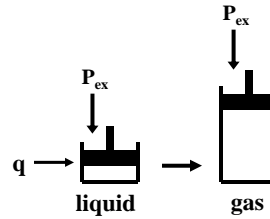


## Reversible Phase Transitions

One example is vaporization (right).

One can also have:

2. condensation
3. fusion (melting)
4. crystallization (freezing)
5. sublimation
6. deposition



Phase transitions (trs in text) occur at constant pressure and temperature

### System

$$\Delta S_{\text{sys}} = \Delta_{\text{trs}} S = \int \frac{dq_{\text{trs}}}{T} = \frac{q_{\text{trs}}}{T} = \frac{\Delta_{\text{trs}} H}{T_{\text{trs}}}$$

### Surroundings

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{trs}}} = \frac{-\Delta_{\text{trs}} H}{T_{\text{trs}}}$$

### Universe

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \frac{\Delta_{\text{trs}} H}{T_{\text{trs}}} + \left[ \frac{-\Delta_{\text{trs}} H}{T_{\text{trs}}} \right] = 0$$

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**Example:** Calculate the entropy changes of the system and surroundings (in J/K) when 195 g of Benzene vapor condenses to the liquid at its normal boiling point.

$$M(\text{C}_6\text{H}_6) = 78 \text{ g/mol}$$

$$\Delta_{\text{vap}} H = 30.8 \text{ kJ/mol}$$

$$T_{\text{b}} = 80 \text{ }^\circ\text{C}$$

$$\Delta S_{\text{sys}} = -218 \text{ J/K}$$

$$\Delta S_{\text{surr}} = +218 \text{ J/K}$$

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**Homework:** Calculate the entropy changes of the system and surroundings (in J/K) when 36 g of H<sub>2</sub>O(s) melts at 0 °C.

$$M(\text{H}_2\text{O}) = 18 \text{ g/mol}$$

$$\Delta_{\text{fus}}H = 6.01 \text{ kJ/mol}$$

$$\Delta S_{\text{sys}} = +44.0 \text{ J/K}$$

$$\Delta S_{\text{surr}} = -44.0 \text{ J/K}$$

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### Trouton's Rule

According to Trouton's Rule, the entropy of vaporization of a substance is approximately:  $\Delta_{\text{vap}}S \approx 85 \text{ J/mol-K}$  at its normal boiling point.

Compound	T <sub>b</sub> [K]	$\Delta_{\text{vap}}H$ [kJ/mol]	$\Delta_{\text{vap}}S$ [J/mol-K]	
H <sub>2</sub> O	373	40.7	109.1	High
CH <sub>3</sub> OH	337	35.3	104.7	
.....				
C <sub>6</sub> H <sub>6</sub>	353	30.8	87.3	$\approx 85 \text{ J/mol-K}$
CCl <sub>4</sub>	350	30.1	86.0	
C <sub>10</sub> H <sub>8</sub>	491	40.5	82.5	
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	308	26.0	84.4	
H <sub>2</sub> S	213	18.7	87.8	
.....				
CH <sub>4</sub>	112	8.2	73.2	Low

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Trouton's Rule can be used to provide an estimate of the Enthalpy of Vaporization of a substance.

**Example:** The normal boiling point of Br<sub>2</sub>(l) is 59 °C

Use Trouton's Rule to estimate the Enthalpy of Vaporization of Br<sub>2</sub>.

$$\Delta_{\text{vap}}H(\text{Est.}) = 28.2 \text{ kJ/mol}$$

$$\Delta_{\text{vap}}H(\text{Exp.}) = 29.5 \text{ kJ/mol}$$

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## Reversible Heating or Cooling (at constant P or V)

### Constant Pressure

**System**

$$\frac{dq_p}{dT} = C_p = nC_{p,m} \longrightarrow dq_p = C_p = nC_{p,m} dT$$

$$\Delta S_{\text{sys}} \equiv \Delta S = \int_{T_1}^{T_2} \frac{dq_p}{T} = \int_{T_1}^{T_2} \frac{nC_{p,m} dT}{T} = nC_{p,m} \ln(T_2 / T_1)$$

if C<sub>p,m</sub> is constant

**Surroundings** dq<sub>surr</sub> = - dq<sub>p</sub>

$$\text{Therefore: } \Delta S_{\text{surr}} = \int_{T_1}^{T_2} \frac{-dq_p}{T} = - \int_{T_1}^{T_2} \frac{nC_{p,m} dT}{T} = -nC_{p,m} \ln(T_2 / T_1)$$

if C<sub>p,m</sub> is constant

Heating (T<sub>2</sub> > T<sub>1</sub>)

$$\Delta S_{\text{sys}} > 0$$

$$\Delta S_{\text{surr}} < 0$$

Cooling (T<sub>2</sub> < T<sub>1</sub>)

$$\Delta S_{\text{sys}} < 0$$

$$\Delta S_{\text{surr}} > 0$$

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**Example:** 2 moles of Ar(g) is initially at 25 °C in a 10 L container.  
 Calculate  $\Delta S (= \Delta S_{\text{sys}})$  if the gas is simultaneously heated to 100 °C  
 and compressed to 5 L.

$$R = 8.31 \text{ J/mol}\cdot\text{K}$$

$$C_{V,m} = (3/2)R = 12.5 \text{ J/mol}\cdot\text{K}$$

Consider this to be a 2 step process: 1. Heat at constant volume to 100 °C  
 2. Compress to 5 L

1. Heating at constant volume from  $T_1 = 298 \text{ K}$  to  $T_2 = 373 \text{ K}$

$$\Delta S_1 = \int_{T_1}^{T_2} \frac{nC_{V,m} dT}{T} = nC_{V,m} \ln(T_2 / T_1) = 2 \text{ mol} (12.5 \text{ J/mol}\cdot\text{K}) \ln(373 / 298) \\ = +5.6 \text{ J/K}$$

2. Compression at constant temperature from  $V_1 = 10 \text{ L}$  to  $V_2 = 5 \text{ L}$

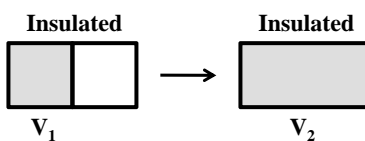
$$\Delta S_2 = nR \ln(V_2 / V_1) = 2 \text{ mol} (8.31 \text{ J/mol}\cdot\text{K}) \ln(5 / 10) \\ = -11.5 \text{ J/K}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = +5.6 - 11.5 = -5.9 \text{ J/K}$$

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## Entropy Changes in Irreversible Processes

### Irreversible Adiabatic Expansion into Vacuum



$$\text{Adiabatic: } dq_{\text{sys}} = dq_{\text{surr}} = 0$$

#### Surroundings

$$\Delta S_{\text{surr}} = \int \frac{dq_{\text{surr}}}{T} = 0$$

#### System

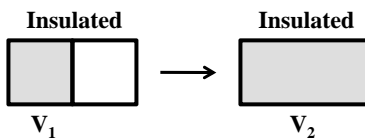
$$\Delta S_{\text{sys}} \neq \int \frac{dq_{\text{sys}}}{T} \neq 0$$

We **cannot** use the heat for this irreversible process to calculate  $\Delta S_{\text{surr}}$ .

