

# ABE 201

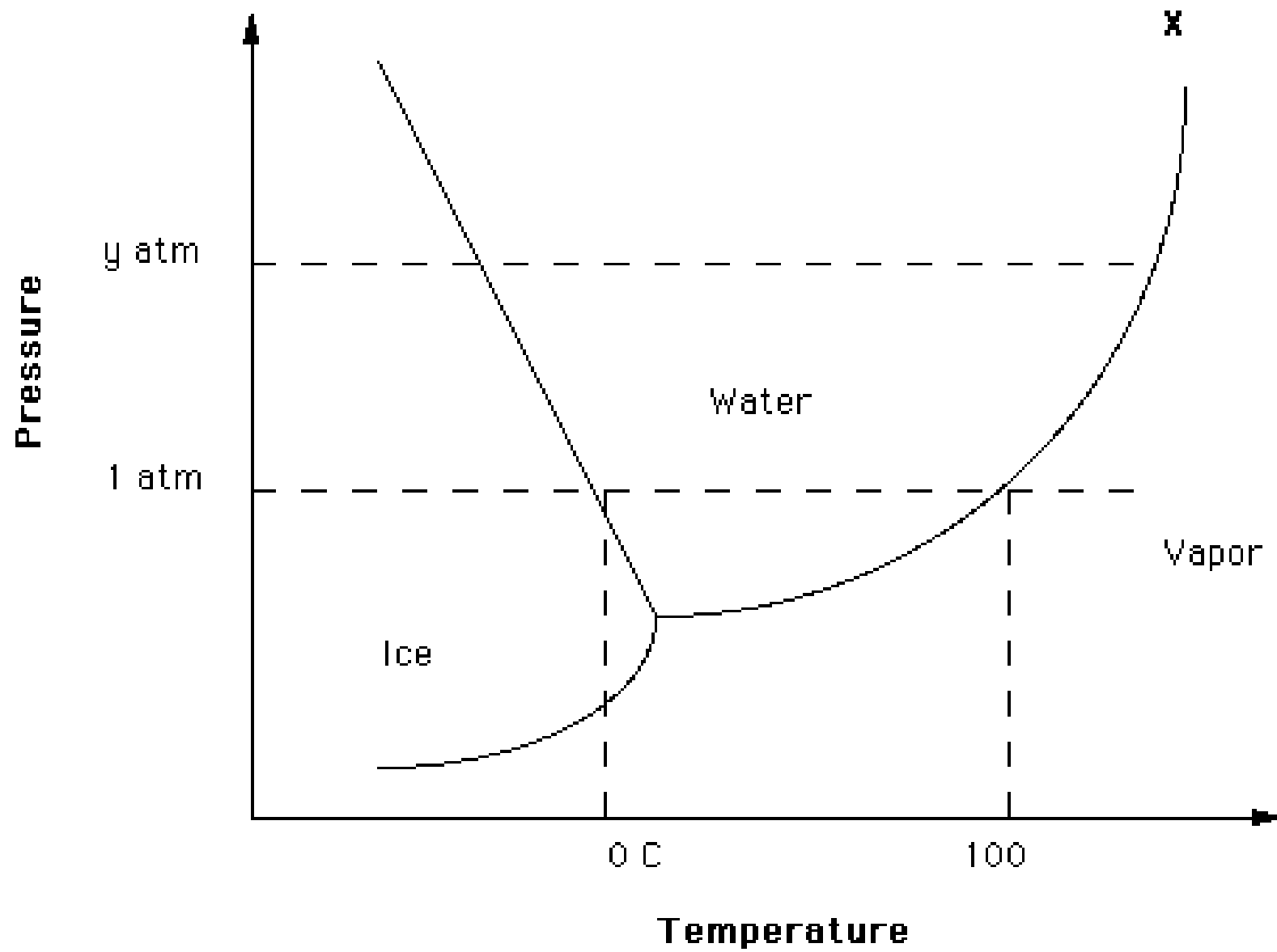
# Biological Thermodynamics 1

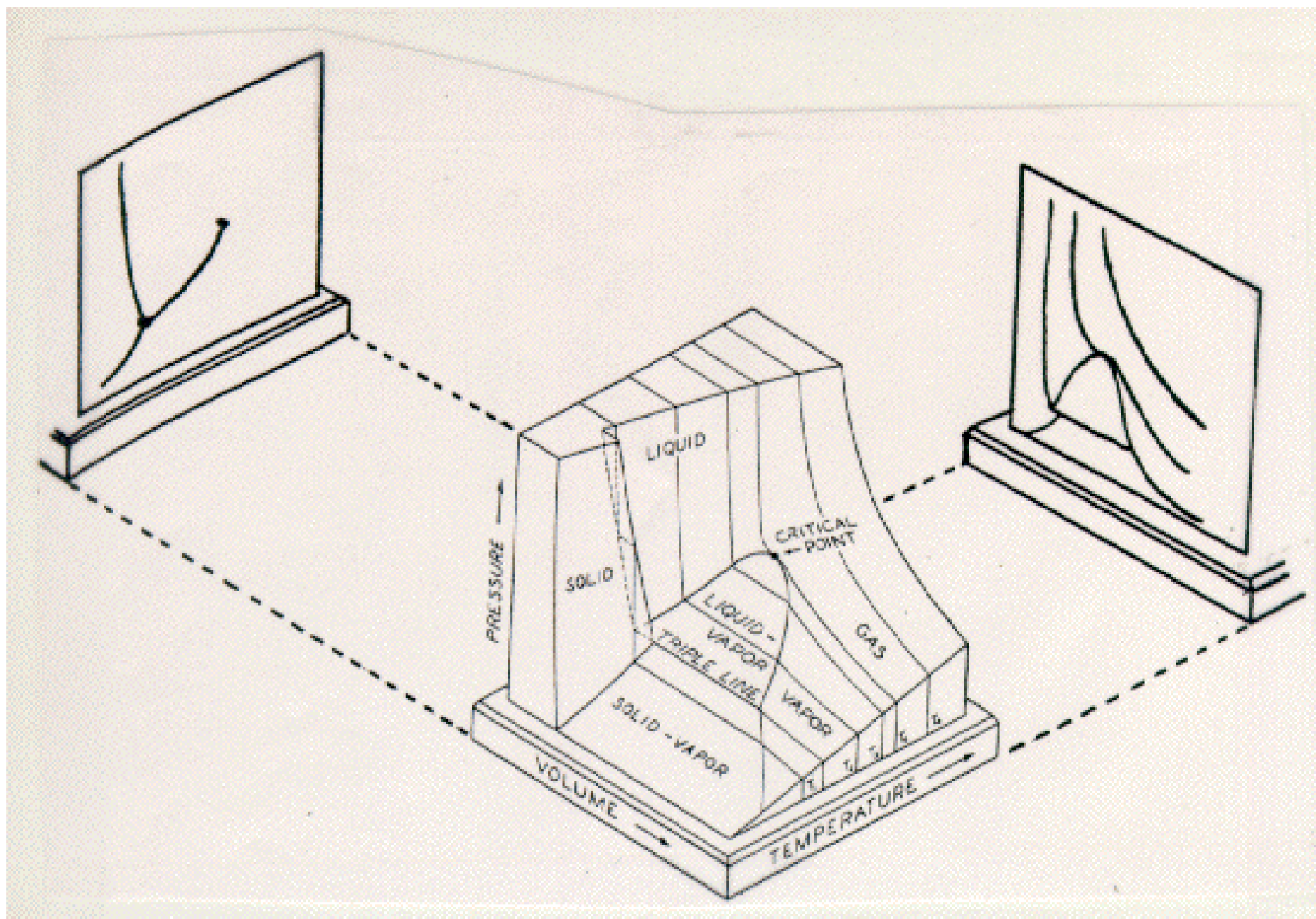
Module 10:  
