Energy Balances – phase change and heat capacity

CHBE 220 Lecture 11

This week

- Lectures – Tues./Thurs. – CHBE 101 @ 8 am
- Office hours – Tuesday 3-4, Thursday 9:30-10:30, or by appointment, CHBE 427
- Individual Assignment 3 – 2 parts – both due Thursday at 9 pm
- Tutorial 5 submission – due Thursday at 9 pm
- Tutorial 6 preparatory exercise – due Thursday at 3:30pm
- Tutorial - Thursday - 3:30 – 5:30 pm in **CHBE 318, 314,** your team can go to either room – the tutorial will focus on describing an energy balance processes of relevance for your project.
- Peer evaluation – Most of you (109 out of 115) have submitted this through iPeer, if you submitted you should have received 0.5/0.5 on canvas.

Last class

You should now be able to:

- **Identify** relevant terms for energy balances for open and closed systems
- **Use** thermodynamic data tables to find internal energy, enthalpy or other thermodynamic properties based on system temperature and pressure
- **Solve** energy balance problems using tabulated thermodynamic data

Learning Objectives

By the end of this lecture you should be able to:

- **Evaluate** the cost of utilities in processes
- **Characterize** energy changes in a system due to changes in temperature
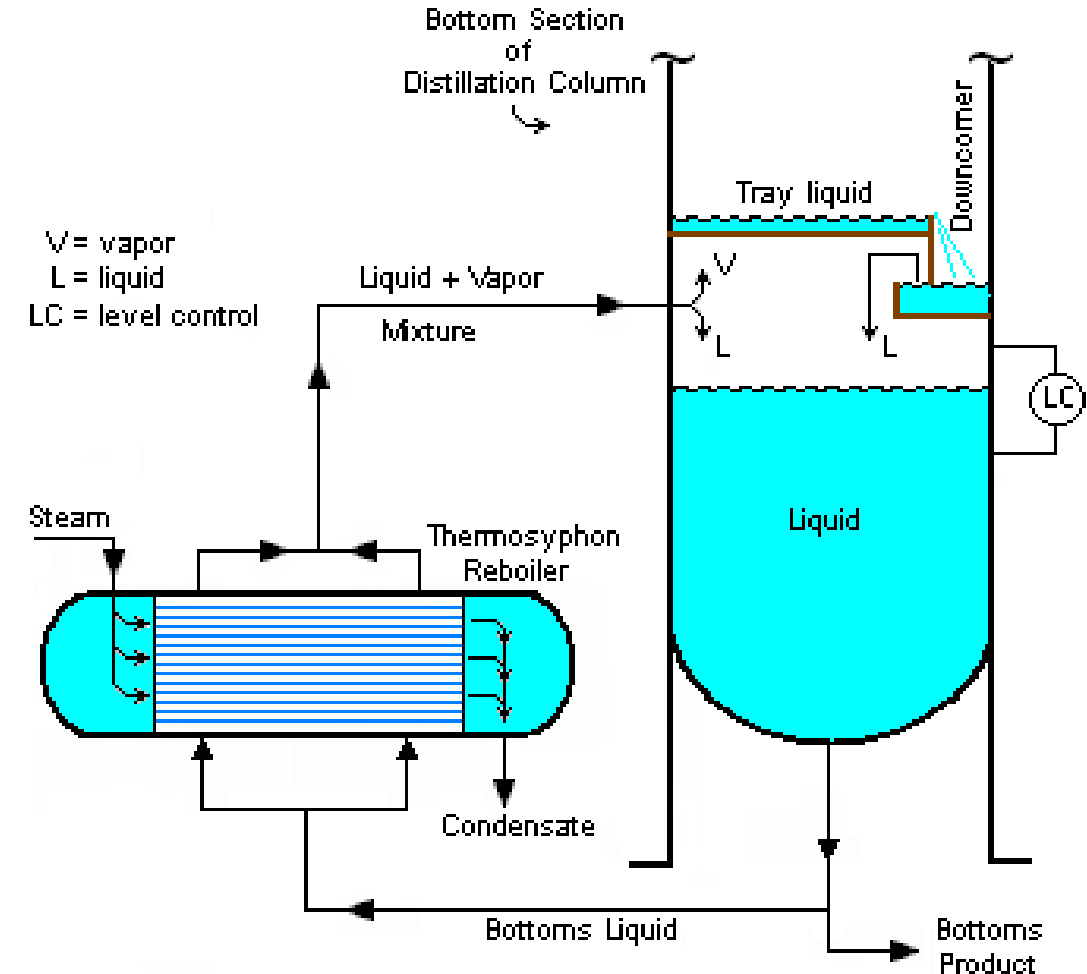- **Analyze** energy balances on processes involving phase changes