We must devise an equivalent **reversible** process to accomplish the same change.

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### Irreversible Adiabatic Expansion into Vacuum



**System: Reversible Path**

$$q = 0$$

$$w = 0$$

$$\text{Therefore: } \Delta U = nC_{v,m}\Delta T = 0 \rightarrow T = \text{constant}$$

The initial and final states of the irreversible adiabatic expansion into vacuum are the same as for a **reversible** isothermal expansion from  $V_1$  to  $V_2$

$$\Delta S_{\text{sys}} = \Delta S_{\text{irrev}} = \Delta S(\text{Rev. Iso. Exp.}) = nR \ln(V_2 / V_1)$$

**Universe**

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = nR \ln(V_2 / V_1) + 0 = nR \ln(V_2 / V_1) > 0$$

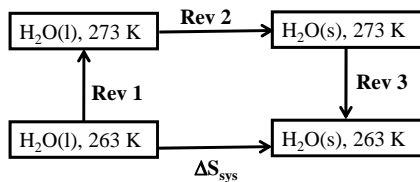
$\Delta S_{\text{univ}} > 0$  for a spontaneous (irrev.) process

### The Freezing of Supercooled Water

Calculate  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$  and  $\Delta S_{\text{univ}}$  when 1 mole of liquid water freezes at  $-10^\circ\text{C}$  ( $=263\text{ K}$ )

**System**

We need a reversible path:



**Data**

$$C_{p,m}(\text{liq}) = 75.3 \text{ J/mol-K}$$

$$C_{p,m}(\text{sol}) = 37.7 \text{ J/mol-K}$$

$$\Delta_{\text{fus}}H(273 \text{ K}) = +6010 \text{ J/mol}$$

$$\Delta S_{\text{sys}} = \Delta S_1 + \Delta S_2 + \Delta S_3 \xrightarrow{\text{In Class}} \Delta S_{\text{sys}} = -20.6 \text{ J/mol-K}$$

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### The Freezing of Supercooled Water

Calculate  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$  and  $\Delta S_{\text{univ}}$  when 1 mole of liquid water freezes at  $-10\text{ }^{\circ}\text{C}$  ( $=263\text{ K}$ )

#### Surroundings

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{263}} = \frac{-q_{\text{sys}}}{T_{263}} = \frac{-\Delta_{\text{crys}}H(263)}{T_{263}}$$

Seems pretty simple from here. **However**, we need the transition  $\Delta H$  at  $263\text{ K}$ , **not**  $273\text{ K}$ .

#### In class

$$\Delta_{\text{crys}}H(263\text{ K}) = -5634\text{ J/mol}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta_{\text{crys}}H(263)}{T_{263}} = \frac{-(-5634\text{ J/mol})}{263\text{ K}} = +21.4\text{ J/mol}\cdot\text{K}$$

#### Universe

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -20.6\text{ J/mol}\cdot\text{K} + 21.4\text{ J/mol}\cdot\text{K} = +0.8\text{ J/mol}\cdot\text{K}$$

$\Delta S_{\text{univ}} > 0$  for a spontaneous (irrev.) process

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### The Boiling of Superheated Benzene

**Homework:** Calculate  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$  and  $\Delta S_{\text{univ}}$  for the vaporization of one mole of liquid Benzene at  $100\text{ }^{\circ}\text{C}$

#### Data

$$T_b = 80\text{ }^{\circ}\text{C} = 353\text{ K}$$

$$C_{\text{p,m}}(\text{liq}) = 138.7\text{ J/mol}\cdot\text{K}$$

$$C_{\text{p,m}}(\text{gas}) = 35.1\text{ J/mol}\cdot\text{K}$$

$$\Delta_{\text{vap}}H(353\text{ K}) = +35.7\text{ kJ/mol}$$

$$\Delta S_{\text{sys}} = +95.4\text{ J/mol}\cdot\text{K}$$

$$\Delta S_{\text{surr}} = -90.2\text{ J/mol}\cdot\text{K}$$

$$\Delta S_{\text{univ}} = +5.2\text{ J/mol}\cdot\text{K}$$

**Note:** For the calculation of  $\Delta S_{\text{surr}}$ , we first computed that

$$\Delta_{\text{vap}}H(373) = +33,630\text{ J/mol}$$

This is Homework #3.7. The complete solution is given with the other homework solutions on the course web site.

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### The Third Law of Thermodynamics

The entropies of all pure crystalline materials at  $T = 0 \text{ K}$  are zero.

$$S_m^\circ(0 \text{ K}) = 0$$

i.e. there is no disorder in a pure crystal at absolute zero.

#### Exceptions

COCCO  
OCCOOC  
COCOOC  
OCOC

Disordered  
Crystals



Amorphous  
Solids

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### Importance of the Third Law

The Third Law permits us to compute absolute entropies of substances at any arbitrary temperature (usually  $25^\circ\text{C}$ )

$$\Delta S = \int \frac{dq_{rev}}{T}$$

$$S_m^\circ(T) - \underset{\parallel}{\cancel{S_m^\circ(0 \text{ K})}} = S_m^\circ(T) = \int_0^T \frac{dq_{rev}}{T}$$

These calculated entropies are tabulated and can be used to determine entropy changes for reactions.

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### The Determination of Third Law Entropies

$$S_m^\circ(T) = S_m^\circ(0) + \int_0^{T_f} \frac{C_p(s)dT}{T} + \frac{\Delta_{\text{fus}}H}{T_f} + \int_{T_f}^{T_b} \frac{C_p(l)dT}{T} + \frac{\Delta_{\text{vap}}H}{T_f} + \int_{T_b}^T \frac{C_p(g)dT}{T}$$

$\parallel$   
 $0$

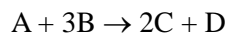
Problem: difficult to measure  $C_p$  near  $T = 0$ . In practice we do an extrapolation. At low  $T$  we find that the expression  $C_p = aT^3$  works well. (Debye Extrapolation)

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### Entropy Changes in Chemical Reactions

Reactants  $\rightarrow$  Products

$$\Delta_r S^\circ = \sum n_{\text{Prod}} S_m^\circ(\text{Prod}) - \sum n_{\text{Rct}} S_m^\circ(\text{Rct})$$



$$\Delta_r S = [2 \cdot S_m^\circ(C) + S_m^\circ(D)] - [S_m^\circ(A) + 3 \cdot S_m^\circ(B)]$$

NOTE:  $S_m^\circ \neq 0$  for elements  
(unlike  $\Delta_f H^\circ$ )

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Example: Use standard molar entropies to calculate  $\Delta_r S^\circ$   
for the reaction,  $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ .

