

**UNIVERSIDADE DE SÃO PAULO
INSTITUTO DE QUÍMICA DE SÃO CARLOS**



Operações Unitárias I

Balanço de Energia

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Capacidade calorífica

Fórmula genérica $C_p = f(T) = a + bT + cT^2 + dT^3$

TABELA D e E (pág. 119 e 120) - ANEXO

Líquidos e sólidos $\Rightarrow C_p = C_v$

Gases ideais $\Rightarrow C_p = C_v + R$

Gases reais \Rightarrow muito complexo e não é objetivo deste curso

Cálculo das Entalpias de misturas

$$C_{p_m}(T) = \sum_{i=1}^n y_i C_{p_i}(T)$$

$$\Delta H_m = \int_{T_1}^{T_2} C_{p_m}(T) dT$$

Capacidade calorífica média, $\overline{C_p}$

Entalpia de alguma substância tabelada relativa ao estado de referência

$$\Delta H = \overline{C_p} \cdot \Delta T \qquad \Delta H = \overline{C_p} \cdot (T - T_{\text{ref}})$$

TABELA E

OU

ΔH para a variação entre duas temperaturas T_1 e T_2

$$\Delta H (T_1 \rightarrow T_2) = \Delta H(T_2) - \Delta H(T_1) = \overline{C_p}_{T_2} (T_2 - T_{\text{ref}}) - \overline{C_p}_{T_1} (T_1 - T_{\text{ref}})$$

Válido porque a entalpia é uma **propriedade de estado**, ou seja, depende apenas do estado inicial e final do processo.

TABELA D: Capacidade Calorífica

Form 1: $C_p(J/mol \cdot ^\circ C)$ or $(J/mol \cdot K) = a + bT + cT^2 + dT^3$

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

Example: $(C_p)_{\text{benzene}} = 71.96 + (20.10 \times 10^{-2})T - (12.78 \times 10^{-3})T^2 + (34.76 \times 10^{-5})T^3$, where T is in $^\circ C$.

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

Compound	Formula	Mol. Wt.	State	Form	Temp. Unit	a	b · 10 ²	c · 10 ⁵	d · 10 ⁹	Range (Units of T)
Acetone	CH ₃ COCH ₃	58.08	l	l	$^\circ C$	123.0	18.6			-30-60
Acetylene	C ₂ H ₂	26.04	g	l	$^\circ C$	71.96	20.10	-12.78	34.76	0-120
Air		29.0	g	l	$^\circ C$	42.43	6.053	-5.033	18.20	0-120
Ammonia	NH ₃	17.03	g	l	K	28.94	0.4147	0.3191	-1.965	0-150
Ammonium sulfate	(NH ₄) ₂ SO ₄	132.15	c	l	K	28.09	0.1965	0.4799	-1.965	273-180
Benzene	C ₆ H ₆	78.11	l	l	$^\circ C$	35.15	2.954	0.4421	-6.686	0-120
Isobutane	C ₄ H ₁₀	58.12	g	l	K	215.9				275-328
n-Butane	C ₄ H ₁₀	58.12	g	l	$^\circ C$	62.55	23.4			279-350
Isobutene	C ₄ H ₈	56.10	g	l	$^\circ C$	74.06	32.95	-25.20	77.57	0-120
Calcium carbide	CaC ₂	64.10	c	2	K	89.46	30.13	-18.91	49.87	0-120
Calcium carbonate	CaCO ₃	100.09	c	2	K	92.30	27.88	-15.47	34.98	0-120
Calcium hydroxide	Ca(OH) ₂	74.10	c	l	K	82.88	25.64	-17.27	50.50	0-120
Calcium oxide	CaO	56.08	c	2	K	68.62	1.19	-8.66 × 10 ¹⁰	—	298-720
Carbon	C	12.01	c	2	K	82.34	4.975	-12.87 × 10 ¹⁰	—	273-10 ³
Carbon dioxide	CO ₂	44.01	g	l	K	89.5				276-37 ³
Carbon monoxide	CO	28.01	g	l	K	41.84	2.03	-4.52 × 10 ¹⁰		273-11 ³
Carbon tetrachloride	CCl ₄	153.84	l	l	K	11.18	1.095	-4.891 × 10 ¹⁰		273-13 ³
Chlorine	Cl ₂	70.91	g	l	$^\circ C$	36.11	4.233	-2.887	7.464	0-150
Copper	Cu	63.54	c	l	$^\circ C$	28.95	0.4110	0.3548	-2.220	0-150
Cumene (Isopropyl benzene)	C ₉ H ₁₂	120.19	g	l	K	93.39	12.98			273-34 ³
Cyclohexane	C ₆ H ₁₂	84.16	g	l	$^\circ C$	33.60	1.367	-1.607	6.473	0-120
Cyclopentane	C ₅ H ₁₀	70.13	g	l	K	22.76	0.6117			273-135
Ethane	C ₂ H ₆	30.07	g	l	$^\circ C$	139.2	53.76	-39.79	120.5	0-12
Ethyl alcohol (Ethanol)	C ₂ H ₅ OH	46.07	l	l	$^\circ C$	94.140	49.62	-31.90	80.63	0-12
Ethylene	C ₂ H ₄	28.05	g	l	$^\circ C$	73.39	39.28	-25.54	68.66	0-12
Ferric oxide	Fe ₂ O ₃	159.70	c	2	K	49.37	13.92	-5.816	7.280	0-12
Formaldehyde	CH ₂ O	30.03	g	l	$^\circ C$	103.1				0
Helium	He	4.00	g	l	$^\circ C$	158.8				100
n-Hexane	C ₆ H ₁₄	86.17	l	l	$^\circ C$	61.34	15.72	-8.749	19.83	0-12
Hydrogen	H ₂	2.016	g	l	$^\circ C$	+40.75	11.47	-6.891	17.66	0-12
Hydrogen sulfide	H ₂ S	34.08	g	l	K	103.4	6.711	-17.72 × 10 ¹⁰	—	273-10
Hydroxyl radical	OH	17.01	g	l	$^\circ C$	34.28	4.268	0.0000	-8.694	0-12
Hydroxyl radical	OH	17.01	g	l	$^\circ C$	20.8				All
Hydroxyl radical	OH	17.01	g	l	$^\circ C$	216.3				20-110
Hydroxyl radical	OH	17.01	g	l	$^\circ C$	137.44	40.85	-23.92	57.66	0-12