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Energy balance equipment

Thermosyphon reboiler

- Many are typically shell and tube, and the Tubular Exchanger Manufacturer's Association (TEMA) has a variety of standards and configurations.
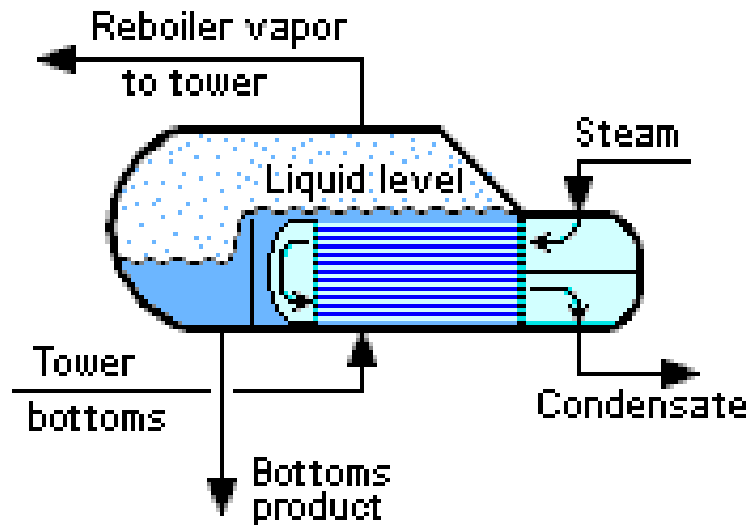
Kettle Reboiler

...and many others

Images: By H Padleckas & Mbeychok CC BY-SA 3.0 via Wikimedia Commons

Energy Balance Equipment

- Almost all energy exchange equipment is either a heat exchanger or jacket. These mostly work with a fluid transferring heat to another (the only exception is electrical heating elements, which are generally rare as they tend to cost more).

Utility	Inlet T (°C)	Outlet T (°C)	P	Cost ($/GJ)
Low-pressure steam	125	124	33 psia (0.22 MPa)	4.54
Medium-pressure steam	175	174	127 psia (0.875 MPa)	4.77
High-pressure steam	250	249	575 psia (3.97 MPa)	5.66
Electricity	N/A	N/A	N/A	18.72
Cooling water	20	25	N/A	0.378
Refrigerated water	5	15	N/A	4.77
Low T refrigerant	-20	-5	N/A	8.49

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Example from last class

A reboiler (a device used to transfer heat at the bottom of a distillation column) is used to evaporate toluene at 190℃ with a heat duty of 3,000,000 kJ/h. Steam is available at the conditions outlined in the table below. Which steam pressure would be used for this system and at what steam flow rate (assuming perfect heat transfer)?

Utility	Inlet T (℃)	Outlet T (℃)	P	Cost ($/GJ)	Cost $/h	Cost $/yr @ 8,000 hrs
High-pressure steam	250	249	575 psia (3.97 MPa)	5.66	16.98	135,840
Electricity	N/A	N/A	N/A	18.72	56.16	449,280

For Steam : $Cost\left(\frac{\$}{hr}\right) = \dot{Q} * cost\left(\frac{\$}{GJ}\right) = 3,000,000\frac{kJ}{h} * \frac{1GJ}{1,000,000kJ} * 5.66\frac{\$}{GJ} = 16.98\frac{\$}{hr}$

