

# Chemistry 163B Winter 2013

## Clausius Inequality and $\Delta S$ ideal gas

Chemistry 163B

$q_{\text{rev}}$ , Clausius Inequality and calculating  
 $\Delta S$  for ideal gas P,V,T changes (HW#5)

Challenged Penmanship  
Notes

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### *statements of the Second Law of Thermodynamics*

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1. Macroscopic properties of an isolated system eventually assume constant values (e.g. pressure in two bulbs of gas becomes constant; two block of metal reach same T) [*Andrews. p37*]
2. It is impossible to construct a device that operates in cycles and that converts heat into work without producing some other change in the surroundings. *Kelvin's Statement [Raff p 157]; Carnot Cycle*
3. It is impossible to have a natural process which produces no other effect than absorption of heat from a colder body and discharge of heat to a warmer body. *Clausius's Statement, refrigerator*
4. In the neighborhood of any prescribed initial state there are states which cannot be reached by any adiabatic process  
~ *Caratheodory's statement [Andrews p. 58]*

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## Clausius Inequality and $\Delta S$ ideal gas

### four steps to exactitude

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$$I. \quad \varepsilon_{\text{CARNOT[ideal gas]}} = \frac{-w_{\text{total}}}{q_U} = 1 - \frac{T_L}{T_U} = 1 + \frac{q_L}{q_U}$$

$$II. \quad \varepsilon_{\text{ANY REVERSIBLE 'TWO TEMPERATURE' MACHINE}} = \varepsilon_{\text{CARNOT[ideal gas]}}$$

or else violation of 2nd Law

$$III. \quad \oint_{\text{cycle}} \frac{\delta q_{\text{rev}}}{T} = 0 \quad \text{eqn 5.11 E \& R; demonstrated for ideal gas Carnot;}$$

general proof for two temperature reversible cycle;  
see "a REALLY BIG RESULT" last lecture  
(Dickerson p. 155; Raff p. 162 - 163)

$$IV. \quad \oint_{\text{cycle}} \frac{\delta q_{\text{rev}}}{T} = 0 \quad \text{for any reversible cyclic process}$$

figure 5.4 E & R  
(Dickerson pp. 156 - 159, Raff pp. 163 - 164)

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### entropy

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$$dS = \frac{\delta q_{\text{rev}}}{T} \quad \text{is an exact differential}$$

S is a state function

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## Clausius Inequality and $\Delta S$ ideal gas

### goals of lecture

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1. Relate  $\Delta S$  and  $q_{\text{irrev}}$
  
2. Calculate  $\Delta S$  for P,V, T changes of ideal gas (HW#5)
  - a. using REVERSIBLE path ( $q_{\text{rev}}$ ) [even for irreversible processes]
  - b. using partial derivatives of S with respect to P, V, T (look ahead)

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### entropy and heat for actual (irreversible processes): $q_{\text{irrev}}$

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a irreversible (actual) **cyclic** engine  $\epsilon_{\text{irrev}}$  coupled with a Carnot refrigerator of  $\epsilon_C$  **will not** violate 2<sup>nd</sup> Law if  $\epsilon_{\text{irrev}} < \epsilon_C$  (viz HO#23 SL 20-26)

$\Delta U_{\text{cyclic}}=0$   
 $-W_{\text{total}}=q_U+q_L$   
 for both rev  
 and irrev

**BUT** what about  $q_{\text{irrev}}$  with  $\epsilon_{\text{irrev}} < \epsilon_C$  ??

$$\epsilon_{\text{irrev}} = \left( \frac{-w_{\text{total}}}{q_U} \right)_{\text{irrev}} = \left( \frac{q_U + q_L}{q_U} \right)_{\text{irrev}} = 1 + \frac{(q_L)_{\text{irrev}}}{(q_U)_{\text{irrev}}} < 1 - \frac{T_L}{T_U} = \epsilon_{\text{reversible}}$$

$$\frac{(q_L)_{\text{irrev}}}{(q_U)_{\text{irrev}}} < -\frac{T_L}{T_U}$$

$$\Delta S_{\text{cyclic engine (reversible or irreversible)}} = \frac{(q_U)_{\text{rev}}}{T_U} + \frac{(q_L)_{\text{rev}}}{T_L} = 0$$

$$\frac{(q_L)_{\text{irrev}}}{T_L} + \frac{(q_U)_{\text{irrev}}}{T_U} < 0 = \Delta S_{\text{cyclic engine (reversible or irreversible)}}$$

$$\frac{\bar{d}q_{\text{rev}}}{T} = dS \quad \frac{\bar{d}q_{\text{irrev}}}{T} < dS \quad \frac{\bar{d}q}{T} \leq dS$$

