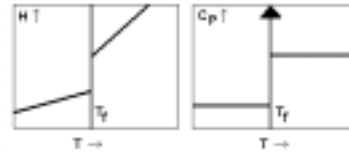


# Physical Chemistry

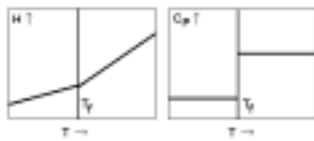
Lecture 22  
Higher-Order Phase Transitions

## First-order phase transition



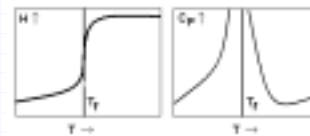
- ◆ Discontinuous enthalpy, entropy and volume change at a specific temperature
- ◆ Common type of phase transition
  - Melting of ice
  - Boiling of water
  - Sublimation of carbon dioxide

## Second-order phase transition



- ◆ Enthalpy, entropy and volume are continuous functions of temperature at  $T_f$ 
  - Change of slope of enthalpy and entropy and volume
- ◆ No "latent enthalpy"
- ◆  $C_p$  exhibits a finite discontinuity at  $T_f$
- ◆ Examples
  - Onset of rotation of  $\text{NH}_4^+$  groups in  $\text{NH}_4\text{Cl}$
  - Semiconductor-to-metal transition
  - Order-disorder transition in alloys

## $\lambda$ Transition of helium-4



- ◆  $C_p$  tends to infinity as  $T$  approaches  $T_f$  from both directions
  - Plot looks like the Greek letter  $\lambda$
- ◆ No "latent heat", although there is a monotonic step in enthalpy
  - Not discontinuous
- ◆ Transition between two forms of liquid He
  - Normal liquid (above 2.17 K)
  - Superfluid (below 2.17K)

## Glass transition of polymers

- ◆ Solid phase of polymeric materials is not highly crystalline
- ◆ The material is disordered and known as a **glass**
  - ◆ Many systems form glasses
    - ◆ Example: Borosilicate glasses
- ◆ Near the glass transition solid "softens" and flows under stress
- ◆ Above the glass-transition temperature, the material is something like an ordinary liquid, although frequently more viscous than small-molecule liquids

## Polymer glass-transition temperatures

Polymer	$T_g$ (K)	Polymer	$T_g$ (K)
Poly(ethylene)	148	Poly(tetrafluoroethylene)	399 (l) 193 (ll)
Atactic poly(propylene)	Atactic -260 Isotactic -265 Syndiotactic 265	Poly(chlorotrifluoroethylene)	373
Poly(1-butylene)	Cis 171 Trans 215	Poly(vinyl chloride)	354
Poly(isoprene)	Atactic 378 Isotactic 313 Syndiotactic 378	Poly(styrene)	373
Poly(butyl methacrylate)	Atactic 293 Isotactic 249	Poly(methyl methacrylate)	Atactic 378 Isotactic 311 Syndiotactic 378

## Summary

- ◆ Phase transitions of many different types are observed
- ◆ First-order transition
  - Usual type of transition
- ◆ Second-order transition
  - Involves some process that does not require a discontinuous change in enthalpy
- ◆ A transition of helium-4
  - Liquid-liquid transition
  - One phase is a superfluid
- ◆ Glass transition
  - Softening, rather than direct melting
  - Glass
  - Polymers