Utility choice can make a big difference

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Vinyl Chloride example from Tut 5
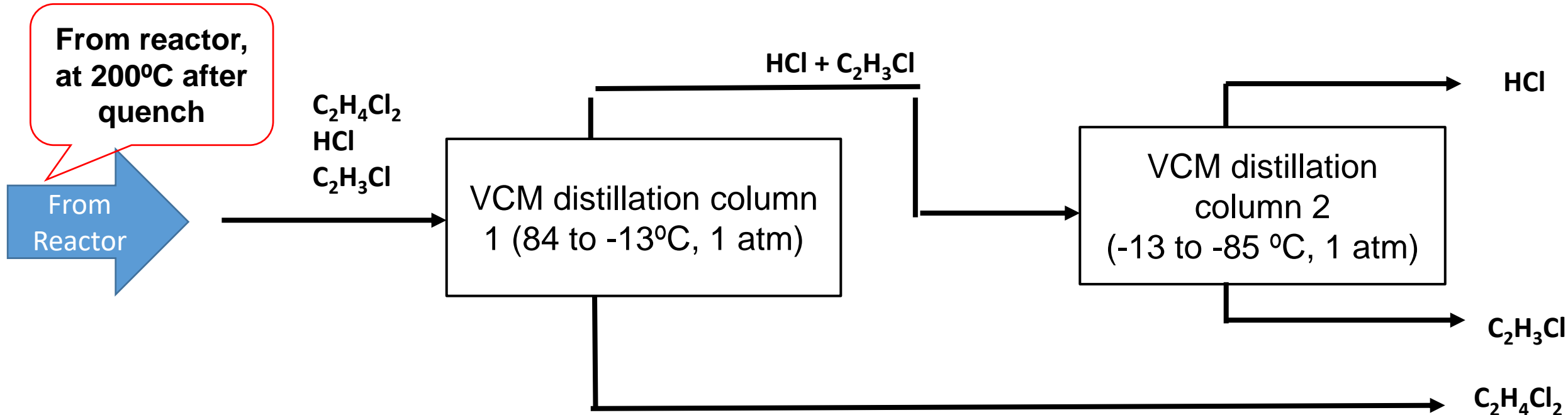
Compound	Formula	Flow to separate (tonne/hr)	Boiling point at 1 atm (°C)	Heat of vapourization at 1 atm (kJ/mol)
EDC	$C_2H_4Cl_2$	47.5008	84	35
HCl	HCl	26.2512	-85	16
VC	C_2H_3Cl	45	-13	21

Say we want this mixture from the reactor to enter the distillation column as a Vapour-liquid mixture at the dew point (since distillation columns work based on V-L equilibrium, we want to be at temperatures where we get V-L equilibrium).
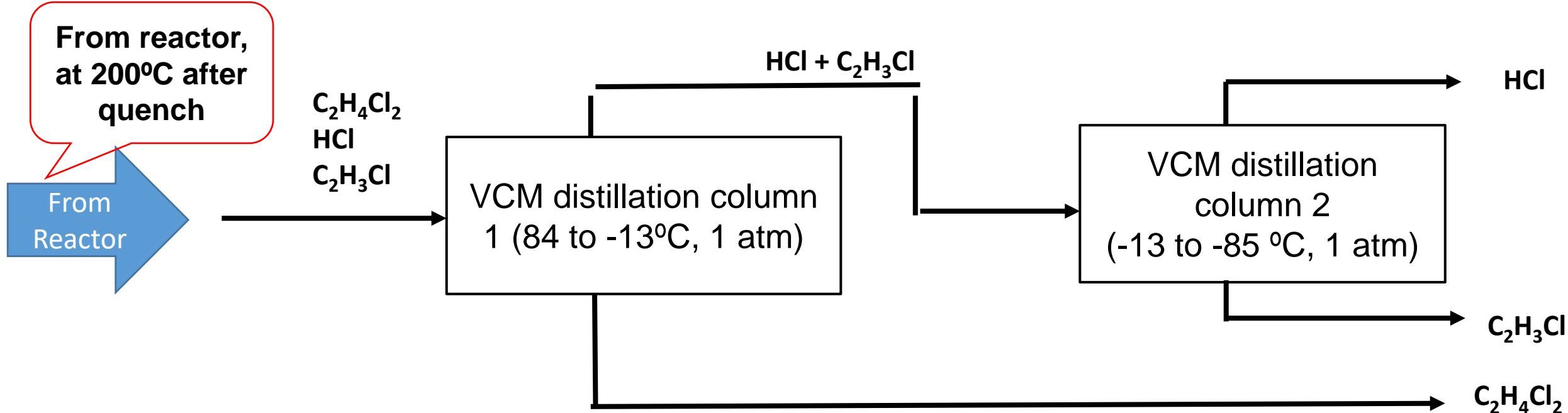
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Need to find yi's (gas mole fractions), so convert flows from tonnes/hr to tonmol/hr and use these to find yi's.
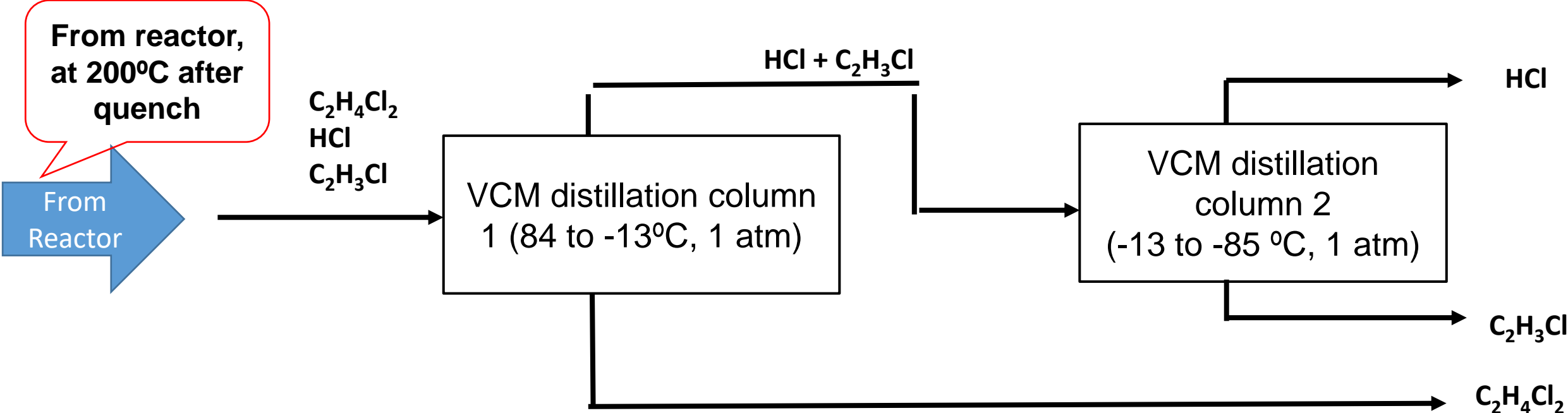
From reactor, at 200ºC after quench

