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Course 56S/66S Lecture Number \_\_\_\_\_ Date 3/6/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

Last Time

Heat Capacity at constant pressure ( $C_p$ )

When  $p$  is constant

$$H = U + pV$$

$$dH = dU + p dV + V dp$$

$= T ds - \cancel{p dV} + \cancel{p dV} + \cancel{V dp} \xrightarrow{\text{Closed System}} + p dV + V dp \quad p = \text{constant}$

$$dH = T ds = \delta q$$

$dH = \delta q$

$$C_p = \left( \frac{\partial q}{\partial T} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p$$

Systems that have "non-zero"  $C_p$  have a T-dependent  $H$  (and  $S$ ).

Integrated Form

$$\Delta H = \int_{H_A}^{H_B} dH = \int_{T_A}^{T_B} C_p dT = C_p (T_B - T_A)$$

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$$\Delta S = \int_{S_A}^{S_B} dS = \int_{T_1}^{T_2} \frac{C_p}{T} dT = C_p \ln \frac{T_2}{T_1}$$

The previous two equations are only true if  $C_p$  does not depend on  $T$ .

### Third Principle of Thermodynamics

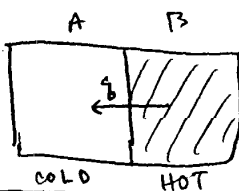
$S=0$  at 0K (i.e. the lowest  $T$  that could be reached in the universe).

$$S = k \ln W \rightarrow W = 1$$

$$S = k \ln 1 = 0$$

Example) Equilibrium  $T$  of objects in thermal contact. At constant  $V$

Q: "T" after thermal equilibrium? (Given  $T_A$  and  $C_A$  and  $T_B, C_B$ .)



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$$\Delta U = \Delta U_A + \Delta U_B = 0$$

$$\begin{aligned} \Delta U_A &= C_{VA} \int_{T_A}^T dT \\ &= C_{VA} (T - T_A) \end{aligned}$$

$$\begin{aligned} \Delta U_B &= C_{VB} \int_{T_B}^T dT \\ &= C_{VB} (T - T_B) \end{aligned}$$

$$C_{VA} (T - T_A) + C_{VB} (T - T_B) = 0$$

$$T (C_{VA} + C_{VB}) = C_{VA} T_A + C_{VB} T_B$$

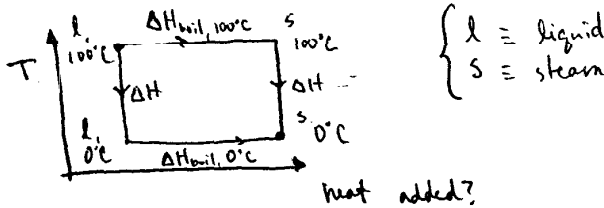
$$T = \frac{C_{VA} T_A + C_{VB} T_B}{C_{VA} + C_{VB}}$$

If  $C_{VA} = C_{VB}$ ,  
$$T = \frac{T_A + T_B}{2}$$

### More About Thermodynamic Cycles:

If a function  $f$  is a state function, then the integral along any cyclic path is equal to zero.

This is not true for non-state functions. ( $\delta q$ ,  $\delta w$ ).



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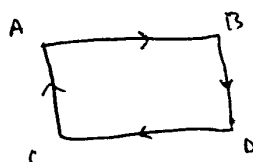
$$\Delta H_{\text{boil}, 100^\circ\text{C}} = 540 \text{ cal g}^{-1}$$

$$C_p = 0.0448 \text{ cal K}^{-1} \text{ g}^{-1} \leftarrow \text{"specific heat" capacity}$$

$$C_p = 1.00 \text{ cal K}^{-1} \text{ g}^{-1}$$

$$\Delta H_{\text{boil}, 0^\circ\text{C}} = \Delta H_{\text{boil}, 100^\circ\text{C}} + \Delta H_{\text{steam}} - \Delta H_{\text{liquid}}$$

For cycles in general of state functions,



$$\Delta Y_{AB} + \Delta Y_{BD} + \Delta Y_{CD} + \Delta Y_{AC} = 0$$

$\boxed{A \rightarrow A}$

$$\Delta Y_{AB} + \Delta Y_{BD} = \Delta Y_{AC} + \Delta Y_{CD}$$

$\boxed{A \rightarrow D}$

### Chapter 9 Maxwell Relations + Gibbs-Duhem Equation

$U = U(S, V)$  at constant  $N$

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$$

$$T = \left( \frac{\partial U}{\partial S} \right)_V \quad -P = - \left( \frac{\partial U}{\partial V} \right)_S$$

$$\frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right) = \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right)$$

$$\frac{\partial T}{\partial V} = - \frac{\partial P}{\partial S} \leftarrow \text{A Maxwell Relation}$$