Cmpd.	$S_m^\circ$
$N_2(g)$	191.6 J/mol·K
$H_2(g)$	130.7
$NH_3(g)$	192.5

$$\begin{aligned}\Delta S &= [2S_m^\circ(NH_3)] - [S_m^\circ(N_2) + 3S_m^\circ(H_2)] \\ &= [2(192.5 \text{ J/mol}\cdot\text{K})] - [191.6 \text{ J/mol}\cdot\text{K} + 3(130.7 \text{ J/mol}\cdot\text{K})] \\ &= -198.7 \text{ J/K}\end{aligned}$$

Note that  $\Delta_r S^\circ \ll 0$ : 4 mol gas  $\rightarrow$  2 mol gas

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### The Temperature Dependence of Reaction Entropies

In Chapter 2, we developed an expression (Kirchoff's Law) to determine the reaction enthalpy at a second temperature,  $\Delta_r H(T_2)$  if we knew  $\Delta_r H(T_1)$ :

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r C_p dT$$

The same method can be used to determine an expression for the the temperature dependence of reaction entropies:

$$\Delta_r S(T_2) = \Delta_r S(T_1) + \int_{T_1}^{T_2} \frac{\Delta_r C_p}{T} dT$$

$$\text{where: } \Delta_r C_p = C_p(P) - C_p(R) = \sum_{\text{Prod}} \nu_{P_i} C_{p,m}(P_i) - \sum_{\text{Rct}} \nu_{R_i} C_{p,m}(R_i)$$

**Note:** If the heat capacities of reactants and products can be taken as approximately constant, then the above equation simplifies to:

$$\Delta_r S(T_2) = \Delta_r S(T_1) + \Delta_r C_p \ln(T_2 / T_1)$$

**You are NOT responsible for the temperature dependence of  $\Delta S$ . I will just comment on it briefly**

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Consider the combustion of hydrogen:  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$

For this reaction at 298 K (=25 °C), the reaction entropy is:

$$\Delta_r H(298 \text{ K}) = -326.7 \text{ kJ}$$

Calculate the reaction entropy at 373 K (=100 °C).

	<b>Species</b>	<b><math>C_{p,m}</math></b>
	$\text{H}_2(\text{g})$	33.6 J/mol-K
	$\text{O}_2(\text{g})$	29.4
	$\text{H}_2\text{O}(\text{l})$	75.3

$$\begin{aligned} \Delta_r C_p &= [2C_{p,m}(\text{H}_2\text{O})] - [2C_{p,m}(\text{H}_2) + C_{p,m}(\text{O}_2)] \\ &= [2(75.3)] - [2(33.6) + 29.4] = +54.0 \text{ J/K} \end{aligned}$$

$$\Delta_r S(T_2) = \Delta_r S(T_1) + \Delta_r C_p \ln(T_2 / T_1)$$

$$\Delta_r S(373 \text{ K}) = \Delta_r S(298 \text{ K}) + \Delta_r C_p \ln(373 / 298)$$

$$= -326.7 \text{ J/K} + (54.0 \text{ J/K}) \ln(373 / 298) = -314.6 \text{ J/K}$$

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### Concentrating on the System

We've learned that the Second Law of Thermodynamics can be utilized to ascertain whether a process is spontaneous (irreversible) or reversible (at equilibrium).

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \begin{matrix} \text{Spont.} \\ \downarrow \\ \geq 0 \\ \uparrow \\ \text{Rev.} \end{matrix}$$

However, we are usually interested primarily in the system, and not the surroundings.

It would be convenient to have criteria for spontaneity that depend solely upon system variables.

Actually, we do have system variables which can determine whether a process is spontaneous under two sets of specific conditions, both of which are very common.

1. The Gibbs Energy:  $G \equiv H - TS$  Constant Temperature and Pressure
2. The Helmholtz Energy:  $A \equiv U - TS$  Constant Temperature and Volume

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## The Gibbs Energy (G)

$$\begin{array}{l}
 \text{T = Constant} \\
 \text{P = Constant}
 \end{array}
 \quad
 \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

Spont. ↓  
 ↑ Rev.

$$\begin{array}{l}
 \text{Constant T} \\
 \text{Constant P}
 \end{array}
 \quad
 \begin{array}{l}
 \Delta S_{\text{sys}} + q_{\text{surr}}/T \geq 0 \\
 \Delta S_{\text{sys}} - q_{\text{sys}}/T \geq 0 \\
 \Delta S_{\text{sys}} - \Delta H_{\text{sys}}/T \geq 0 \\
 T\Delta S - \Delta H \geq 0
 \end{array}$$

Spont. ↓  
 ↑ Rev.

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$$\begin{array}{c}
 \text{Spont.} \\
 \downarrow \\
 \Delta H - T\Delta S \leq 0 \\
 \uparrow \\
 \text{Rev.}
 \end{array}$$

Define:  $G \equiv H - TS$

$$\Delta G = \Delta H - \Delta(TS)$$

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

$$\begin{array}{c}
 \text{Spont.} \\
 \downarrow \\
 \text{Therefore: } \Delta G \leq 0 \\
 \uparrow \\
 \text{Rev.}
 \end{array}$$

If  $\Delta G > 0$ , the process is spontaneous in the reverse direction.

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## The Helmholtz Energy (A)

$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$

Spont. ↓  
 ↑ Rev.

**T = Constant**  
**V = Constant**

**Difference from G**

Constant T      $\Delta S_{\text{sys}} + q_{\text{surr}}/T \geq 0$   
 $\Delta S_{\text{sys}} - q_{\text{sys}}/T \geq 0$

**Constant V**      $\Delta S_{\text{sys}} - \Delta U_{\text{sys}}/T \geq 0$      **Difference from G**

$T\Delta S - \Delta U \geq 0$   
 Spont. ↓  
 $\Delta U - T\Delta S \leq 0$   
 ↑ Rev.

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Spont. ↓  
 $\Delta U - T\Delta S \leq 0$   
 ↑ Rev.