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## *2<sup>nd</sup> Law of Thermodynamics in terms of entropy*

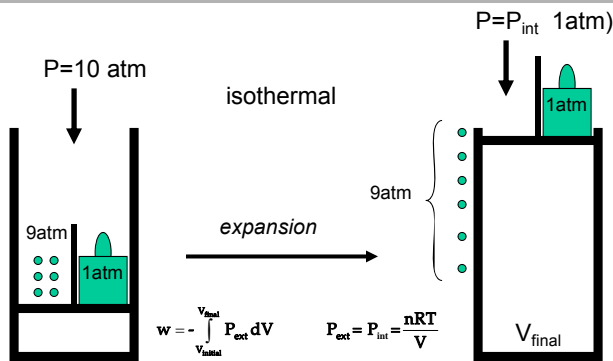
• **S is a STATE FUNCTION**

$$\Delta S = \int_{rev} \frac{\delta q_{rev}}{T} > \int_{irrev} \frac{\delta q_{irrev}}{T}$$

**E&R eqn 5.33 Clausius inequality**

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### Lecture 3: *Pressure-Volume work reversible isothermal expansion; $P_{ext}=P_{int}$*



1mole  
300K  
10 atm  
 $V_1$

$$w = - \int_{V_{initial}}^{V_{final}} P_{ext} dV \quad P_{ext} = P_{int} = \frac{nRT}{V}$$

$$w = - \int_{V_{initial}}^{V_{final}} \frac{nRT}{V} dV = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV = -nRT \ln \frac{V_2}{V_1}$$

1mole  
300K  
1 atm  
 $V_2$

$$V_2 = \frac{300K R (1mol)}{1 atm} \quad V_1 = \frac{300K R (1mol)}{10 atm}$$

$$w = - (300 K \cdot mol) R \ln \frac{10 atm}{1 atm}$$

$w = -5743 J = -5.743 kJ$   
(more work done ON surroundings  
by reversible than irreversible;  $w_{irrev} = -2.244 kJ$ )

$q_{rev} = -w = +5.743 kJ$

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**Lecture 3:**  
**Isothermal expansion:  $P_{ext} = \text{const}$  ideal gas (irreversible)**

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isothermal  $\Delta T = 0$

$w = - \int_{V_{initial}}^{V_{final}} P_{ext} dV$        $PV = nRT$   
 $w = -1 \text{ atm} (V_2 - V_1)$   
 $V_2 = \frac{300 \text{ K } R (1 \text{ mol})}{1 \text{ atm}}$        $V_1 = \frac{300 \text{ K } R (1 \text{ mol})}{10 \text{ atm}}$   
 $w = -(300 \text{ K} \cdot \text{mol}) R \left( \frac{1}{1 \text{ atm}} - \frac{1}{10 \text{ atm}} \right)$   
 $w = -2244 \text{ J} = -2.244 \text{ kJ}$   
 (- sign implies net work done ON surrounding)

1 mole  
300K  
10 atm  
 $V_1$

1 mole  
300K  
1 atm  
 $V_2$

**$q_{irrev} = -w = +2.244 \text{ kJ}$**

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**EXAMPLE from early lectures: isothermal expansion**

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$(P_1 = 10 \text{ atm}, T_1 = 300 \text{ K}, V_1) \rightarrow (P_2 = 1 \text{ atm}, T_2 = 300 \text{ K}, V_2)$   
 initial    →    final

same initial and final

$\int \frac{dq}{T} = \frac{q}{T}$  for isothermal process       $\Delta S$

$P_{ext} = P_{int};$        $q_{rev} = 5743 \text{ J}$        $\frac{q}{T} = 19.14 \text{ J K}^{-1}$       ?

$P_{ext} = \text{const } 1 \text{ atm};$        $q_{irrev} = 2244 \text{ J}$        $\frac{q}{T} = 7.48 \text{ J K}^{-1}$       ?

