Find equilibrium urea yield

This nomograph quickly determines the equilibrium constant for recycled ammonia and carbon dioxide conversion to urea in commercial plants

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UREA is synthesized from NH_3 and CO_2 according to the following:

$$2\,NH_3 + CO_2 \rightleftarrows NH_4CO_2NH_2 - 38{,}000\ \text{KgCal/Mole} \quad (1)$$

Ammonium Carbamate

$$NH_4CO_2NH_4 \rightleftarrows NH_2CONH_2 + H_2O + 7{,}000\ \text{KgCal/Mole} \quad (2)$$

Urea

Reaction (1) is strongly exothermic, almost instantaneous and complete. Reaction (2) is endothermic, much slower and does not go to completion.

Both reactions are usually carried out simultaneously in a single reactor, in which the exothermic heat of reaction (1) is directly utilized to sustain reaction (2).

Unconverted ammonium carbamate is usually separated from the aqueous urea product solution by low pressure decomposition to NH_3 and CO_2 gas. Such gas is then absorbed in water and the aqueous solution of ammonium carbamate formed is recycled to the reactor for recovery.

In practice, the following equilibrium exists in a urea synthesis reactor operating within a liquid recycle urea synthesis process:

Reactor feed streams — Reactor effluent solution

$$a\,NH_3 + b\,H_2O + CO_2 \rightleftarrows x\,NH_2CONH_2 + (1-x)\,NH_4CO_2NH_2 + (a-2)\,NH_3 + (b+x)\,H_2O \quad (3)$$

Excess ammonia shifts Reaction (3) to the right, and excess water shifts it to the left.

Thus, based on Reactions (1) and (2), the equilibrium constant "K" for the above mixture in equilibrium is presented by:

$$K = \frac{x\,(b+x)\,(1+a+b-x)}{(1-x)\,(a-2x)^2} \quad (4)$$

Frejacques[1] first determined the values for the equilibrium constant "K" with respect to temperature in a batch autoclave and worked out an approximated nomographic presentation of formula (4).

However, tests by the writer on commercial urea synthesis reactors indicate much higher values for the equilibrium constant "K" in relation to temperature. Constants by Frejacques and the writer are tabulated below.

Temperature °C	Values for the equilibrium constant "K" — Determined by Frejacques	Determined in continuous reactors
150	0.8.	0.84
160	0.92	1.07
170	1.07	1.37
180	1.23	1.80
190	1.45	2.38
200	1.70	3.10

These findings have been incorporated in the revised nomograph which is the exact mathematical presentation of equation (4), with the temperature scale (No. 1) added for easy determination of the "K" value in relation to reactor operating temperature.