Define:  $A \equiv U - TS$      **Difference from G**

$\Delta A = \Delta U - \Delta(TS)$   
 $\Delta A = \Delta U - T\Delta S$

Spont. ↓  
 Therefore:  $\Delta A \leq 0$   
 ↑ Rev.

If  $\Delta A > 0$ , the process is spontaneous in the reverse direction.

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**The material below is FYI. You are not responsible for it.**

### **The Helmholtz Energy and Maximum Work**

It can be shown (Sect. 3.5c) that the maximum work is related to  $\Delta A$  by:

Maximum work that can be performed by system:

$$-w_{\max} = -\Delta A$$

### **The Gibbs Energy and Maximum non-Expansion Work**

It can be shown (Sect. 3.5c) that the maximum non-expansion work (i.e. non-PV work) is related to  $\Delta G$  by:

Maximum non-expansion work that can be performed by system:

$$(-w_{\max})_{\text{non-PV}} = -\Delta G$$

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### **Factors Influencing Spontaneity (const T and p)**

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

$\Delta H$	$\Delta S$	$\Delta G$	
-	+	-	Spontaneous at all temperatures
+	-	+	Not Spontaneous at any temperature
+	+	+	Not Spontaneous at low temperature
		-	Spontaneous at high temperature Entropically driven reaction
-	-	+	Not Spontaneous at high temperature
		-	Spontaneous at low temperature Enthalpically driven reaction

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## Standard Reaction Gibbs Energies

Reactants  $\rightarrow$  Products

One method to calculate  $\Delta G^\circ$  for a reactions is:

- (1) Calculate  $\Delta H^\circ$  from values of  $\Delta_f H^\circ$  (Enthalpies of Formation)
- (2) Calculate  $\Delta S^\circ$  from values of  $S_m^\circ$  (Absolute Entropies)
- (3) Calculate  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

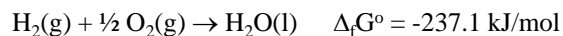
A second, direct, method is to use Gibbs Energies of Formation.

This method is closely analogous to the use of Enthalpies of Formation to determine reaction enthalpies (Chapter 2).

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## Gibbs Energy of Formation

The Gibbs Energy of Formation ( $\Delta_f G^\circ$ ) of a compound is the Gibbs energy to form one mole of the compound from the elements in their standard state; e.g.



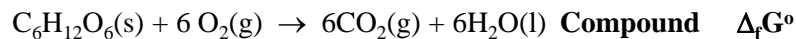
The Gibbs Energy change for a reaction is then given by:

$$\Delta_r G^\circ = \Delta_f G^\circ(\text{Prod}) - \Delta_f G^\circ(\text{Rct})$$

$$\Delta_r G^\circ = \sum_{\text{Prod}} \nu_{P_i} \Delta_f G^\circ(P_i) - \sum_{\text{Rct}} \nu_{R_i} \Delta_f G^\circ(R_i)$$

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Use the data in the table to calculate  $\Delta G^\circ$  for the reaction



Compound	$\Delta_f G^\circ$
$\text{C}_6\text{H}_{12}\text{O}_6$	-908.9 kJ/mol
$\text{CO}_2$	-394.4
$\text{H}_2\text{O}$	-237.1

$$\Delta_r G^\circ = [6\Delta_f G^\circ(\text{CO}_2) + 6\Delta_f G^\circ(\text{H}_2\text{O})] - [\Delta_f G^\circ(\text{C}_6\text{H}_{12}\text{O}_6) + 6\Delta_f G^\circ(\text{O}_2)]$$

$$\Delta_r G^\circ = [6(-394.4) + 6(-237.1)] - [(-908.9) + 6(0)]$$

$$\Delta_r G^\circ = -2880 \text{ kJ}$$

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## Combining the First and Second Laws

### Preliminary: Exact Differentials and Maxwell Relations

We have a number of State Functions in Thermodynamics, including U, H, S, A and G.

Earlier we learned that the differential of a State Function is an exact differential.

Now we will introduce a mathematical relation between the partial derivatives of exact differentials. Consider the total differential of a State Function  $z = z(x,y)$ :

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = Mdx + Ndy$$

A mathematical property of State Functions with exact differentials is that the values of the "mixed" partial derivatives is independent of the order of differentiation; i.e.

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y \quad \text{or} \quad \boxed{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y}$$

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### The Fundamental Equation

The First Law of Thermodynamics (in differential form) is:

$$dU = dq + dw$$

Assuming (1) reversible processes, (2) only PV work, and (3) a closed system, one has:

$$dS = \frac{dq}{T} \rightarrow dq = TdS \text{ and } dw = -pdV$$

Therefore:  $dU = TdS - pdV$

Using  $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

One can write a Maxwell relation from dU:  $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$

**Note:** This Maxwell Relation is not as useful as a couple of others coming up.

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### Expressions for dH, dA and dG + corresponding Maxwell Relations

#### Internal Energy (U)

$$dU = TdS - pdV \quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

#### Enthalpy (H)

$$H = U + pV$$

$$dH = d(U + pV) = dU + d(pV)$$

$$dH = (TdS - pdV) + (pdV + Vdp)$$

$$\boxed{dH = TdS + Vdp} \rightarrow \boxed{\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p}$$

Also not particularly useful, but hang in there.

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## Expressions for dH, dA and dG + related Maxwell Relations

### Helmholtz Energy (A)

$$A = U - TS$$

↓ In class

$$dA = -SdT - pdV \xrightarrow{\text{In class}} \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad \text{This Maxwell Relation is very useful}$$

### Gibbs Energy (G)

$$G = H - TS = U + pV - TS$$

↓ In class

$$dG = -SdT + Vdp \xrightarrow{\text{In class}} \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad \text{So is this one}$$

**Suggestion:** It is far easier to learn how to "derive" the above equations than to try to memorize all of them.

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## Applications of the Equations

### The Dependence of Internal Energy on Volume

In Chapter 2, we learned that the Internal Energy depends upon both the temperature and volume,  $U=U(V, T)$ :

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = \pi_T dV + C_V dT$$

$C_V = \left(\frac{\partial U}{\partial T}\right)_V$  Constant V Heat Capacity

$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$  Internal Pressure

However, we had no method to calculate the Internal Pressure,  $\pi_T$ .  
Now we do!!

$$dU = TdS - pdV \quad \text{Divide by } dV \text{ and hold } T \text{ constant.}$$

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - p \quad \text{That's nice, but how do we evaluate } (\partial S/\partial V)_T ?$$

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$dU = TdS - pdV$  Divide by  $dV$  and hold  $T$  constant.