From Reactor

$C_2H_4Cl_2$
HCl
C_2H_3Cl

HCl + C_2H_3Cl

VCM distillation column 1 (84 to -13ºC, 1 atm)

VCM distillation column 2 (-13 to -85 ºC, 1 atm)

HCl

C_2H_3Cl

$C_2H_4Cl_2$

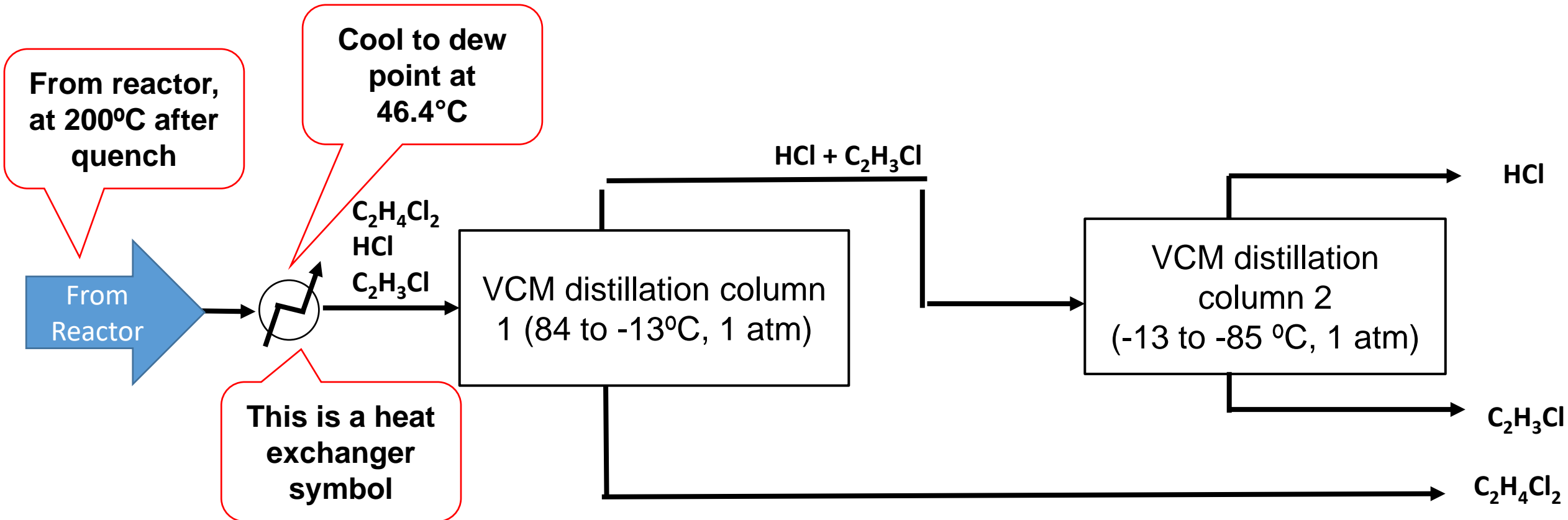| Compound	Formula	Flow to separate (tonne/hr)	Flow to separate (tonnne-mol/h)	yi (gas mole fractions)
EDC	$C_2H_4Cl_2$	47.5008	0.48	0.25
HCl	HCl	26.2512	0.72	0.375
VC	C_2H_3Cl	45	0.72	0.375