T P H and U Relationships

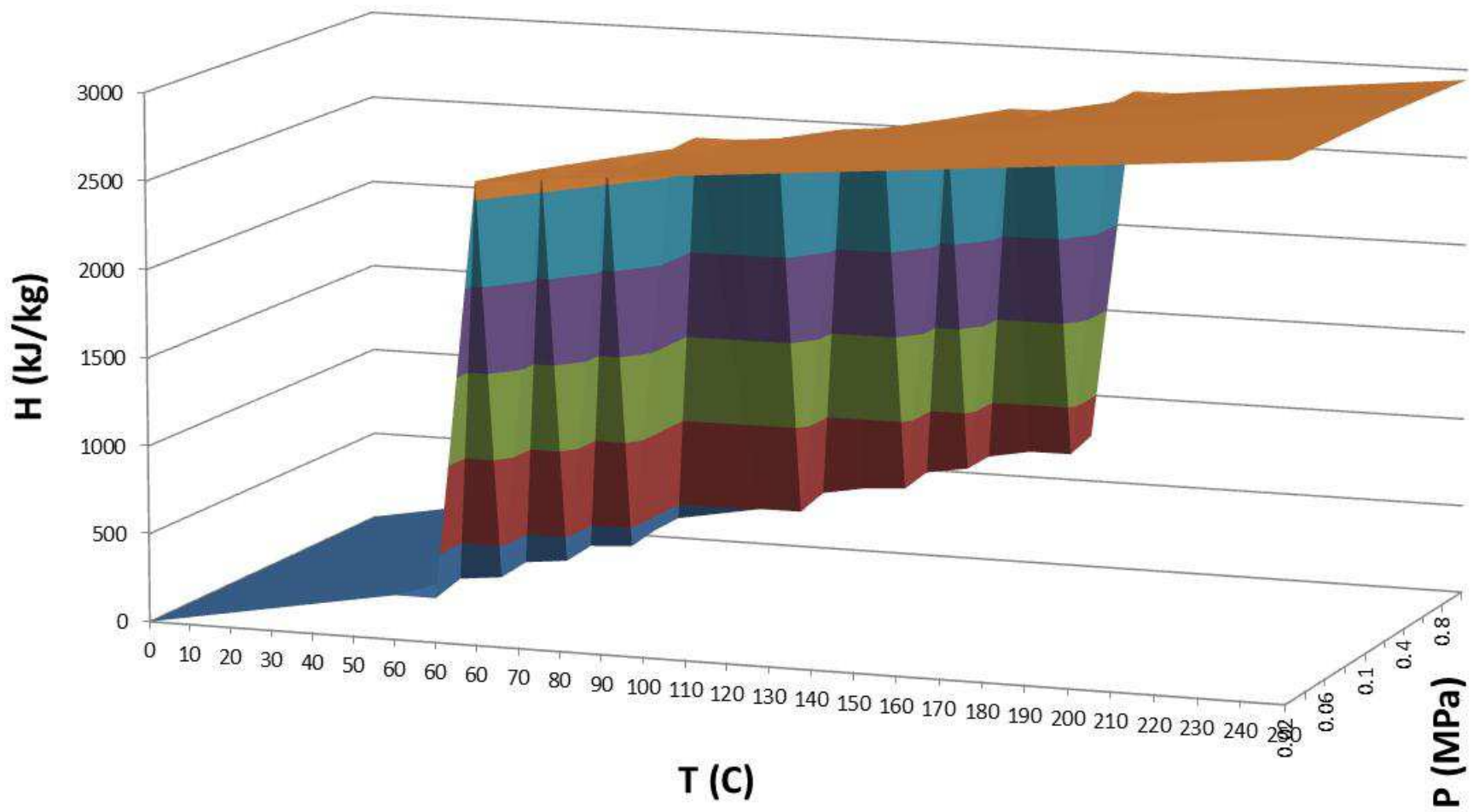
# Outline

- Representing the relationship between T, P, and H graphically
- Sensible versus Latent Heat
- Calculating sensible and latent heat changes
- Estimating heat capacity for biological materials