TABELA I

TABELA D

Compound	Formula	Mol. Wt.	State	Form	Temp. Unit	α	$b \cdot 10^2$	$c \cdot 10^4$	$d \cdot 10^6$	Range (Units of T)
Hydrogen	H ₂	2.016	g	1	°C	28.84	0.00765	0.3288	-0.8698	0-12
Hydrogen bromide	HBr	80.92	g	1	°C	29.10	-0.0227	0.9887	-4.858	0-12
Hydrogen chloride	HCl	36.47	g	1	°C	29.13	-0.1341	0.9715	-4.335	0-12
Hydrogen cyanide	HCN	27.03	g	1	°C	35.3	2.908	1.092		0-12
Hydrogen sulfide	H ₂ S	34.08	g	1	°C	33.51	1.547	0.3012	-3.292	0-12
Magnesium chloride	MgCl ₂	95.23	c	1	K	72.4	1.58			273-92
Magnesium oxide	MgO	40.32	c	2	K	45.44	0.5008	-8.732 × 10 ¹⁰		273-21
<u>Methane</u>	CH ₄	16.04	g	1	°C	<u>34.31</u>	<u>5.469</u>	<u>0.3661</u>	-11.00	0-120
			g	1	K	19.87	5.021	1.268	-11.00	273-120
Methyl alcohol (Methanol)	CH ₃ OH	32.04	l	1	°C	75.86				0
						82.59				40
			g	1	°C	42.93	8.301	-1.87	-8.03	0-71
Methyl cyclohexane	C ₇ H ₁₄	98.18	g	1	°C	121.3	56.53	-37.72	100.8	0-12
Methyl cyclopentane	C ₆ H ₁₂	84.16	g	1	°C	98.83	45.857	-30.44	83.81	0-12
Nitric acid	HNO ₃	63.02	l	1	°C	110.0				25
Nitric oxide	NO	30.01	g	1	°C	29.50	0.8188	-0.2925	0.3652	0-3
<u>Nitrogen</u>	N ₂	<u>28.02</u>	g	1	°C	<u>29.00</u>	<u>0.2199</u>	<u>0.5723</u>	-2.871	0-12
Nitrogen dioxide	NO ₂	46.01	g	1	°C	36.07	3.97	-2.88	7.87	0-12
Nitrogen tetraoxide	N ₂ O ₄	92.02	g	1	°C	75.7	12.5	-11.3		0-3
Nitrous oxide	N ₂ O	44.02	g	1	°C	37.66	4.151	-2.694	10.57	0-12
Oxygen	O ₂	32.00	g	1	°C	29.10	1.158	-0.6076	1.311	0-12
n-Pentane	C ₅ H ₁₂	72.15	l	1	°C	155.4	43.68			0-3
			g	1	°C	114.8	34.09	-18.99	42.26	0-12
Propane	C ₃ H ₈	44.09	g	1	°C	68.032	22.59	-13.11	31.71	0-12
Propylene	C ₃ H ₆	42.08	g	1	°C	59.580	17.71	-10.17	24.60	0-12
Sodium carbonate	Na ₂ CO ₃	105.99	c	1	K	121				288-3
Sodium carbonate decahydrate	Na ₂ CO ₃ · 10H ₂ O	286.15	c	1	K	535.6				298
Sulfur	S	32.07	c	1	K	15.2	2.68			273-3
			(Rhombic)							
			c	1	K	18.3	1.84			368-3
			(Monoclinic)							
Sulfuric acid	H ₂ SO ₄	98.08	l	1	°C	139.1	15.59			10-4
Sulfur dioxide	SO ₂	64.07	g	1	°C	38.91	3.904	-3.104	8.606	0-12
Sulfur trioxide	SO ₃	80.07	g	1	°C	48.50	9.188	-8.540	32.40	0-12
<u>Toluene</u>	C ₇ H ₈	92.13	l	1	°C	<u>148.8</u>				0
			l	1	°C	<u>181.2</u>				100
			g	1	°C	<u>94.18</u>	38.00	-27.86	80.33	0-12
Water	H ₂ O	<u>18.016</u>	l	1	°C	75.4				0-12
			g	1	°C	33.46	0.6880	0.7604	-3.593	0-12