Find T = 46.4°C,

Can also calculate xi (liquid mole fractions) using Raoult's law:

$$x_i = \frac{p_i^*}{y_i \times P}$$

Compound	Formula	Flow to separate (tonne/hr)	Flow to separate (tonnne-mol/h)	yi (gas mole fractions)	xi (liquid mole fractions)
EDC	$C_2H_4Cl_2$	47.5008	0.48	0.25	.94
HCl	HCl	26.2512	0.72	0.375	0.005
VC	C_2H_3Cl	45	0.72	0.375	0.053

This is what we expect as EDC is the largest molecule, with the most interactions and the least volatile (also we saw this with the boiling T)

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Now, how much energy is removed to cool this exit stream down from 200°C to 46.4°C?

Compound	Formula	Flow to separate (tonne/hr)	Flow to separate (tonnne-mol/h)	yi (gas mole fractions)	xi (liquid mole fractions)
EDC	$C_2H_4Cl_2$	47.5008	0.48	0.25	.94
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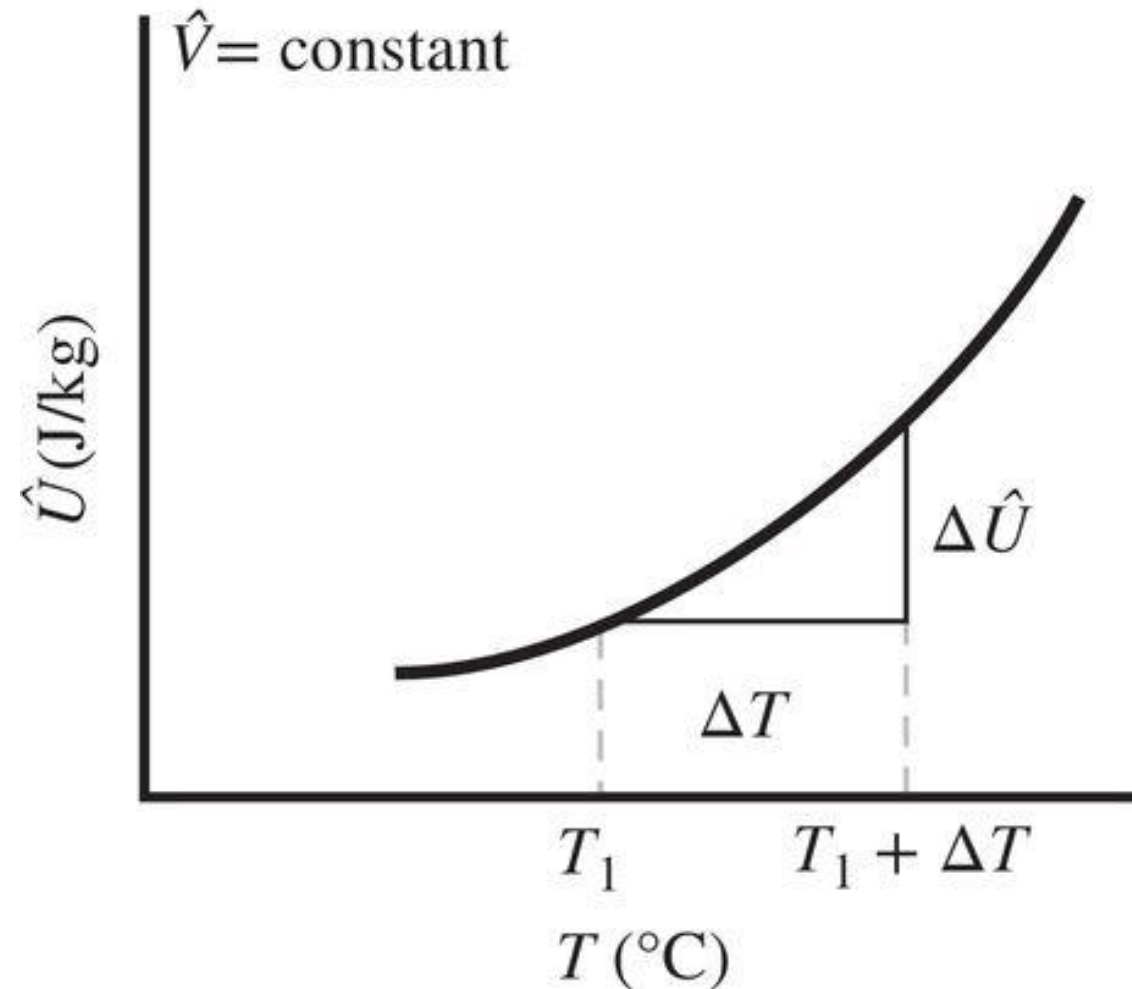# Changes in temperature, holding other variables constant