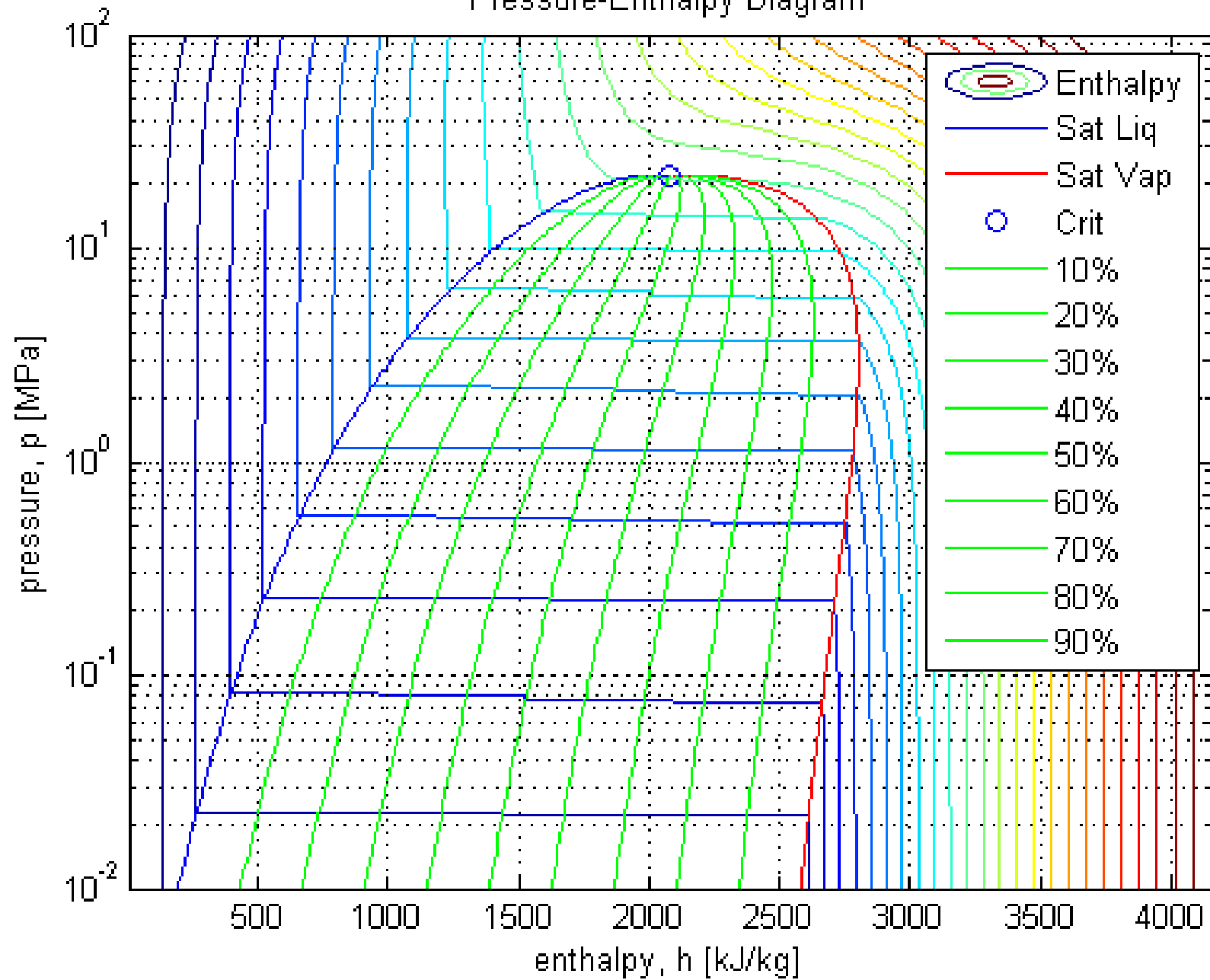
The Phase Diagram For Water

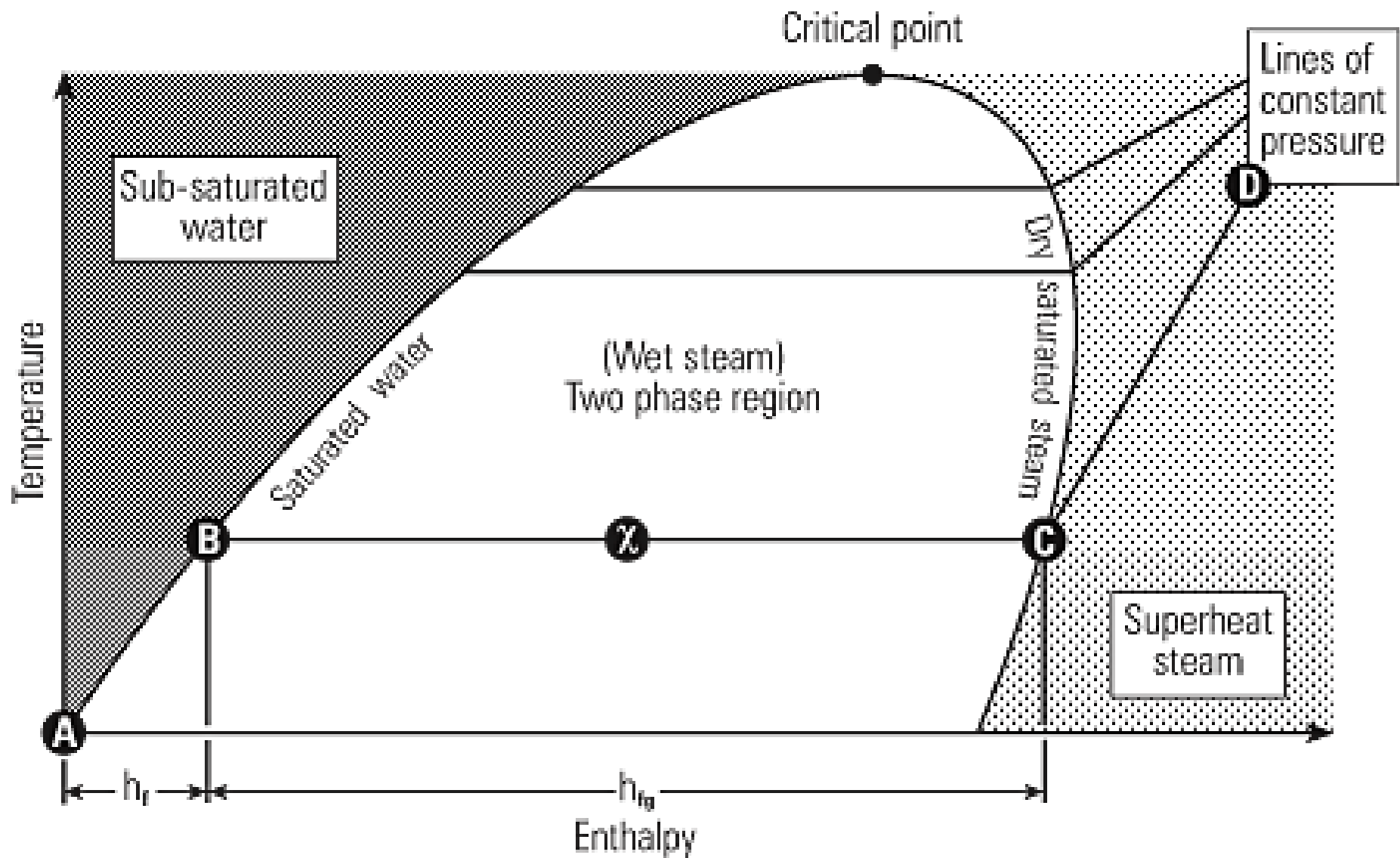






Pressure-Enthalpy Diagram





# Constant Temperature Processes

- For Liquids and solids, specific volume and internal energy depend heavily on temperature, and little on pressure

For constant T:

$$(\Delta \hat{U})_T \approx 0$$

$$(\Delta \hat{H})_T = (\Delta \hat{U})_T + \Delta(P\hat{V})_T = \cancel{(\Delta \hat{U})_T} + \hat{V}\Delta P + P\Delta \hat{V} \approx 0$$

for water  $\hat{V} = 0.00100$  to  $0.00116$  between  $0.01^\circ\text{C}$  to  $200^\circ\text{C}$

If water compressed at  $20^\circ\text{C}$  from  $2\text{ Pa}$  (saturation) to  $200\text{ kPa}$ ,

$\Delta H = 0.2\text{ kJ/kg}$ , from  $84.0$ - $84.2\text{ kJ/kg}$  - a change of  $0.2\%$



# T, P, H and Phase

- Phase changes represent a “discontinuity” to the relationship between T, P, and H.
- This discontinuity can be expressed by thinking about these relationships as distinct, separate phenomena.
- When no phase change occurs T, P, and H are straight-forward functions of one another.
- When a phase change occurs, T & P are constant while H undergoes a significant change as 100% of the liquid becomes 100% vapor