TABELA E: Capacidade Calorífica Média de Gases Combustíveis Ideais: Unidades em SI.

T(°C)	\bar{C}_p (J/mol·°C)						
	Air	O ₂	N ₂	H ₂	CO	CO ₂	H ₂ O
0	28.94	29.24	29.03	28.84	29.00	36.63	33.55
25	29.05	29.39	29.06	28.84	29.06	37.15	33.63
100	29.21	29.80	29.16	28.86	29.23	38.63	33.92
200	29.45	30.32	29.32	28.90	29.47	40.45	34.34
300	29.71	30.80	29.52	28.95	29.72	42.10	34.80
400	29.97	31.24	29.74	29.03	29.99	43.59	35.29
500	30.25	31.65	29.98	29.12	30.27	44.93	35.81
600	30.53	32.02	30.24	29.23	30.56	46.14	36.36
700	30.81	32.39	30.51	29.35	30.85	47.23	36.92
800	31.10	32.71	30.79	29.48	31.14	48.20	37.49
900	31.38	33.02	31.07	29.63	31.42	49.07	38.08
1000	31.65	33.30	31.34	29.78	31.70	49.85	38.66
1100	31.92	33.55	31.62	29.94	31.97	50.54	39.24
1200	32.18	33.79	31.88	30.12	32.23	51.18	39.81
1300	32.42	34.02	32.13	30.29	32.47	51.75	40.37
1400	32.65	34.23	32.37	30.47	32.69	52.28	40.91
1500	32.85	34.42	32.58	30.66	32.89	52.77	41.42