Closed system

$$Q = \Delta \widehat{U}$$

No work since $\widehat{V}$ is constant

$$C_v(T) = \lim_{\Delta T \to 0} \frac{\Delta \widehat{U}}{\Delta T} = \left(\frac{\partial \widehat{U}}{\partial T} \right)_V$$

Above expression relates the heat capacity at a constant volume (C_v) to the partial derivative of internal energy ($\widehat{U}$) over temperature (T) at a constant volume (V).

Fig from: Elementary Principles of Chemical Processes, 4/E by Richard M. Felder, Ronald W. Rousseau, and Lisa G. Bullard Copyright © 2016 by John Wiley & Sons, Inc.

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$$C_v(T) = \lim_{\Delta T \to 0} \frac{\Delta \widehat{U}}{\Delta T} = \left(\frac{\partial \widehat{U}}{\partial T}\right)_V$$

Note $C_v(T)$ is heat capacity as a function of temperature, not multiplication $C_v \times T$.

Re-arrange and integrate

$$d\widehat{U} = C_v(T)dT$$
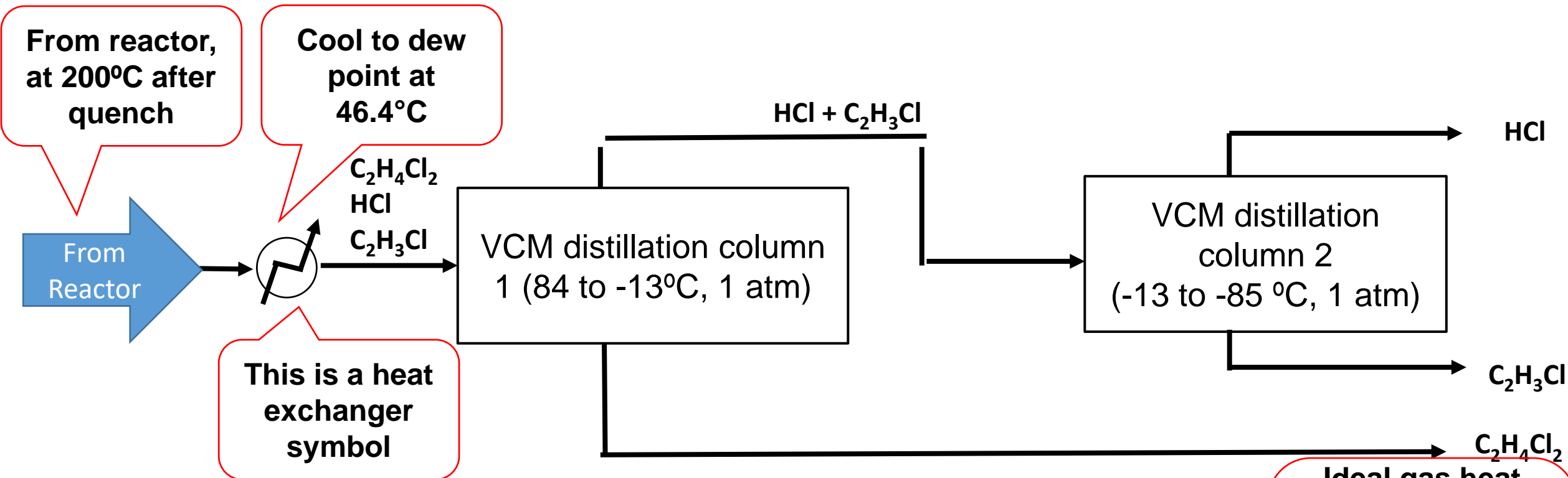
$$\Delta \widehat{U} = \int_{T_1}^{T_2} C_v(T)dT$$

