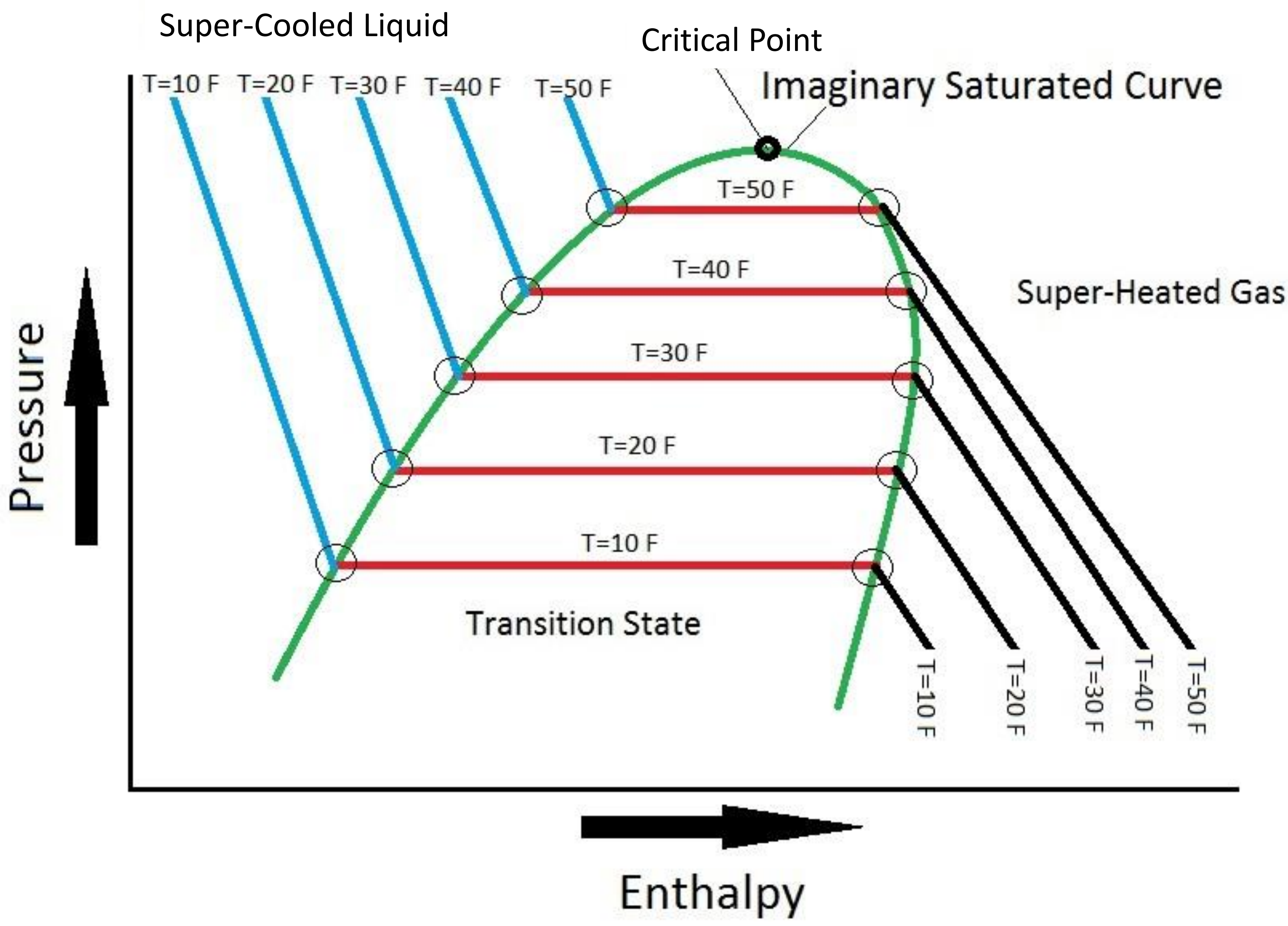