$\Delta S = \int_{initial}^{final} \frac{dq_{rev}}{T}$   
some reversible path

to calculate  $\Delta S$  must use **reversible** path initial → final

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## Clausius Inequality and $\Delta S$ ideal gas

$$\Delta S_{\text{universe}} \geq 0$$


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soon :

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}} \geq 0$$

***disorder increases***

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### calculating entropy (see summary on review handout)

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- Thermal properties of entropy and entropy calculations
  - $dS = \frac{\delta q_{\text{rev}}}{T}$ ;  $\Delta S = \int \frac{\delta q_{\text{rev}}}{T}$ ;  $\oint \frac{\delta q_{\text{rev}}}{T} = 0$
  - $\Delta S \geq \int \frac{\delta q}{T}$ ;  $0 \geq \oint \frac{\delta q}{T}$ ; (= for reversible process; > for spontaneous ['real'] process)
  - $\Delta S_{\text{total universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$
  - S is a state function; dS is an exact differential
  - Dependence of S on
    - T:  $\left(\frac{\partial \bar{S}}{\partial T}\right)_{P_i} = \frac{\bar{C}_V}{T}$ ;  $\left(\frac{\partial \bar{S}}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$
    - P:  $\left(\frac{\partial \bar{S}}{\partial P}\right)_T = -\left(\frac{\partial \bar{V}}{\partial T}\right)_P$
    - V:  $\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_P$
    - Phase:  $\Delta S = \frac{\Delta H_{\text{equilibrium phase change}}}{T_{\text{equilibrium phase change}}}$
  - Calculation of entropy changes for changes in P, V, T, phase
  - Third Law and calculations using Third Law Entropies:  $\bar{S}^\circ(T)$
  - $\Delta S_{\text{mixing}}^\circ(T) = \sum_i \nu_i \bar{S}_i^\circ(T)$
  - Entropy of mixing:  $\Delta S = -n_{\text{total}} R \sum_i X_i \ln X_i$  where  $X_i = \frac{n_i}{n_{\text{total}}}$

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## Clausius Inequality and $\Delta S$ ideal gas

look ahead -  $\Delta S$  for changes in  $T, V$ ; (always  $\Delta S = \int_{initial}^{final} \frac{dq_{rev}}{T}$  )

also:

$S(T, V)$ :

$$dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV$$

coming soon

$$\left( \frac{\partial S}{\partial T} \right)_V = \frac{n\bar{C}_V}{T} \quad \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V$$

so:  $dS = \frac{n\bar{C}_V}{T} dT + \left( \frac{\partial P}{\partial T} \right)_V dV$  **always (no  $w_{other}$ , closed system)**

**ideal gas**

$$dS = \frac{n\bar{C}_V}{T} dT + \frac{nR}{V} dV \quad \Delta S = \int_{rev \text{ const } V \text{ path}} \frac{n\bar{C}_V}{T} dT + \int_{rev \text{ const } T \text{ path}} \frac{nR}{V} dV$$

$$\Delta S = n\bar{C}_V \ln \left( \frac{T_{final}}{T_{initial}} \right) + nR \ln \left( \frac{V_{final}}{V_{initial}} \right) \quad \text{E\&R eqn 5.18}$$

$q_{rev}$  T vary  
const V path

$q_{rev}$  V vary  
const T path

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look ahead-  $\Delta S$  for changes in  $T, P$ ; (always  $\Delta S = \int_{initial}^{final} \frac{dq_{rev}}{T}$  )

also:

$S(T, P)$ :

$$dS = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP$$

coming soon

$$\left( \frac{\partial S}{\partial T} \right)_P = \frac{n\bar{C}_P}{T} \quad \left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P$$

so:  $dS = \frac{n\bar{C}_P}{T} dT - \left( \frac{\partial V}{\partial T} \right)_P dP$  **always (no  $w_{other}$ , closed system)**

**ideal gas**

$$dS = \frac{n\bar{C}_P}{T} dT - \frac{nR}{P} dP \quad \Delta S = \int_{rev \text{ const } P \text{ path}} \frac{n\bar{C}_P}{T} dT - \int_{rev \text{ const } T \text{ path}} \frac{nR}{P} dP$$

$$\Delta S = n\bar{C}_P \ln \left( \frac{T_{final}}{T_{initial}} \right) - nR \ln \left( \frac{P_{final}}{P_{initial}} \right) \quad \text{E\&R eqn 5.19}$$

$q_{rev}$  vary T  
const P path

$q_{rev}$  vary P  
const T path

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*End of Lecture*

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