The reader must be cautioned that the conversion values

About the author

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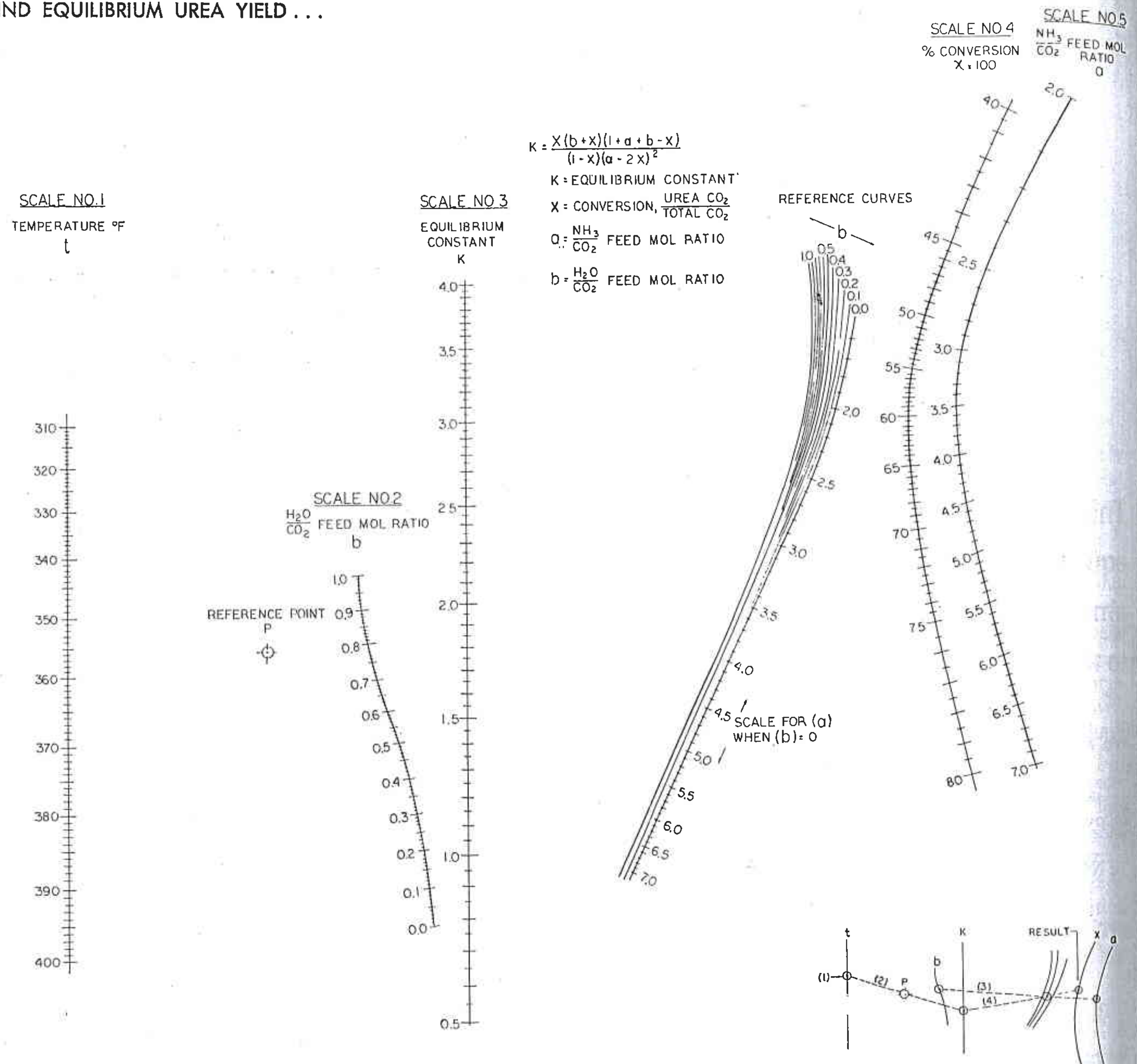

STEP NO. 1. SELECT OPERATING TEMPERATURE (t) ON SCALE NO.1

STEP NO.2. DRAW A STRAIGHT LINE FROM (t) THROUGH THE FIXED REFERENCE POINT (P) TO INTERSECT SCALE NO.3. READ THE VALUE FOR K AT INTERSECTION.

STEP NO.3. SELECT VALUE FOR (a) ON SCALE NO.5 AND VALUE FOR (b) ON SCALE NO.2. CONNECT (a) AND (b) AND MARK THE POINT OF INTERSECTION OF THIS LINE WITH THE APPROPRIATE REFERENCE CURVE CORRESPONDING TO THE SAME VALUE OF (b)

STEP NO.4. DRAW A STRAIGHT LINE FROM (K) AS DETERMINED IN STEP NO.2 THROUGH THE REFERENCE POINT AS DETERMINED IN STEP NO.3 AND INTERSECT SCALE NO.4 READ THE VALUE FOR CONVERSION (X) AT THE INTERSECTION.

FOR A SPECIAL CASE WHEN (b) = 0, (a) MAY BE READ DIRECTLY ALONG THE REFERENCE CURVE FOR b = 0, THUS ELIMINATING STEP NO.3.

EXAMPLE:

FOR: t = 365°F
a = 3.6
b = 0.5
K = 2.06
X = 67%

Fig. 1—Knowing reactor temperature, this nomograph gives equilibrium conversion for recycled ammonia and carbon dioxide to urea.

indicated in the graph can only be attained in practice in properly designed continuous reactors.

In addition to the standard reactor design criteria, other parameters as the combination of operating pressure, temperature, NH_3 and H_2O to CO_2 mol ratios, reactants residence time in the reactor and their proper homogenizing must be taken in consideration in order to optimize the overall conversion of CO_2 to urea.

Prints of the nomograph are available in 8½" x 11"; 11" x 17"; and in its original size 28" x 36", by request on company's letterhead to: Ivo Mavrovic, Consulting Engineer, Room #3624, 500 Fifth Avenue, New York, N.Y. 10036.

REFERENCES

[1] Frejacques; "The Industrial Synthesis of Urea"; Chimie et Industrie, Vol 60 #1; Jul. 1948.

Indexing Terms: Ammonia-1, Carbon Dioxide-1, Conversion-8, Urea-2.