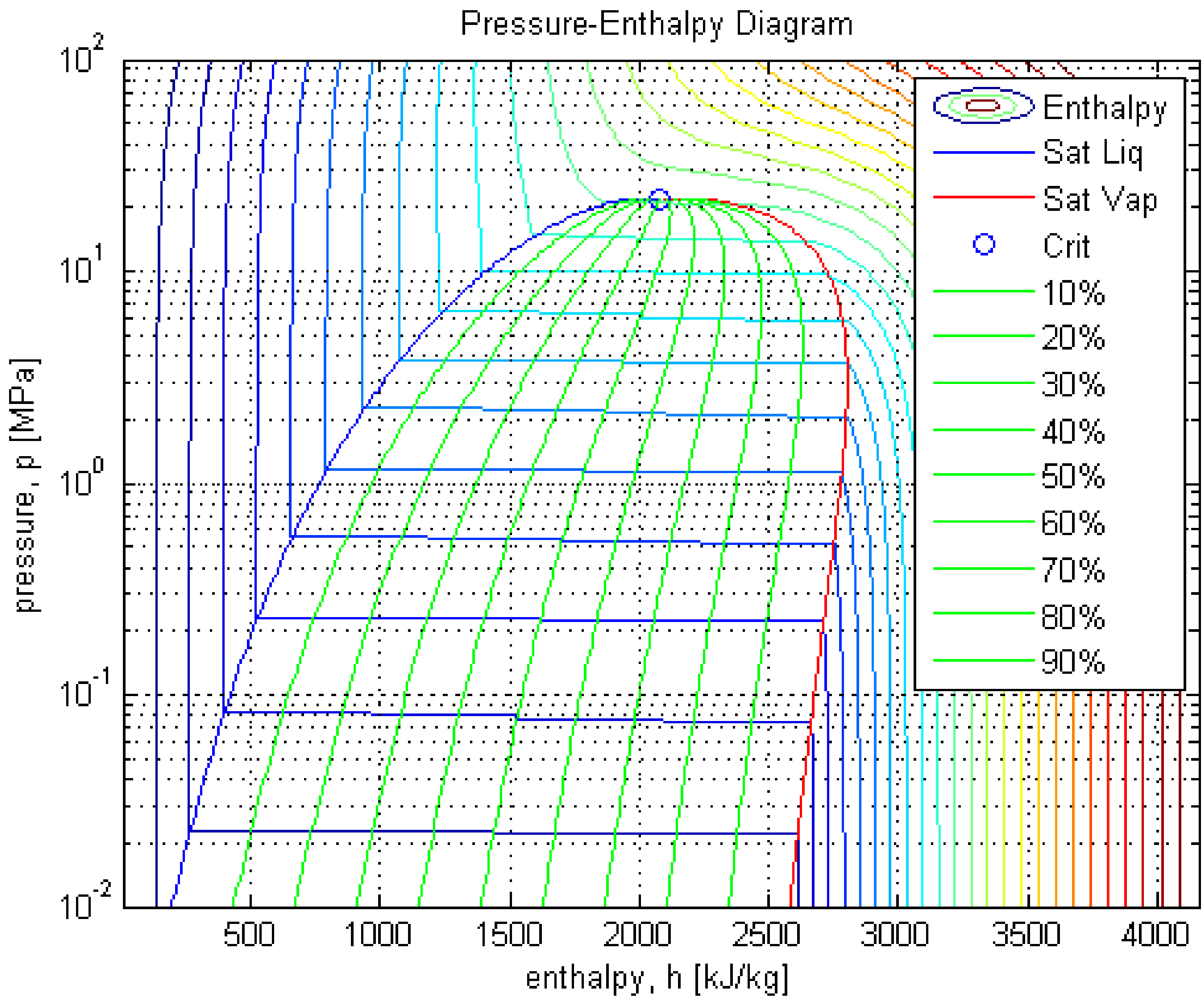
ABE 201
Biological Thermodynamics 1