In open systems, we use heat capacity at constant pressure

$$C_p(T) = \lim_{\Delta T \to 0} \frac{\Delta \widehat{H}}{\Delta T} = \left(\frac{\partial \widehat{H}}{\partial T}\right)_P$$

Re-arrange and integrate

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

Now, how much energy is removed to cool this exit stream down from 200°C to 46.4°C? Calculate this energy change for the 3 compounds.

Compound	Formula	Flow to separate (tonne/hr)	Flow to separate (tonnne-mol/h)	Cp (J/mol K)
EDC	$C_2H_4Cl_2$	47.5008	0.48	29
HCl	HCl	26.2512	0.72	29
VC	C_2H_3Cl	45	0.72	29

Ideal gas heat capacities, as there was no listed heat capacities for these gases I could find

For EDC: $\Delta \dot{H} = \dot{n} \int_{T_1}^{T_2} C_p(T) dT = .48 \frac{\text{tonnne}-\text{mol}}{\text{h}} * 1{,}000{,}000 \frac{\text{mol}}{tonne-\text{mol}} * 29 \frac{J}{\text{molK}} * (200°C - 46.4°C) * \frac{1K}{1°C} = 2.14 \times 10^9 J/h$

For HCl or VC: $\Delta \dot{H} = \dot{n} \int_{T_1}^{T_2} C_p(T) dT = .72 \frac{\text{tonnne}-\text{mol}}{\text{h}} * 1{,}000{,}000 \frac{\text{mol}}{tonnne-\text{mol}} * 29 \frac{J}{\text{molK}} * (200°C - 46.4°C) * \frac{1K}{1°C} =$
$3.21 \times 10^9 J/h$

Total: $8.55 \times \frac{10^9 J}{h} = 8.55$ GJ/hr

Note that here we assume the interaction between species does not affect the heat capacity

How to remove this 8.55 GJ/h from our stream going from 200°C to 46.4°C?

Option	Utility	Inlet T (°C)	Outlet T (°C)	P	Cost ($/GJ)
A	Cooling water	20	25	N/A	0.378
B	Refrigerated water	5	15	N/A	4.77
C	Low T refrigerant	-20	-5	N/A	8.49

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Cooling water is the least expensive and it follows our rule of thumb of having at least 10°C of difference with our process stream.

$$\text{For water}: Cost\left(\frac{\$}{hr}\right) = \dot{Q} * cost\left(\frac{\$}{GJ}\right) = 8.55\frac{GJ}{h} * 0.378\frac{\$}{GJ} = 3.23\frac{\$}{hr}$$

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How much water is needed to remove this 8.55 GJ/h from our stream?

Option	Utility	Inlet T (°C)	Outlet T (°C)	P	Cost ($/GJ)
A	Cooling water	20	25	N/A	0.378

The heat capacity coefficients are used in the equation:

$$C_P = A + BT + CT^2 + DT^3$$

where T is in K and C_P in J/mol-K The heat capacities tabulated

	$\Delta H_{f,298.15}$	$\Delta G_{f,298.15}$	Heat Capacity Constants			
	kJ/mol	kJ/mol	A	B	C	D
Water	-285.83	-237.214	7.243E+01	1.039E-02	-1.497E-06	

> For this small temperature range we could assume a constant heat capacity of 76 J/mol K, but we will compare this to textbook data. Generally the larger the T range, the better it is to use the variable Cp.