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - p \quad \text{That's nice, but how do we evaluate } (\partial S/\partial V)_T?$$

Remember that:  $dA = -SdT - pdV \rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

And so, Voila:  $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - p = T \left(\frac{\partial p}{\partial T}\right)_V - p$

This equation is often termed a **Thermodynamic Equation of State** because it relates the pressure to thermodynamic properties of the system.

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**Review Example 1:** Evaluate the internal pressure,  $\pi_T$ , for a Perfect Gas  
(We performed this calculation in Chapter 2)

$$\pi_T = (\partial U/\partial V)_T = 0$$

So we have now proven that the Internal Energy is independent of volume for a Perfect Gas.

**Review Example 2:** The van der Waals Equation of State is:

(A) Develop an expression for  $\pi_T$  for a van der Waals gas

(We performed this calculation in Chapter 2)

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = a \left(\frac{n}{V}\right)^2 \quad \left[ p + a \left(\frac{n}{V}\right)^2 \right] [V - nb] = nRT$$

(B) For  $\text{CO}_2(\text{g})$ ,  $a = 3.61 \text{ atm L}^2/\text{mol}^2$ . What is  $\Delta U$  (in J) when 1 mol of  $\text{CO}_2$  is compressed from 1.0 L to 0.2 L? 1 L-atm = 101 J

$$\Delta U = -14.4 \text{ L-atm} \approx -1.5 \text{ kJ}$$

Note that  $\Delta U < 0$ , which is what one expects for an attractive gas when the molecules get closer together.

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### $C_p - C_V$ Revisited

In Chapter 2, starting with:  $C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V$

We derived the equation:  $C_p - C_V = \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_p$

We then presented the relation (without proof):  $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$

We now see where this relation comes from.

We used the expression for  $(\partial U/\partial V)_T$  to obtain the final equation for  $C_p - C_V$ :

$$C_p - C_V = TV \frac{\alpha^2}{\kappa_T} \quad \text{where } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \quad \text{and } \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$

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$$C_p - C_V = \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_p = TV \frac{\alpha^2}{\kappa_T}$$

**Comment:** We showed earlier that, for a van der Waals gas,  
 $(\partial U/\partial V)_p = a(n/V)^2$

This term is positive, as it will be for all "attractive" gases.

This result implies that  $C_p - C_V > R$  for all gases in which attractive forces predominate.

This is intuitively consistent with the expectation that it will be harder to separate molecules if there are attractive forces than if there are no interactions (i.e. a Perfect Gas)

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## Applications of the Equations

### The Dependence of Enthalpy on Pressure

In Chapter 2, we learned that the the Enthalpy depends upon both the temperature and pressure,  $H=H(p,T)$ :

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT = \left(\frac{\partial H}{\partial p}\right)_T dp + C_p dT \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

Constant Pressure Heat Capacity

In order to evaluate the first term in this equation, we presented (without proof):

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$$

We now have the tools to derive the above expression.

Let's prove this equation for  $\left(\frac{\partial H}{\partial p}\right)_T$  **in class**.

You should know how to perform this type of calculation (and similar ones).

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$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$$

Consider a gas which obeys the Equation of State:

$$pV = nRT - Bp \quad , \quad B = 2.0 L$$

Calculate the Enthalpy change,  $\Delta H$  (in J), when one mole of this gas is compressed isothermally (at 25 °C) from 1. atm to 10. atm.

$$1 \text{ L}\cdot\text{atm} = 101 \text{ J}$$

$$\left(\frac{\partial H}{\partial p}\right)_T = -B$$

$$\begin{aligned} \Delta H &= -B[p_2 - p_1] = -18 L \cdot \text{atm} \cdot \frac{101 \text{ J}}{1 L \cdot \text{atm}} \\ &= -1820 \text{ J} = -1.8 \text{ kJ} \end{aligned}$$

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### The Dependence of Thermodynamic Quantities on Volume for a non-Perfect Gas

Consider a hypothetical gas that obeys the Equation of State:  $pV^2 = nRT$

If this gas undergoes an isothermal expansion from  $V_1$  to  $V_2$ , develop **integrated** expressions for the following quantities in terms of  $n$ ,  $R$ ,  $T$ ,  $V_1$  and  $V_2$ :  $\Delta S$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta A$  and  $\Delta G$ .

Do **not** use either  $\Delta A = \Delta U - T\Delta S$  or  $\Delta G = \Delta H - T\Delta S$  except as a consistency check on your calculations.

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V^2} \rightarrow \Delta S = nR \left[ \frac{1}{V_1} - \frac{1}{V_2} \right] \quad \left(\frac{\partial A}{\partial V}\right)_T = -\frac{nRT}{V^2} \rightarrow \Delta A = -nRT \left[ \frac{1}{V_1} - \frac{1}{V_2} \right]$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \rightarrow \Delta U = 0 \quad \left(\frac{\partial G}{\partial V}\right)_T = -\frac{2nRT}{V^2} \rightarrow \Delta G = -2nRT \left[ \frac{1}{V_1} - \frac{1}{V_2} \right]$$

$$\left(\frac{\partial H}{\partial V}\right)_T = -\frac{nRT}{V^2} \rightarrow \Delta H = -nRT \left[ \frac{1}{V_1} - \frac{1}{V_2} \right]$$

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### The Dependence of Thermodynamic Quantities on Pressure for a non-Perfect Gas

Consider a hypothetical gas that obeys the Equation of State:  $pV = nRT^2$

If this gas undergoes an isothermal compression from  $p_1$  to  $p_2$ , develop **integrated** expressions for the following quantities in terms of  $n$ ,  $R$ ,  $T$ ,  $p_1$  and  $p_2$ :  $\Delta S$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta A$  and  $\Delta G$ .

Do **not** use either  $\Delta A = \Delta U - T\Delta S$  or  $\Delta G = \Delta H - T\Delta S$  except as a consistency check on your calculations.

$$\left(\frac{\partial S}{\partial p}\right)_T = -\frac{2nRT}{P} \rightarrow \Delta S = -2nRT \ln(p_2/p_1) \quad \left(\frac{\partial A}{\partial p}\right)_T = +\frac{nRT^2}{p} \rightarrow \Delta A = +nRT^2 \ln(p_2/p_1)$$

$$\left(\frac{\partial U}{\partial p}\right)_T = -\frac{nRT^2}{P} \rightarrow \Delta U = -nRT^2 \ln(p_2/p_1) \quad \left(\frac{\partial G}{\partial p}\right)_T = +\frac{nRT^2}{p} \rightarrow \Delta G = +nRT^2 \ln(p_2/p_1)$$

$$\left(\frac{\partial H}{\partial p}\right)_T = -\frac{nRT^2}{P} \rightarrow \Delta H = -nRT^2 \ln(p_2/p_1)$$

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**Homework:**

Consider a hypothetical gas that obeys the Equation of State:  $p^2V = nRT$

If this gas undergoes an isothermal compression from  $p_1$  to  $p_2$ , develop **integrated** expressions for the following quantities in terms of  $n$ ,  $R$ ,  $T$ ,  $p_1$  and  $p_2$ :  $\Delta S$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta A$  and  $\Delta G$ .

