

Chemistry 163B Winter 2013

Clausius Inequality and ΔS ideal gas

Chemistry 163B

q_{rev} , Clausius Inequality and calculating ΔS for ideal gas P,V,T changes (HW#5)

Challenged Penmanship Notes

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statements of the Second Law of Thermodynamics

- 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]
- 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*
- 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*
- 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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four steps to exactitude

- I. $\epsilon_{CARNOT[ideal\ gas]} = \frac{-w_{total}}{q_U} = 1 - \frac{T_L}{T_U} = 1 + \frac{q_L}{q_U}$
- II. $\epsilon_{ANY\ REVERSIBLE\ 'TWO\ TEMPERATURE'\ MACHINE} = \epsilon_{CARNOT[ideal\ gas]}$
or else violation of 2nd Law
- III. $\oint_{cycle} \frac{dq_{rev}}{T} = 0$ 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. $\oint_{cycle} \frac{dq_{rev}}{T} = 0$ for any reversible cyclic process
figure 5.4 E & R
(Dickerson pp.156 - 159, Raff pp.163 - 164)

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entropy

$dS = \frac{dq_{rev}}{T}$ is an exact differential

S is a state function

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goals of lecture

- Relate ΔS and q_{irrev}
- Calculate ΔS for P,V, T changes of ideal gas (HW#5)
 - a. using REVERSIBLE path (q_{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_{irrev}

a irreversible (actual) **cyclic** engine ϵ_{irrev} coupled with a Carnot refrigerator of ϵ_C will not violate 2nd Law if $\epsilon_{irrev} < \epsilon_C$ (viz HOR23 SL 20-26)

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

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

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

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

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

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

$\frac{dq_{rev}}{T} = dS$ $\frac{dq_{irrev}}{T} < dS$ $\frac{dq}{T} \leq dS$

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2nd Law of Thermodynamics in terms of entropy

• S is a STATE FUNCTION

• $\Delta S = \int_{rev} \frac{dq_{rev}}{T} > \int_{irrev} \frac{dq_{irrev}}{T}$

E&R eqn 5.33 Clausius inequality

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

isothermal expansion

$w = - \int_{V_1}^{V_2} P_{ext} dV$ $P_{ext} = P_{int} = \frac{nRT}{V}$

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

1 mole 300K 10 atm V_1 \rightarrow 1 mole 300K 1 atm V_2

$w = - (300 \text{ K-mol}) R \ln \frac{10 \text{ atm}}{1 \text{ atm}}$
 $w = -5743 \text{ J} = -5.743 \text{ kJ}$

$q_{rev} = -w = +5.743 \text{ kJ}$
(more work done ON surroundings by reversible than irreversible; $w_{irrev} = -2.244 \text{ kJ}$)

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

isothermal $\Delta T=0$

expansion

$w = - \int_{V_1}^{V_2} P_{ext} dV$ $PV=nRT$

$w = -1 \text{ atm} (V_2 - V_1)$ $PV=nRT$

1 mole 300K 10 atm V_1 \rightarrow 1 mole 300K 1 atm V_2

$w = - (300 \text{ K-mol}) R \left(\frac{1}{1 \text{ atm}} - \frac{1}{10 \text{ atm}} \right)$
 $w = -2244 \text{ J} = -2.244 \text{ kJ}$ **$q_{irrev} = -w = +2.244 \text{ kJ}$**
(- sign implies net work done ON surrounding)

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EXAMPLE from early lectures: isothermal expansion

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

initial \rightarrow final

same initial and final $\int \frac{dq}{T} = \frac{q}{T}$ for isothermal process ΔS

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

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

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

some reversible path

to calculate ΔS must use **reversible** path initial \rightarrow final

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$\Delta S_{universe} \geq 0$

SOON :

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

disorder increases

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calculating entropy (see summary on review handout)

- Thermal properties of entropy and entropy calculations
 - $dS = \frac{dq_{rev}}{T}$; $\Delta S = \int \frac{dq_{rev}}{T}$; $\int \frac{dq_{rev}}{T} = 0$
 - $\Delta S \geq \int \frac{dq}{T}$; $0 \geq \int \frac{dq}{T}$; ($=$ for reversible process; $>$ for spontaneous ["real"] process)
 - $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$
 - **S is a state function; dS is an exact differential**
 - Dependence of S on
 - T: $\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_p}{T}$; $\left(\frac{\partial S}{\partial T} \right)_V = \frac{C_v}{T}$
 - P: $\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$
 - V: $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$
 - Phase: $\Delta S = \frac{\Delta H_{equilibrium phase change}}{T_{equilibrium phase change}}$
- Calculation of entropy changes for changes in P, V, T, phase
- Third Law and calculations using Third Law Entropies: $S^\circ(T)$
- $\Delta S^\circ_{mix}(T) = - \sum_i \nu_i S^\circ_i(T)$
- Entropy of mixing: $\Delta S = -R \sum_i \nu_i \ln X_i$ where $X_i = \frac{n_i}{n_{total}}$

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

also: coming soon

$S(T, V)$:

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

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

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

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

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

\downarrow
 q_{rev} vary
const V path

\downarrow
 q_{rev} vary
const T path

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

also: coming soon

$S(T, P)$:

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

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

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

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

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

\downarrow
 q_{rev} vary T
const P path

\downarrow
 q_{rev} vary P
const T path

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End of Lecture

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