# Sensible Heating

- Defined as heat transferred to raise or lower the temperature of the substance

$$Q = \Delta U = \text{function of temperature}$$

$$\dot{Q} = \Delta \dot{H} = \text{function of temperature}$$

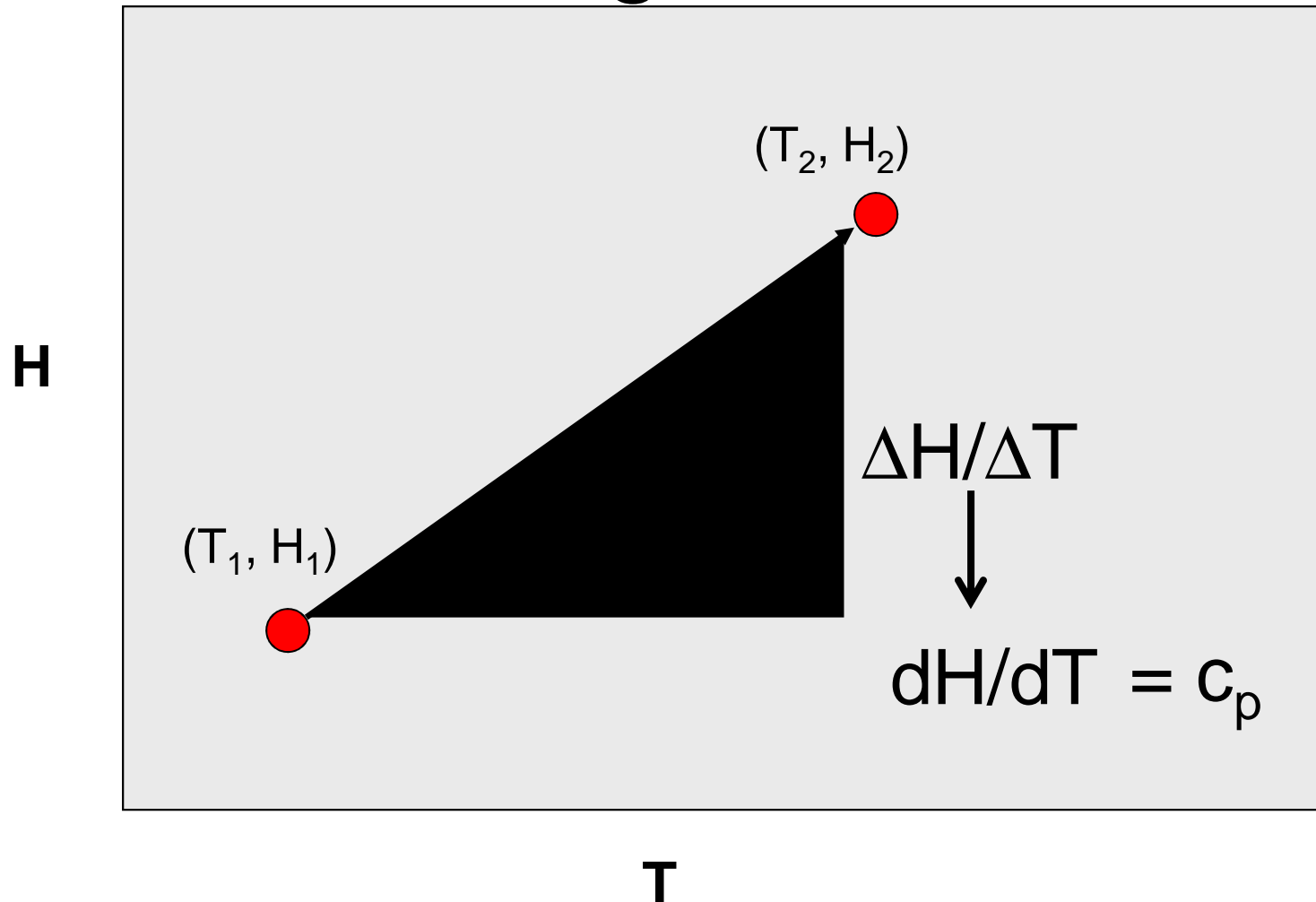
# Latent Heating

- Defined as heat transferred to change the phase of the substance

$$Q = \Delta U_v, \Delta U_m$$

$$\dot{Q} = \Delta \dot{H}_v, \Delta \dot{H}_m$$

# State Change Without Phase Change, $P=\text{constant}$



# Enthalpy is a Strong Function of Temperature

- For incremental changes in temperature at constant ***pressure***, the enthalpy change is approximated by the slope of the plotted relationship.
- As the incremental temperature change approaches zero, the limiting slope defines the ***heat capacity at constant pressure***.

$$C_p(T)$$

# Using $C_p$

- For ideal gas:

$$\Delta\hat{H} = 0 + \int_{T_1}^{T_2} C_p(T) dT$$

- For Liquid or solids:

$$\Delta\hat{H} = \hat{V}\Delta P + \int_{T_1}^{T_2} C_p(T) dT \approx \int_{T_1}^{T_2} C_p(T) dT$$

- For nonideal gases this approach is valid only if  $P$  is constant. Note in most cases of liquids and solids the first term including  $\Delta P$  is usually small relative to the second term.