Do **not** use either  $\Delta A = \Delta U - T\Delta S$  or  $\Delta G = \Delta H - T\Delta S$  except as a consistency check on your calculations.

**Answers:**

$$\left(\frac{\partial S}{\partial p}\right)_T = -\frac{nR}{p^2} \rightarrow \Delta S = -nR \left[ \frac{1}{p_1} - \frac{1}{p_2} \right] \quad \left(\frac{\partial A}{\partial p}\right)_T = +\frac{2nRT}{p^2} \rightarrow \Delta A = +2nRT \left[ \frac{1}{p_1} - \frac{1}{p_2} \right]$$

$$\left(\frac{\partial U}{\partial p}\right)_T = +\frac{nRT}{p^2} \rightarrow \Delta U = +nRT \left[ \frac{1}{p_1} - \frac{1}{p_2} \right] \quad \left(\frac{\partial G}{\partial p}\right)_T = +\frac{nRT}{p^2} \rightarrow \Delta G = +nRT \left[ \frac{1}{p_1} - \frac{1}{p_2} \right]$$

$$\left(\frac{\partial H}{\partial p}\right)_T = 0 \rightarrow \Delta H = 0$$

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**Examples of Non-PV Work****This is FYI: You are NOT responsible for non-PV work**

One occasionally encounters other types of non-Pressure-Volume work in thermodynamics:

If an elastic material (e.g. a rubber band) is stretched, the work is:  $dw = +fdL$

F is the force and L is the length.

If an electric field is applied to a polarizable material, the work involved is:  $dw = -DdE$

E is the electric field strength and D is the resulting electrical displacement.

If a liquid with surface tension spreads on a solid surface, the work involved is:  $dw = +\gamma dA$

A is the surface area and  $\gamma$  is the surface area.

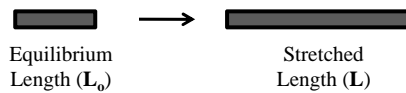
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## Thermodynamics of Rubber Elasticity This is FYI only

Pressure-Volume work is only one type of thermodynamic work that can be performed on a system.

Another type of work which very important in the rubber/elastomer industry is the work involved in stretching an elastomeric material (e.g. a rubber band) from it's equilibrium length.

We shall demonstrate that, although some of the equations will change, the same methods which we have learned can be used to calculate the thermodynamic quantities involved in this process.



The infinitesimal value of the work involved in stretching the rubbery material from  $L$  to  $L+dL$  is:  $dw = +fdL$

This is analogous to the term,  $dw = -pdV$ , in systems where there is pressure-volume work.

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The infinitesimal value of the work involved in stretching the rubbery material from  $L$  to  $L+dL$  is:  $dw = +fdL$

The First Law expression for  $dU$  is:  $dU = dq + dw = TdS + fdL$

The equations for the related thermodynamic quantities ( $H$ ,  $A$  and  $G$ ) are:

$$H = U - fL$$

$$A = U - TS$$

$$G = H - TS$$

Let's use the thermodynamic methods we've learned for P-V work to derive the following expressions for  $dH$ ,  $dA$  and  $dG$ :

$$dH = TdS - Ldf$$

$$dA = -SdT + fdL$$

$$dG = -SdT - LdF$$

We can also use  $dA$  and  $dG$  to obtain the following Maxwell Relations (**in class**):

$$\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L \quad \text{and} \quad \left(\frac{\partial S}{\partial f}\right)_T = +\left(\frac{\partial L}{\partial T}\right)_f$$

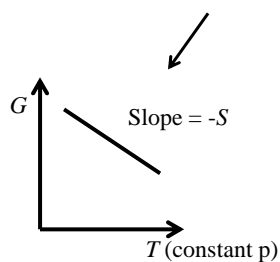
72



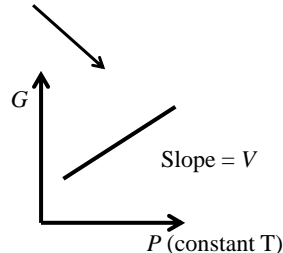
### Properties of the Gibbs Energy

$$dG = -SdT + Vdp = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

Thus:  $\left(\frac{\partial G}{\partial T}\right)_p = -S$  and  $\left(\frac{\partial G}{\partial p}\right)_T = +V$



$S$  is positive ( $-S$  is negative)  
so  $G$  is decreasing with  
increasing  $T$



$V$  is positive so  $G$  is  
increasing with  
increasing  $p$

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### Variation of the Gibbs Energy with Temperature

**Note:** We are performing the derivation below solely to obtain an equation useful when determining the temperature dependence of the equilibrium constant. You are **NOT** responsible for this derivation.

$$dG = -SdT + Vdp = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

Therefore:  $\left(\frac{\partial G}{\partial T}\right)_p = -S$

It is more convenient to put the variation of  $G$  in terms of  $H$ , rather than  $S$ .

$$G = H - TS \rightarrow S = \frac{H}{T} - \frac{G}{T} \rightarrow \left(\frac{\partial G}{\partial T}\right)_p = -\left(\frac{H}{T} - \frac{G}{T}\right) = -\frac{H}{T} + \frac{G}{T}$$

It is also more convenient (i.e. simpler functionality) to solve for the derivative of  $G/T$  (rather than of  $G$ ):

After a number of algebraic manipulations (for which you are **not** responsible), it can be shown that:

$$\left(\frac{\partial (G/T)}{\partial T}\right)_p = -\frac{H}{T^2}$$

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$$\left( \left( \frac{G}{T} \right) \right)_p = -\frac{H}{T^2}$$

If one is considering a reaction,  $R \rightarrow P$ , then the above equation can be applied to both reactants and products to get:

$$\left( \left( \frac{\Delta G}{T} \right) \right)_p = -\frac{\Delta H}{T^2} \quad \text{where } \Delta G = G_P - G_R \quad \text{and} \quad \Delta H = H_P - H_R$$

We will not discuss or use this equation at this time.