TABELA E

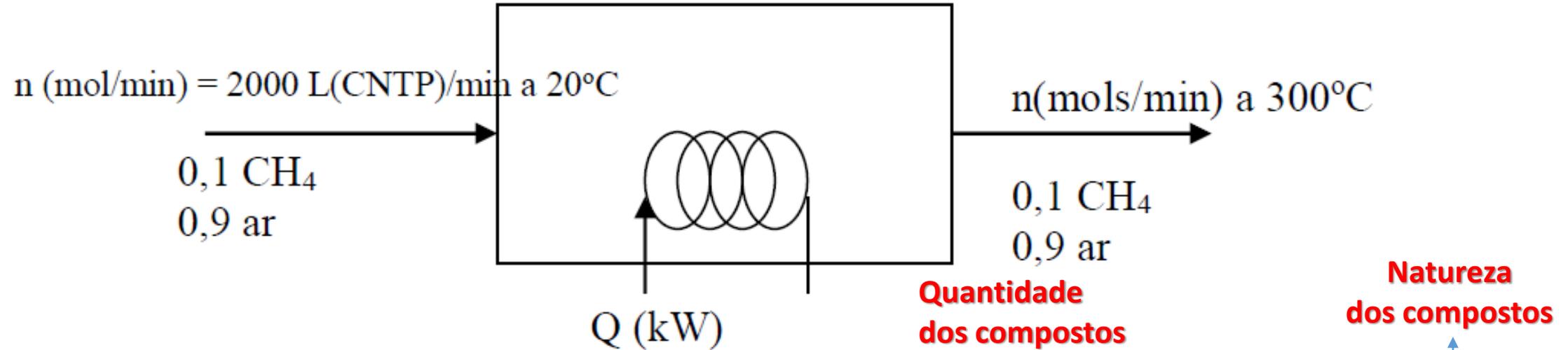
$$H = C_{p_T} \cdot (T - T_{ref})$$

* Calculated from the heat capacity formulas of Table D

Example: The enthalpy of oxygen at 700°C relative to O₂ at 25°C [or the enthalpy change for the process O₂(25°C) → O₂(700°C)] is

$$\begin{aligned} \bar{H}_{O_2}(700^\circ\text{C}) &= (\bar{C}_p)_{700^\circ\text{C}}(700^\circ\text{C} - 25^\circ\text{C}) \\ &= \left(32.39 \frac{\text{J}}{\text{mol}\cdot^\circ\text{C}} \right) (675^\circ\text{C}) = 21\,860 \text{ J/mol} \end{aligned}$$

Exercício III.6) Uma corrente contendo 10% CH₄ e 90% de ar em volume deve ser aquecida de 20 a 300°C. Calcule a taxa de calor requerida em kW se a vazão volumétrica do gás é 2,00x10³ L (CNTTP)/min



- **Metano (CH₄) => Simples**
- **Ar => mistura**

$$Q = \Delta H = \sum_{\text{saída}} n_i H_i - \sum_{\text{entrada}} n_i H_i$$

TABELA E: Capacidade Calorífica Média de Gases Combustíveis Ideais: Unidades em SI.

T(°C)	\bar{C}_p (J/mol·°C)						
	Air	O ₂	N ₂	H ₂	CO	CO ₂	H ₂ O
0	28.94	29.24	29.03	28.84	29.00	36.63	33.55
25	29.05	29.39	29.06	28.84	29.06	37.15	33.63
100	29.21	29.80	29.16	28.86	29.23	38.63	33.92
200	29.45	30.32	29.32	28.90	29.47	40.45	34.34
300	29.71	30.80	29.52	28.95	29.72	42.10	34.80
400	29.97	31.24	29.74	29.03	29.99	43.59	35.29
500	30.25	31.65	29.98	29.12	30.27	44.93	35.81
600	30.53	32.02	30.24	29.23	30.56	46.14	36.36
700	30.81	32.39	30.51	29.35	30.85	47.23	36.92
800	31.10	32.71	30.79	29.48	31.14	48.20	37.49
900	31.38	33.02	31.07	29.63	31.42	49.07	38.08
1000	31.65	33.30	31.34	29.78	31.70	49.85	38.66
1100	31.92	33.55	31.62	29.94	31.97	50.54	39.24
1200	32.18	33.79	31.88	30.12	32.23	51.18	39.81
1300	32.42	34.02	32.13	30.29	32.47	51.75	40.37
1400	32.65	34.23	32.37	30.47	32.69	52.28	40.91
1500	32.85	34.42	32.58	30.66	32.89	52.77	41.42

TABELA E

* Calculated from the heat capacity formulas of Table D

Example: The enthalpy of oxygen at 700°C relative to O₂ at 25°C [or the enthalpy change for the process O₂(25°C) → O₂(700°C)] is

$$\begin{aligned} \bar{H}_{\text{O}_2}(700^\circ\text{C}) &= (\bar{C}_p)_{700^\circ\text{C}}(700^\circ\text{C} - 25^\circ\text{C}) \\ &= \left(32.39 \frac{\text{J}}{\text{mol}\cdot^\circ\text{C}} \right) (675^\circ\text{C}) = 21\,860 \text{ J/mol} \end{aligned}$$