# Heat Capacity Formulas

- Table B.2
- Conversion between  $C_p$  and  $C_v$ :
  - Liquids and Solids:

$$C_p \approx C_v$$

- Ideal Gases:

$$C_p \approx C_v + R$$

- Non ideal gases (not easily determined relation)

# Simple Derivation

- We can derive the relation between the heat capacities from the definitions we all ready have:

$$\Delta \hat{H} = \Delta \hat{U} + \Delta(P\hat{V})$$

$$\Delta \hat{H} = \Delta \hat{U} + \Delta(RT)$$

$$\Delta \hat{H} = \Delta \hat{U} + R\Delta(T)$$

- Now let us look at the incremental changes for this integral balance and differentiate with respect to temperature:

$$\frac{d\hat{H}}{dT} = \frac{d\hat{U}}{dT} + R \frac{dT}{dT}$$

$$C_p = C_v + R$$



# Calculating Heat Capacities

Table B.2

Form 1

$$C_p = a + bT + cT^2 + dT^3$$

Form 2

$$C_p = a + bT + cT^{-2}$$

**Table B.2** Heat Capacities<sup>a</sup>

$$\text{Form 1: } C_p[\text{kJ}/(\text{mol}\cdot^\circ\text{C})] \text{ or } [\text{kJ}/(\text{mol}\cdot\text{K})] = a + bT + cT^2 + dT^3$$

$$\text{Form 2: } C_p[\text{kJ}/(\text{mol}\cdot^\circ\text{C})] \text{ or } [\text{kJ}/(\text{mol}\cdot\text{K})] = a + bT + cT^{-2}$$

Example:  $(C_p)_{\text{acetone(g)}} = 0.07196 + (20.10 \times 10^{-5})T - (12.78 \times 10^{-8})T^2 + (34.76 \times 10^{-12})T^3$ , where  $T$  is in  $^\circ\text{C}$ .

Note: The formulas for gases are strictly applicable at pressures low enough for the ideal gas equation of state to apply.

Compound	Formula	Mol. Wt.	State	Form	Temp. Unit	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$	Range (Unit of $T$ )
Acetone	$\text{CH}_3\text{COCH}_3$	58.08	l	1	$^\circ\text{C}$	123.0	18.6			-30-60
			g	1	$^\circ\text{C}$	71.96	20.10	-12.78	34.76	0-12
Acetylene	$\text{C}_2\text{H}_2$	26.04	g	1	$^\circ\text{C}$	42.43	6.053	-5.033	18.20	0-12
Air		29.0	g	1	$^\circ\text{C}$	28.94	0.4147	0.3191	-1.965	0-15
			g	1	K	28.09	0.1965	0.4799	-1.965	273-18
Ammonia	$\text{NH}_3$	17.03	g	1	$^\circ\text{C}$	35.15	2.954	0.4421	-6.686	0-12
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	132.15	c	1	K	215.9				275-32
Benzene	$\text{C}_6\text{H}_6$	78.11	l	1	$^\circ\text{C}$	126.5	23.4			6-67
			g	1	$^\circ\text{C}$	74.06	32.95	-25.20	77.57	0-12
Isobutane	$\text{C}_4\text{H}_{10}$	58.12	g	1	$^\circ\text{C}$	89.46	30.13	-18.91	49.87	0-12
n-Butane	$\text{C}_4\text{H}_{10}$	58.12	g	1	$^\circ\text{C}$	92.30	27.88	-15.47	34.98	0-12
Isobutene	$\text{C}_4\text{H}_8$	56.10	g	1	$^\circ\text{C}$	82.88	25.64	-17.27	50.50	0-12
Calcium carbide	$\text{CaC}_2$	64.10	c	2	K	68.62	1.19	$-8.66 \times 10^{10}$	—	298-72
Calcium carbonate	$\text{CaCO}_3$	100.09	c	2	K	82.34	4.975	$-12.87 \times 10^{10}$	—	273-10
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	74.10	c	1	K	89.5				276-37
Calcium oxide	$\text{CaO}$	56.08	c	2	K	41.84	2.03	$-4.52 \times 10^{10}$		273-11
Carbon	C	12.01	c	2	K	11.18	1.095	$-4.891 \times 10^{10}$		273-13
Carbon dioxide	$\text{CO}_2$	44.01	g	1	$^\circ\text{C}$	36.11	4.233	-2.887	7.464	0-15
Carbon monoxide	CO	28.01	g	1	$^\circ\text{C}$	28.95	0.4110	0.3548	-2.220	0-15
Carbon tetrachloride	$\text{CCl}_4$	153.84	l	1	K	93.39	12.98			273-34
Chlorine	$\text{Cl}_2$	70.91	g	1	$^\circ\text{C}$	33.60	1.367	-1.607	6.473	0-12
Copper	Cu	63.54	c	1	K	22.76	0.6117			273-13