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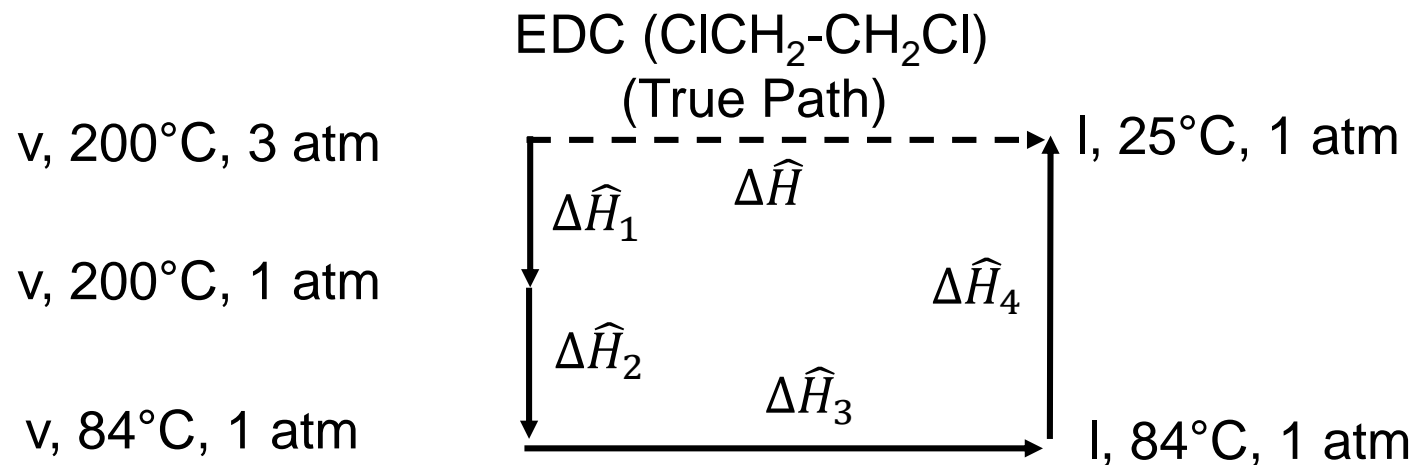$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p(T)dT = 76\frac{J}{molK} * (25°C - 20°C)\frac{K}{°C} = 380\frac{J}{mol}$$

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

$$\dot{n} = \frac{\dot{Q}}{\Delta \hat{H}} = \frac{8.55\frac{GJ}{h} * 1E9\frac{J}{GJ}}{380\,J/mol} = 2.25 \times 10^7 mol/h$$

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Values from: Introductory Chemical Engineering Thermodynamics, second edition by Elliott and Lira

Hypothetical process paths

$\widehat{U}$ & $\widehat{H}$ are state properties, and depend on state, rather than the path to that state.

Eg. Enthalpy change ($\Delta\widehat{H}$) related to transformation of dichloroethane (EDC) from vapour at 200°C and 3 atm to liquid at 25°C and 1 atm.

EDC (ClCH$_2$-CH$_2$Cl)
(True Path)

v, 200°C, 3 atm $\dashrightarrow$ l, 25°C, 1 atm

$\Delta\widehat{H}_1$ $\Delta\widehat{H}$

v, 200°C, 1 atm $\Delta\widehat{H}_4$

$\Delta\widehat{H}_2$

v, 84°C, 1 atm $\Delta\widehat{H}_3$ l, 84°C, 1 atm

What would you look up to calculate the above energy transitions?

Why do we split this transition up?

Easier to calculate energy transitions with only 1 variable changing

Data tables may not provide the exact information we want. We seen how to calculate the energy of each of these transitions:

A. Changes in T at constant P and state of aggregation

B. Phase changes at constant T, P

C. Chemical reaction at constant T, P

Learning Objectives

By the end of this lecture you should be able to:

- **Evaluate** the cost of utilities in processes
- **Characterize** energy changes in a system due to changes in temperature
- **Analyze** energy balances on processes involving phase changes