However, the equation will be very useful when we study the temperature dependence of equilibrium constants in Chapter 6 because  $\ln(K_{\text{eq}}) = -\Delta G^\circ/RT$

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### Variation of the Gibbs Energy with Pressure

$$dG = -SdT + Vdp = \left( \frac{\partial G}{\partial T} \right)_p dT + \left( \frac{\partial G}{\partial p} \right)_T dp$$

Therefore:  $\left( \frac{\partial G}{\partial p} \right)_T = +V$

For an isothermal change in pressure, one has:

$$\Delta G = G(p_{\text{fin}}) - G(p_{\text{init}}) = \int_{p_{\text{init}}}^{p_{\text{fin}}} \left( \frac{\partial G}{\partial p} \right)_T dp = \int_{p_{\text{init}}}^{p_{\text{fin}}} V dp$$

If we're dealing with the Molar Gibbs Energy, the equation is easily modified.

$$\Delta G_m = G_m(p_{\text{fin}}) - G_m(p_{\text{init}}) = \int_{p_{\text{init}}}^{p_{\text{fin}}} \left( \frac{\partial G}{\partial p} \right)_T dp = \int_{p_{\text{init}}}^{p_{\text{fin}}} V_m dp$$

or  $G_m(p_{\text{fin}}) = G_m(p_{\text{init}}) + \int_{p_{\text{init}}}^{p_{\text{fin}}} V_m dp$

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$$G_m(p_{fin}) = G_m(p_{init}) + \int_{p_{init}}^{p_{fin}} V_m dp$$

If the initial pressure is  $p^\circ = 1 \text{ bar}$ , then the above equation can be written as:

$$G_m(p) = G_m^\circ + \int_{p^\circ}^p V_m dp$$

### Liquid and Solids

Unlike gases, the molar volume of condensed phase materials (liquids and solids) is almost completely independent of pressure. Therefore, the above equation simplifies to:

$$G_m(p) = G_m^\circ + V_m \int_{p^\circ}^p dp = G_m^\circ + V_m (p - p^\circ)$$

**Example:** Calculate the change (in J) in the molar Gibbs energy  $[G_m(p) - G_m(p^\circ)]$  of one mole of ice at  $-10^\circ\text{C}$  when the applied pressure is increased from 1 bar to 5 bar.

$$G_m(p) - G_m(p^\circ) = 7.8 \text{ J} \approx 8 \text{ J}$$

$$1 \text{ L-bar} = 100 \text{ J}$$

$$M = 18 \text{ g/mol}$$

$$d = 0.92 \text{ g/cm}^3$$

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### The Synthesis of Diamond

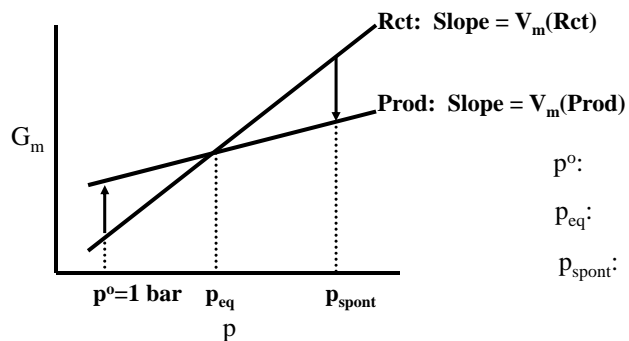
Consider a solid or liquid phase reaction:  $\text{Rct} \rightarrow \text{Prod}$

$$G_m(\text{Rct}) = G_m^\circ(\text{Rct}) + V_m(\text{Rct})(P - P^\circ)$$

$$G_m(\text{Prod}) = G_m^\circ(\text{Prod}) + V_m(\text{Prod})(P - P^\circ)$$

$$\Delta G_m = G_m(\text{Prod}) - G_m(\text{Rct}) \quad \Delta G_m^\circ = G_m^\circ(\text{Prod}) - G_m^\circ(\text{Rct})$$

$$\Delta G_m = \Delta G_m^\circ + \Delta V_m(p - p^\circ) \quad \Delta V_m = V_m(\text{Prod}) - V_m(\text{Rct})$$



$$p^\circ: \quad \Delta G_m > 0$$

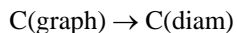
$$p_{eq}: \quad \Delta G_m = 0$$

$$p_{spont}: \quad \Delta G_m < 0$$

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$$\Delta G_m = \Delta G_m^\circ + \Delta V_m(p-p^\circ)$$

Let's apply this equation to the synthesis of diamond from graphite:



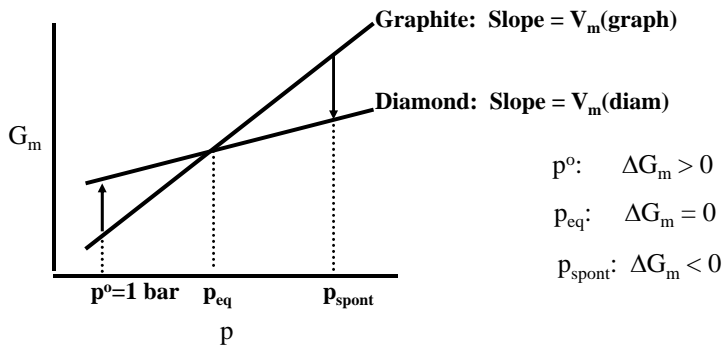
$$\begin{aligned} \text{At } 25^\circ\text{C, } \Delta G_m^\circ &= \Delta_f G^\circ(\text{diam}) - \Delta_f G^\circ(\text{graph}) \\ &= 2.90 \text{ kJ/mol} - 0 && \text{Reaction not} \\ &= 2.90 \times 10^3 \text{ J/mol} && \text{spontaneous} \\ &= 2.90 \times 10^3 \text{ kPa}\cdot\text{L/mol} && \text{at } P^\circ = 1 \text{ bar} \end{aligned}$$

$$\begin{aligned} V_m(\text{graph}) &= 5.33 \text{ mL/mol} && \text{Increased pressure} \\ V_m(\text{diam}) &= 3.42 \text{ mL/mol} && \text{would favor diamond} \end{aligned}$$

$$\begin{aligned} \Delta V_m &= V_m(\text{diam}) - V_m(\text{graph}) \\ &= 3.42 \text{ mL/mol} - 5.33 \text{ mL/mol} \\ &= -1.91 \text{ mL/mol} \\ &= -1.91 \times 10^{-3} \text{ L/mol} \end{aligned}$$

At what pressure are graphite and diamond in equilibrium?