# Using Heat Capacity Formulas

$$\Delta\hat{H}=\hat{V}\Delta P+\int_{T_1}^{T_2} C_p(T)dT$$

$$\Delta\hat{H}=\hat{V}\Delta P+\int_{T_1}^{T_2} \left(a+bT+cT^2+dT^3\right)dT$$

$$\Delta\hat{H}=0+\left|aT+\frac{b}{2}T^2+\frac{c}{3}T^3+\frac{d}{4}T^4\right|_{T_1}^{T_2}$$

$$\Delta\hat{H}\approx a\Delta T=c_p\Delta T$$

# Using Sensible and Latent Heat in 1<sup>st</sup> Law Energy Balances

$$\Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p = \dot{Q} - \dot{W}_s$$

$$\Delta\dot{H} = \left[ \Sigma \left( \hat{H}_{i,out} \dot{m}_{i,out} \right) - \Sigma \left( \hat{H}_{i,in} \dot{m}_{i,in} \right) \right]$$

$$\Delta\dot{H} = \Delta\hat{H}_{sensible} \dot{m} + \Delta\hat{H}_{latent} \dot{m}$$

$$\Delta\dot{H} = \int_{T_1}^{T_2} \left( a + bT + cT^2 + dT^3 \right) dT \cdot \dot{m} + \Delta\hat{H}_{latent} \dot{m}$$

# Heat Capacities of Biological Materials

- Usually treated as a constant (b=c=d=0)

$$\Delta\hat{H} \approx a\Delta T = c_p\Delta T$$

- Tabulated Values
  - Very specific (pure biochemicals)
  - Limited range (moisture, composition)
  - Limited utility (variability of biomaterials)
- Calculated Values
  - Estimates based on composition or moisture content

# Tabulated Heat Capacities

<b>Material</b>	<b><math>C_p</math> (kJ/kg-K)</b>
Flour	1.80-1.88
Ice Cream (liquid)	3.27
Ice Cream (frozen)	1.88
Milk, whole	3.85
Olive Oil	2.01
Green Beans (fresh)	3.81
Green Beans (frozen)	1.97

# Predicting Heat Capacity in Biological Materials

- There are several equations that can be used to predict unknown specific heats for food and biological materials
- Two Examples
  - Seibels Equations
  - Choi and Okos Equation

# Seibels Equations

- Based on the wet basis moisture content of the biomaterial
- $MC(wb) = \text{mass of water} / \text{total mass}$
- $MC(wb) = \text{mass fraction of water}$
- Specific Heat (kJ/(kg-K))

Above freezing:  $c_p = 0.837 + 3.348 * x_{\text{water}}$

Below freezing:  $c_p = 0.837 + 1.256 * x_{\text{water}}$



# Choi and Okos Equation

- Estimates the specific heat for foods in kJ/(kg-K) as weighted average of composition.

Water

$$C_p = 4.180 * X_w + 1.711 * X_p + 1.928 * X_f + 1.547 * X_c + 0.908 * X_a$$

Ice

$$C_p = 1.998 * X_w + 1.711 * X_p + 1.928 * X_f + 1.547 * X_c + 0.908 * X_a$$

w = water, p = protein, f = fat, c = carbohydrate, a = ash

# Summary

- Thermodynamic properties (T, P, H, etc.) are related to one another by smooth functions with discontinuities at phase change boundaries
- This can be simplified as two types of thermal relationships: sensible and latent energy
- Heat capacities for biological materials can be measured, use tabulated values, or be estimated from the composition.