Module 10:

T P H and U Relationships


Super-Cooled Liquid
Critical Point
Imaginary Saturated Curve
T=10 F
T=20 F
T=30 F
T=40 F
T=50 F
T=50 F
T=40 F
T=30 F
T=20 F
T=10 F
Super-Heated Gas
Transition State
T=10 F
T=20 F
T=30 F
T=40 F
T=50 F
Pressure
Enthalpy



Pressure-Enthalpy Diagram
pressure, p [MPa]
enthalpy, h [kJ/kg]
10^-2
10^-1
10^0
10^1
10^2
500
1000
1500
2000
2500
3000
3500
4000
Enthalpy
Sat Liq
Sat Vap
Crit
10%
20%
30%
40%
50%
60%
70%
80%
90%

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 enthalpy (or internal energy)

$$\Delta H = \Delta H_{sensible} + \Delta H_{latent}$$

- Latent heat/enthalpy is the energy of phase change:

$$\Delta \mathrm{H}_{\mathrm{latent}} = \Delta \mathrm{H}_{\mathrm{LV}} \text{ or } \Delta \mathrm{H}_{vaporization} \text{ or } \Delta \mathrm{H}_{melting}$$

- <u>Sensible heat/enthalpy</u> can be calculated using heat capacity (Cp) as a function <u>integrated</u> over a temperature range.

$$\Delta H_{sensible} = \int_{T_1}^{T_2} m \cdot C_p dT$$

- Heat capacities for solids and most liquids are <u>constants</u> over large ranges of temperatures

$$\Delta H_{sensible} = \int m \cdot C_p dT = m \cdot C_p \int dT = m \cdot C_p \cdot \Delta T$$

- Heat capacities for biological materials can be measured, use tabulated values, or be estimated from the composition.

Finding Heat Capacities

- Table B.2
  - What is Cp for Water (liquid) at 50 C?
  - What is Cp for Water (vapor) at 50 C?

From B.2 : Liquid H_2O

$C_p = 0.0754$ kJ/mol-K for T(0 – 100 C)

= 4.19 kJ/Kg-K

For Vapor

$$C_p = .03346 + 6.88 \times 10^{-6} \times T + 7.604 \times 10^{-9} \times T^2 - 3.593 \times 10^{-12} \times T^3$$

= 0.0338 kJ/mol-K = 1.88 kJ/kg-K

Example

- In a cooling process hydrogen (H_2) is cooled from 800°C to 200°C. If 10 kmol/min is delivered to the cooler, calculate the heat removal rate in kW using the heat capacity formulas (Table B.2)

Table B.2 Heat Capacities[a]

Form 1: C_p[kJ/(mol·°C)] or [kJ/(mol·K)] $= a + bT + cT^2 + dT^3$
Form 2: C_p[kJ/(mol·°C)] or [kJ/(mol·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 °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 (Units of T)
Acetone	CH_3COCH_3	58.08	l	1	°C	123.0	18.6			−30–60
			g	1	°C	71.96	20.10	−12.78	34.76	0–1200
Acetylene	C_2H_2	26.04	g	1	°C	42.43	6.053	−5.033	18.20	0–1200
Air		29.0	g	1	°C	28.94	0.4147	0.3191	−1.965	0–1500
			g	1	K	28.09	0.1965	0.4799	−1.965	273–1800
Ammonia	NH_3	17.03	g	1	°C	35.15	2.954	0.4421	−6.686	0–1200
Ammonium sulfate	$(NH_4)_2SO_4$	132.15	c	1	K	215.9				275–328
Benzene	C_6H_6	78.11	l	1	°C	126.5	23.4			6–67
			g	1	°C	74.06	32.95	−25.20	77.57	0–1200
Isobutane	C_4H_{10}	58.12	g	1	°C	89.46	30.13	−18.91	49.87	0–1200
n-Butane	C_4H_{10}	58.12	g	1	°C	92.30	27.88	−15.47	34.98	0–1200
Isobutene	C_4H_8	56.10	g	1	°C	82.88	25.64	−17.27	50.50	0–1200
Calcium carbide	CaC_2	64.10	c	2	K	68.62	1.19	-8.66×10^{10}	—	298–720
Calcium carbonate	$CaCO_3$	100.09	c	2	K	82.34	4.975	-12.87×10^{10}	—	273–1033
Calcium hydroxide	$Ca(OH)_2$	74.10	c	1	K	89.5				276–373
Calcium oxide	CaO	56.08	c	2	K	41.84	2.03	-4.52×10^{10}		273–1173
Carbon	C	12.01	c	2	K	11.18	1.095	-4.891×10^{10}		273–1373
Carbon dioxide	CO_2	44.01	g	1	°C	36.11	4.233	−2.887	7.464	0–1500
Carbon monoxide	CO	28.01	g	1	°C	28.95	0.4110	0.3548	−2.220	0–1500
Carbon tetrachloride	CCl_4	153.84	l	1	K	93.39	12.98			273–343
Chlorine	Cl_2	70.91	g	1	°C	33.60	1.367	−1.607	6.473	0–1200
Copper	Cu	63.54	c	1	K	22.76	0.6117			273–1357

[a]Adapted in part from D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering,* 3rd Edition, © 1974, Table E.1. Adapted by permission of Prentice-Hall, Inc., Englewood Cliffs, NJ.