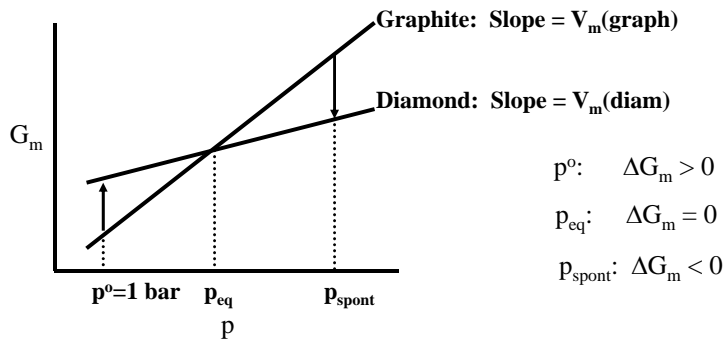
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$$\begin{aligned} \Delta G_m &= G_m(\text{diam}) - G_m(\text{graph}) && \Delta G_m^\circ = G_m^\circ(\text{diam}) - G_m^\circ(\text{graph}) \\ \Delta G_m &= \Delta G_m^\circ + \Delta V_m(p-p^\circ) && \Delta V_m = V_m(\text{diam}) - V_m(\text{graph}) \end{aligned}$$

Equilibrium: At  $p_{\text{eq}}$ ,  $\Delta G_m = 0$

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$$p^0: \Delta G_m > 0$$

$$p_{\text{eq}}: \Delta G_m = 0$$

$$p_{\text{spont}}: \Delta G_m < 0$$

$$0 = \Delta G_m^{\circ} + \Delta V_m(p_{\text{eq}} - p^{\circ})$$

$$p_{\text{eq}} - p^{\circ} = -\frac{\Delta G_m^{\circ}}{\Delta V_m} = -\frac{2.9 \times 10^3 \text{ kPa} \cdot \text{L/mol}}{-1.91 \times 10^{-3} \text{ L/mol}}$$

$$= 1.52 \times 10^6 \text{ kPa}$$

$$p_{\text{eq}} = p^{\circ} + 1.52 \times 10^6 \text{ kPa}$$

$$= 100 \text{ kPa} + 1.52 \times 10^6 \text{ kPa}$$

$$= \boxed{1.52 \times 10^6 \text{ kPa}}$$

$$p_{\text{eq}} = 1.52 \times 10^6 \text{ kPa} \cdot 1 \text{ bar}/100 \text{ kPa}$$

$$= \boxed{15,200 \text{ bar}}$$

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## A Postscript

Synthetic diamond was first produced successfully in 1954 at the General Electric Research Laboratories

Because the reaction to form diamond is extremely slow at room temperature, they performed the experiment at 1650 °C

At the higher temperature,  $\Delta G_m = 8.16 \text{ kJ/mol}$ , leading to  $P_{\text{eq}} = 43,000 \text{ bar}$ .

An actual pressure of 95,000 bar was applied to force the reaction to be very spontaneous.

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### Variation of the Gibbs Energy with Pressure

$$G_m(p) = G_m^\circ + \int_{p^\circ}^p V_m dp$$

Gases

Obviously, we cannot consider the molar volume of a gas to be independent of pressure. However, if we assume the gas obeys the Perfect Gas equation, we have:

$$G_m(p) = G_m^\circ + \int_{p^\circ}^p V_m dp = G_m^\circ + \int_{p^\circ}^p \frac{RT}{p} dp$$

If the pressure on the gas is increased isothermally, then

$$G_m(p) = G_m^\circ + RT \int_{p^\circ}^p \frac{1}{p} dp = G_m^\circ + RT \ln\left(\frac{p}{p^\circ}\right)$$

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$$G_m(p) = G_m^\circ + RT \int_{p^\circ}^p \frac{1}{p} dp = G_m^\circ + RT \ln\left(\frac{p}{p^\circ}\right)$$

**Example:** Calculate the change (in J) in the molar Gibbs energy  $[G_m(p) - G_m^\circ]$  of one mole of water vapor at 110 °C when the applied pressure is increased from 1 bar to 5 bar.

$$G_m(p) - G_m^\circ = 5120 \text{ J} \approx 5 \text{ kJ} \quad R = 8.31 \text{ J/mol-K}$$

Note that the increase in Gibbs energy of the gas is almost 3 orders of magnitude higher than the liquid (<10 J).

This is reasonable when one remembers that the molar volumes of gases are ~3 orders of magnitude higher than liquids or solids.

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## Chemical Potential ( $\mu$ )

Pure Substances

$$dG = -SdT + Vdp$$

If we're dealing with one mole of a substance, this equation becomes

$$dG_m = -S_m dT + V_m dp$$

The Gibbs Energy per mole of a substance,  $G_m$ , is given a fancy title, Chemical Potential and symbol,  $\mu$

$$d\mu = -S_m dT + V_m dp$$

It seems a little foolish to give the Molar Gibbs Energy a new name. However, when we deal with mixtures it becomes more important.

For a pure substance, though:  $\mu \equiv G_m$

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## Chemical Potential ( $\mu$ )

Mixtures

For mixtures, one must consider variations in G results from changes in temperature and pressure PLUS changes in the number of moles of each component.

Let's consider a mixture with two components (A and B):

$$\begin{aligned} dG &= \left(\frac{\partial G}{\partial T}\right)_{p, n_A, n_B} dT + \left(\frac{\partial G}{\partial p}\right)_{T, n_A, n_B} dp + \left(\frac{\partial G}{\partial n_A}\right)_{T, p, n_B} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{T, p, n_A} dn_B \\ &= -SdT + Vdp + \left(\frac{\partial G}{\partial n_A}\right)_{T, p, n_B} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{T, p, n_A} dn_B \end{aligned}$$

The Chemical Potential of each component is given by:

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T, p, n_B} \quad \text{and} \quad \mu_B = \left(\frac{\partial G}{\partial n_B}\right)_{T, p, n_A}$$

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### Chemical Potential ( $\mu$ )

$$dG = -SdT + Vdp + \left(\frac{\partial G}{\partial n_A}\right)_{T,p,n_B} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{T,p,n_A} dn_B$$

The Chemical Potential of each component is given by:

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T,p,n_B} \quad \text{and} \quad \mu_B = \left(\frac{\partial G}{\partial n_B}\right)_{T,p,n_A}$$

Therefore, the equation for dG becomes:

$$dG = -SdT + Vdp + \mu_A dn_A + \mu_B dn_B$$

The chemical potential of a component in a mixture depends upon its environment.

For example, the chemical potential of pure  $\text{CHCl}_3$  is different from its chemical potential in a mixture of  $\text{CHCl}_3$  with  $\text{CH}_3\text{COCH}_3$

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### Multicomponent Mixtures

In a two component mixture, dG is given by:

$$dG = -SdT + Vdp + \mu_A dn_A + \mu_B dn_B$$

If there are N components, one can write:

$$dG = -SdT + Vdp + \sum_{i=1}^N \mu_i dn_i$$

where:  $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n'}$  n' indicates that all  $n_j \neq n_i$  are held constant

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