59-240 Lecture 9 First Law Machinery

State vs. Path Functions

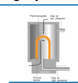
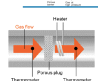
State
- define state of substance
- independent of preparation
- *U, H, p, V, T*
- Exact differentials: $\Delta U = U_f - U_i$
- Independent of path
- $$\Delta U = \int_i^f dU$$
- dU is an exact differential

Path
- preparation of state
- *q, w*
- Inexact differentials
- Dependent on path
- $$q = \int_{i,\ \text{path}}^{f} dq$$
- *dq, dw* are inexact differentials

Changes in internal energy
- $U(V, T)$
- Total Differential Equation (TDE):
- $$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$
- dV and dT represent infinitesimal changes
- In parentheses are the partial differentials (PD)
- $(\partial U/\partial T)_V = C_V$, so
- $$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + C_V\, dT$$

Internal Pressure
- $$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$
- measure of cohesive forces
- $$dU = \pi_T\, dV + C_V\, dT$$
- $\pi_T = 0$ for perfect gas
- π_T becomes important as pressure increases and attractive or repulsive forces come into play (see Lecture 4)
- Joule appartus
  - tried to measure π_T
  - expanded gas into a vacuum
  - his measurements determined: w = 0, q = 0, $\Delta U = 0$ and $\pi_T = 0$
  - however, his apparatus was too crude to accurately measure π_T

Relation between C_p and C_V
- Perfect gas, $\pi_T = 0$
- $$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_p$$
- Prove that *(know this proof)*:
- $$C_p - C_V = \frac{\alpha^2 TV}{\kappa_T}$$

Joule-Thomson effect
- Important in liquefaction of gases
- Cooling by adiabatic expansion
- 
  Apparatus #1: $\mu = (dT/dP)_H$ Isenthalpic
- 
  Apparatus #2 $\mu_T = (dH/dP)_T$ Isothermal
- Linde refrigerator
- μ and $\mu_T = 0$ for perfect gases
- attractive and repulsive interactions determine the signs of μ and μ_T
- All real gases have inversion temperatures

Changes in *H*, const. *V*
- $$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$
- $$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + C_p\, dT$$
- Rearrange to (know this proof)
- $$\left(\frac{\partial H}{\partial T}\right)_V = \left(1 - \frac{\alpha\mu}{\kappa_T}\right) C_p$$
- Isothermal compressibility $$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$
- examples of using κ_T
- JT coefficient $$\mu = \left(\frac{\partial T}{\partial p}\right)_H$$

Changes in *U*, const. *p*
- $$dU = \pi_T\, dV + C_V\, dT$$
- Take derivative wrt *p* (know this proof)
- $$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V$$
- New: expansion coefficient, α
- $$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$
- Large α, big responses to change in *T*