Answer:

- Part a: (Use table B.2)

$$\dot{Q} = \dot{n}\Delta\hat{H}$$

$$\Delta\hat{H} = \int_{800}^{200} C_p dT = \int_{800}^{200} (a + b \cdot T + c \cdot T^2 + d \cdot T^3) dT$$

$$\Delta\hat{H} = \left[a \cdot T + \frac{b \cdot T^2}{2} + \frac{c \cdot T^3}{3} + \frac{d \cdot T^4}{4} \right]_{800}^{200} = -17.29 kJ / mol$$

$$a = 28.84x10^{-3}, b = 0.00765x10^{-5}, c = 0.3288x10^{-8}, d = -0.8698x10^{-12}$$

$$\Delta H = \frac{-17.29kJ}{mol} \frac{10kmol}{\min} \frac{1000mol}{1kmol} \frac{1\min}{60\sec} = -2882 \text{ kW}$$

Using Tabulated Values

- How much heat must be removed to cool 2.5 kg green beans (85% moisture content) from 20 C to -20 C?

Tabulated Heat Capacities for Selected Biological Materials

from Transport Processes and Unit Operations 3rd Ed. by Geankoplis

Material	C_p (kJ/kg-K)	Material	C_p (kJ/kg-K)
Oak	2.39	Flour	1.80-1.88
Pine, yellow	2.81	Ice Cream (liquid)	3.27
Wool	1.36	Ice Cream (frozen)	1.88
Starch	1.218	Milk, whole	3.85
Glycerol	1.382	Olive Oil	2.01
Lactose	1.202	Green Beans (fresh)	3.81
Apples	3.73-4.02	Green Beans (frozen)	1.97
Bacon	3.43	Potatoes	3.52
Beef	3.43	Poultry (fresh)	3.31
Bread, white	2.72-2.85	Poultry (frozen)	1.55
Butter	2.30		
Eggs	3.18		
Corn (fresh)	3.32		
Corn (frozen)	1.77		

$\Delta H + \Delta E_k + \Delta E_p = Q - W_s$
$\Delta H = Q$

Break up into 3 parts
1: Cool from 20C to 0C
2: Freezing Process (phase change)
3: Cool from 0C to -20C
$Q = \Delta H_1 + \Delta H_2 + \Delta H_3$

1:
$\Delta H_1 = m * c_{p(fresh)} * (T2 - T1) = 2.5 \text{ kg } (3.81 \text{ kJ/kg-C}) (0 - 20) = -190.5 \text{ kJ}$

Heat of melting (table B.1 -> water dHm = 6.0095 kJ/mol
2: $\Delta H_2 = m * xwater * \Delta H_{freezing}$
$= 2.5(0.85) * (6.0095 \text{ kJ/mol})(1 \text{ mol}/18\text{g})(1000\text{g}/1\text{kg}) = -709.5 \text{ kJ}$

3: $\Delta H_3 = m * cp(frozen) * (T2 - T1) = 2.5 * (1.97)(-20 - 0) = -98.5 \text{ kJ}$

$Q = \Delta H_1 + \Delta H_2 + \Delta H_3 = -190.5 - 709.5 - 98.5 = -998.5 \text{ kJ}$

Green Beans

- Using the Seibels Equation, what are:
  - The heat capacity of fresh green beans (85% MC)?
  - The heat capacity of frozen green beans (85% MC)?

Fresh Green Beans:

$C_p = 0.837 + 3.348*(0.85) = 3.68$ kJ/kg-K

Compare to tabulated value: $C_p = 3.81$ kJ/kg-K

Frozen Green Beans:

$C_p = 0.837 + 1.256*(0.85) = 1.91$ kJ/kg-K

Compare to tabulated value: $C_p = 1.97$ kJ/kg-K

Using Choi and Okos Equation

- Calculate the heat capacity of a bacterial cell slurry that contains a bioproduct

Slurry Composition

75.0% water

17.5% carbohydrates

5.0% protein

2.0% lipids (fat)

0.5% ash

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

$$= 4.18(0.75) + 1.711(0.05) + 1.928(0.02) + 1.547(0.175) + 0.908(0.005)$$

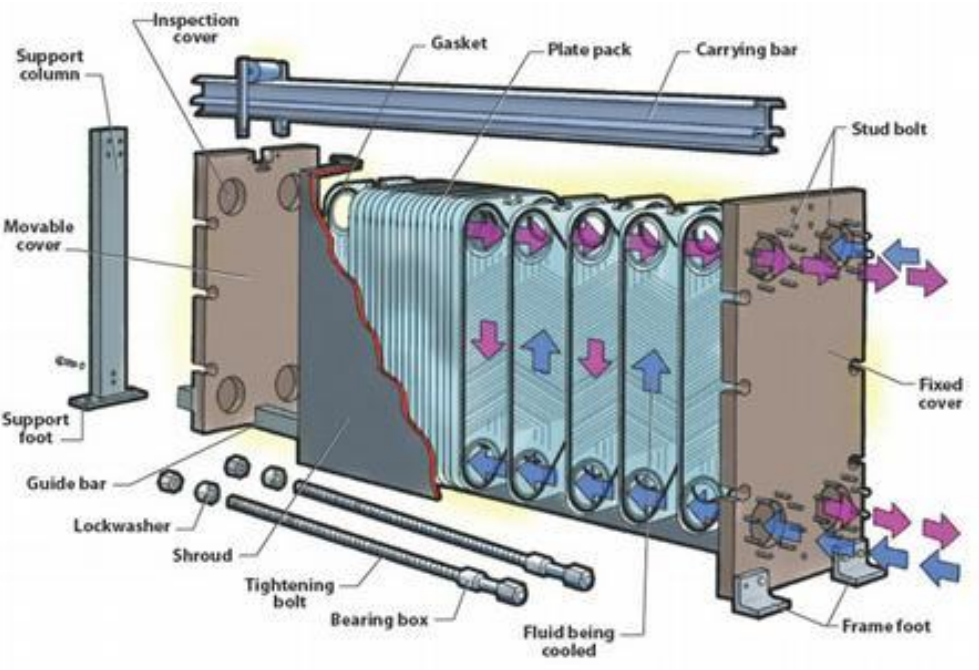
$$= 3.53 \text{ kJ/kg-K}$$

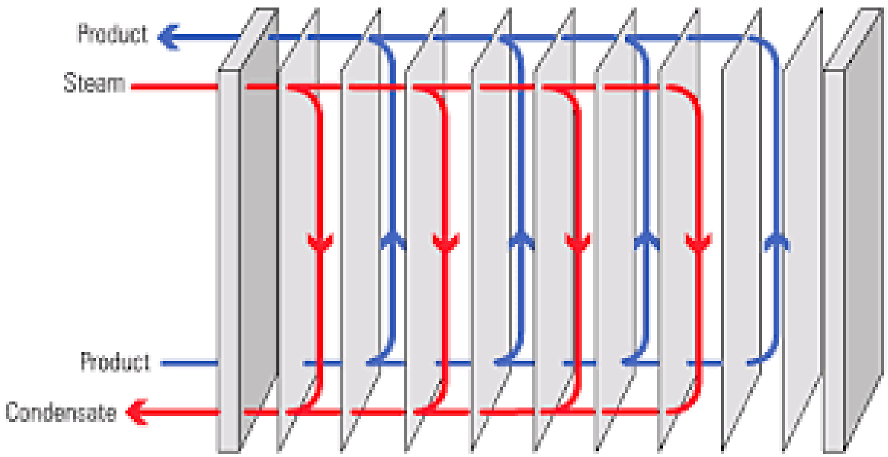
Mass and Energy Balance

Whole milk is pasteurized at a rate of 250 kg/hr by heating from 4 C to 72C in an adiabatic plate-and-frame heat exchanger using superheated steam (2 bar, 140 C) at a rate of 12.5 kg/hr.

If the steam leaves the heat exchanger at 2 bar, what is the final conditions of the steam?

Plate and Frame Heat Exchangers





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Corn (frozen)	1.77		

$\Delta H + \Delta E_k + \Delta E_p = Q - W_s$
$\Delta H = 0$

$\Delta H_{milk} = \Delta H_{steam}$

$\Delta H_{milk} = m*c_p*(T2 - T1) = 250$ kg/hr (3.85 kJ/kg-C) (72 – 4)
= 65450 kJ/hr

$\Delta H_{steam} = m_{steam}* (H_{initial,2bar,\ 140C} - H_{final})$
$= 12.5(2748.3 \text{ kJ/kg} - H_{final}) = 34353.75 - 12.5* H_{final}$

$H_{final} = 2487.7$ kJ/kg

$H_{sat(2bar,v)} = 2706.2$ kJ/kg
$H_{sat(2bar,l)} = 504.70$ kJ/kg
$H_{final} = xH_{sat(2bar,v)} + (1\text{-}x)\ H_{sat(2bar,l)}$
Where x = quality
2487.7 = x(2706.2) + (1-x) 504.70
x = 0.90

Outlet steam is saturated steam (120.2 C, 2 bar) at 90% quality.